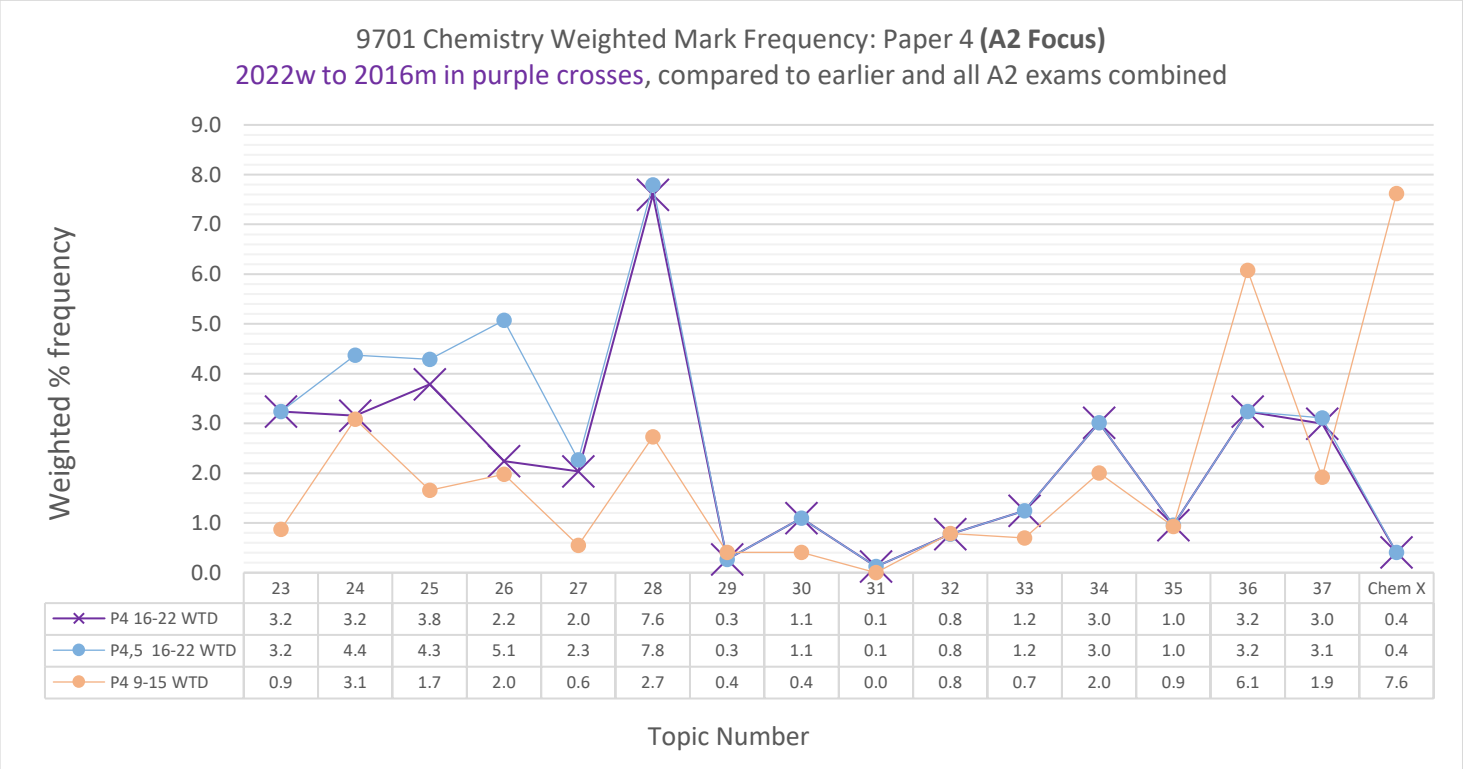
Name: Class: Date:

A Level Chem 34 EQ 22m to 09w **Paper 4** Nitrogen compounds 217marks

As you start and work through this worksheet you can tick off your progress to show yourself how much you have done, and what you need to do next. The first task is just to read the first question and should take you less than 3 minutes to complete.

Paper 4 Topic Checklist Tick each task off as you go along	RANK:	P4 Noob	P4 Novice	P4 Bronze	P4 Silver	P4 Gold	P4[1] Winner	P4 Hero	P4 Legend
	Marks	1 Q Started	1 Q done	10% of marks	25% of marks	40% of marks	50% of marks	75% of marks	100% of marks
Topic 34 (marks)	217		4	22	54	87	109	163	217
Time - 72 seconds per mark (minutes)	264		5	26	66	106	132	198	264



	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	Chem X
P4 16-22 WTD	3.2	3.2	3.8	2.2	2.0	7.6	0.3	1.1	0.1	0.8	1.2	3.0	1.0	3.2	3.0	0.4
P4,5 16-22 WTD	3.2	4.4	4.3	5.1	2.3	7.8	0.3	1.1	0.1	0.8	1.2	3.0	1.0	3.2	3.1	0.4
P4 9-15 WTD	0.9	3.1	1.7	2.0	0.6	2.7	0.4	0.4	0.0	0.8	0.7	2.0	0.9	6.1	1.9	7.6

What the most thoughtful students will get out of their extensive studying will be a capacity to do meaningful brain-based work even under stressful conditions, which is a part of the self-mastery skillset that will continue to deliver value for the whole of their lives. Outstanding grades will also happen, but the most important outcome from skillful action in study is being better at any important tasks even if circumstances are do not feel ideal.

Learning how to manage oneself so we can more reliably get ambitious and successful outcomes out of our challenges in a productive and positive way is one aspect of life's most valuable pursuit summarised and inscribed on the Temple of Apollo at Delphi: "know thyself".

1. To complete these questions, as important as your answer, is checking your answer against the mark scheme.
2. For each question, or page, convert your mark score into a percentage. This will allow you to see (and feel) your progress as you get more experience and understanding with each topic.
3. If you find you get a higher percentage answering short answer questions than multiple choice questions that often means you are using the marking scheme correctly; your correct answer might not be fully complete. The marks easiest to miss rely on providing more details fully described.

[1] **DO NOT** work on these higher levels of completion unless you have also achieved at least a "Silver" (25%) in the same topic in Paper 5, if it exists.

34 Nitrogen compounds

34.1 Primary and secondary amines

Learning outcomes

Candidates should be able to:

1 recall the reactions (reagents and conditions) by which primary and secondary amines are produced:
   (a) reaction of halogenoalkanes with NH_3 in ethanol heated under pressure
   (b) reaction of halogenoalkanes with primary amines in ethanol, heated in a sealed tube / under pressure
   (c) the reduction of amides with $LiAlH_4$
   (d) the reduction of nitriles with $LiAlH_4$ or H_2 / Ni
2 describe the condensation reaction of ammonia or an amine with an acyl chloride at room temperature to give an amide
3 describe and explain the basicity of aqueous solutions of amines

34.2 Phenylamine and azo compounds

Learning outcomes

Candidates should be able to:

1 describe the preparation of phenylamine via the nitration of benzene to form nitrobenzene followed by reduction with hot Sn/concentrated HCl, followed by NaOH(aq)
2 describe:
   (a) the reaction of phenylamine with Br_2(aq) at room temperature
   (b) the reaction of phenylamine with HNO_2 or $NaNO_2$ and dilute acid below 10 °C to produce the diazonium salt; further warming of the diazonium salt with H_2O to give phenol
3 describe and explain the relative basicities of aqueous ammonia, ethylamine and phenylamine
4 recall the following about azo compounds:
   (a) describe the coupling of benzenediazonium chloride with phenol in NaOH(aq) to form an azo compound
   (b) identify the azo group
   (c) state that azo compounds are often used as dyes
   (d) that other azo dyes can be formed via a similar route

34.3 Amides

Learning outcomes

Candidates should be able to:

1 recall the reactions (reagents and conditions) by which amides are produced:
   (a) the reaction between ammonia and an acyl chloride at room temperature
   (b) the reaction between a primary amine and an acyl chloride at room temperature
2 describe the reactions of amides:
   (a) hydrolysis with aqueous alkali or aqueous acid
   (b) the reduction of the CO group in amides with $LiAlH_4$ to form an amine
3 state and explain why amides are much weaker bases than amines

34.4 Amino acids

Learning outcomes

Candidates should be able to:

1 describe the acid / base properties of amino acids and the formation of zwitterions, to include the isoelectric point
2 describe the formation of amide (peptide) bonds between amino acids to give di- and tripeptides
3 interpret and predict the results of electrophoresis on mixtures of amino acids and dipeptides at varying pHs (the assembling of the apparatus will not be tested)

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(c) A student studies the reaction of $CH_3CHClCOOH$ with aqueous NH_3 to determine the reaction mechanism.

The student finds that when $CH_3CHClCOOH$ and NH_3 are added in a 1 : 1 stoichiometric ratio, the conjugate acid and base of the reactants are quickly formed.

reaction 1 $CH_3CHClCOOH + NH_3 \rightarrow CH_3CHClCOO^- + NH_4^+$

In an excess of NH_3, $CH_3CHClCOO^-$ undergoes a nucleophilic substitution reaction.

reaction 2 $CH_3CHClCOO^- + NH_3 \rightarrow CH_3CH(NH_2)COO^- + H^+ + Cl^-$

(vi) When an excess of $CH_3CHClCOO^-$ is used, further substitution reactions occur. One product has the formula $C_6H_9NO_4^{2-}$.

Suggest the structure of $C_6H_9NO_4^{2-}$.

[1]

[Total: 21]

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5 2-Chloropropanoic acid, $CH_3CHClCOOH$, is used in many chemical syntheses.

(b) When $CH_3CHClCOOH$ reacts with aqueous NH_3, alanine forms.

alanine

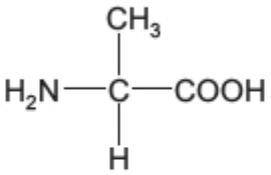

Fig. 5.1

Alanine is an amino acid. Its isoelectric point is 6.1.

(i) State what is meant by isoelectric point.

.....

..... [1]

(ii) Give the structural formula of alanine at pH 2.

..... [1]

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8 Phenylamine, $C_6H_5NH_2$, and ethylamine, $C_2H_5NH_2$, can be distinguished by adding aqueous bromine.

(a) State what is seen when aqueous bromine is added to phenylamine.

.....

..... [2]

(b) Suggest what is seen when aqueous bromine is added to ethylamine.

..... [1]

(c) Draw the structure of the organic product formed when an excess of aqueous bromine is added to phenylamine.

[1]

(d) Name the product you have drawn in **(c)**.

..... [1]

[Total: 5]

10 Valine (Val) and lysine (Lys) are amino acids. The structures of these amino acids can be found in the *Data Booklet*.

The isoelectric point of an amino acid is the pH at which it exists as a zwitterion. The isoelectric point of valine is 6.0. The isoelectric point of lysine is 9.7.

(a) Draw the structure of valine at pH 6.0.

[1]

(b) A solution of lysine is produced with pH 9.7. Dilute sulfuric acid is added slowly until the pH of the solution is 1.0. The sulfuric acid reacts with lysine to produce different organic ions that are not present in significant concentrations at pH 9.7.

Draw the structures of three of the organic ions that form during the addition of sulfuric acid in the boxes. Draw the organic ion present at pH 1.0 in box C.

A	B	C (pH 1.0)

[3]

(c) Draw the structure of the dipeptide Val-Lys. The peptide bond should be shown fully displayed.

[2]

[Total: 6]

(b) A mixture of serine, $HOCH_2CH(NH_2)CO_2H$, and lysine, $H_2N(CH_2)_4CH(NH_2)CO_2H$, reacts to form several different products.

(i) Draw the structures of the two structural isomers with the molecular formula $C_6H_{12}N_2O_5$ that could be present in the product mixture.

The functional group formed in each case should be displayed.

[3]

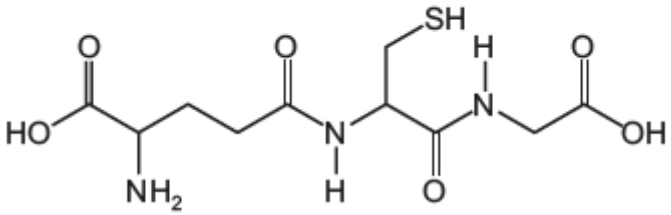
(ii) Predict the number of different structural isomers with the molecular formula $C_9H_{19}N_3O_4$ that could be present in the product mixture.

molecular formula	number of structural isomers formed
$C_9H_{19}N_3O_4$	

[1]

(c) Glutathione is a naturally occurring compound found in plants.

glutathione



(ii) Draw the structures of the three products formed after complete acid hydrolysis of glutathione. Assume the thiol group, –SH, does not react.

[2]

(iii) Glutathione is soluble in water.

By referring to the structure of glutathione, explain why glutathione is soluble in water.

.....

.....

..... [1]

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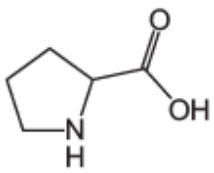
7 Proline (Pro) is a naturally occurring amino acid.

proline



(a) Proline is often found bonded to glycine (Gly) in a protein.

(i) Draw the dipeptide Pro-Gly.

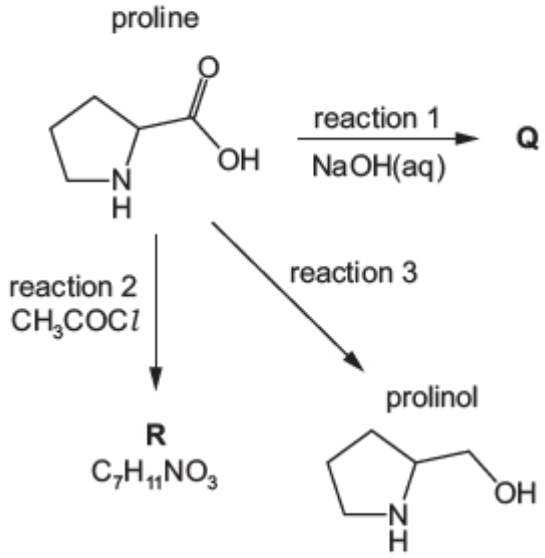
The peptide bond must be shown fully displayed.

[2]

(ii) Name the type of reaction that forms a dipeptide from two amino acids.

..... [1]

(b) The reaction scheme shows several reactions of proline.



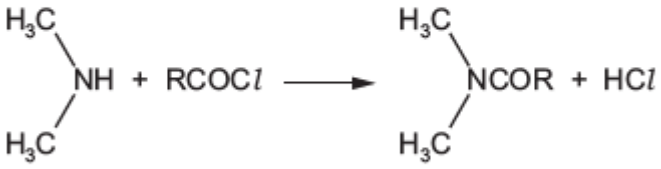
(i) Write an equation for the reaction of proline with NaOH(aq) in reaction 1.

$C_4H_7NHCO_2H$ + ... [1]

(ii) Proline has a secondary amine functional group.

Secondary amines react with acyl chlorides. For example, dimethylamine reacts with RCOC*l* according to the following equation.

dimethylamine



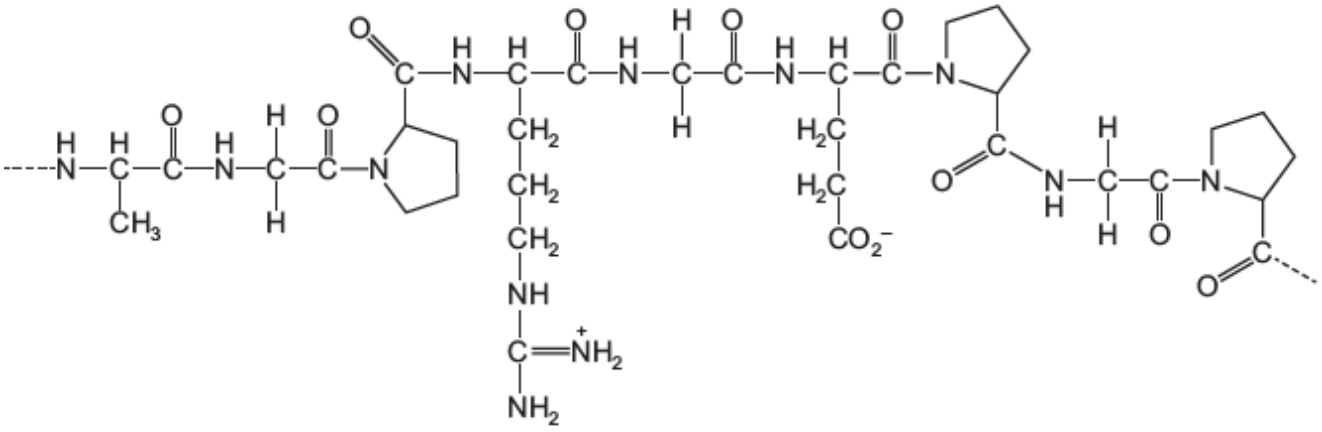
Suggest the skeletal structure of **R**, $C_7H_{11}NO_3$, the product of reaction 2.

[1]

(iii) Suggest the reagent required for reaction 3.

..... [1]

(d) Part of the structure of gelatin is shown.



Identify the number of amino acid units in the structure shown.

..... [1]

(e) (i) At pH 6.5, proline exists in aqueous solution as a zwitterion.

Draw the structure of the zwitterion of proline.

Explain how the zwitterion of proline forms.

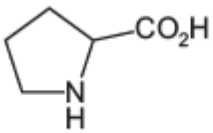
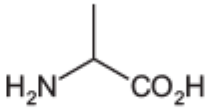
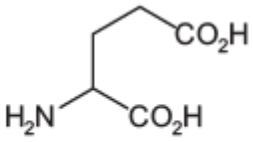
.....

.....

..... [2]

(ii) The isoelectric point of an amino acid is the pH at which it exists as a zwitterion.

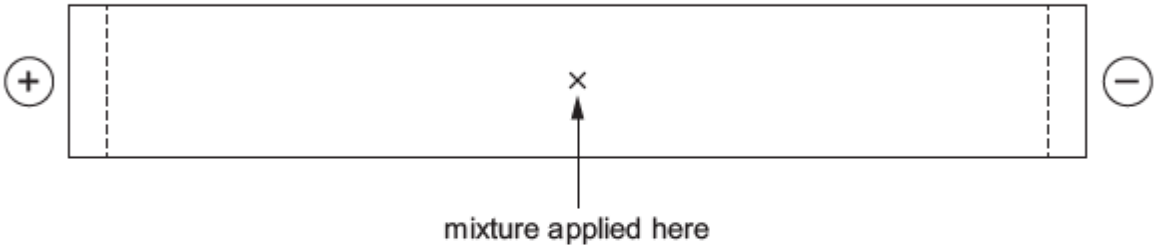
Three of the amino acids in gelatin are proline, alanine and glutamic acid. Their isoelectric points are shown.

amino acid	proline 	alanine 	glutamic acid 
isoelectric point	6.5	6.0	3.1

A mixture of these amino acids was analysed by electrophoresis using a buffer solution at pH 4.0.

Draw and label three spots on the diagram of the electropherogram to indicate the likely position of each of these three species after electrophoresis.

Explain your answer.



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..... [4]

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(b) 2-aminopropanoic acid, $CH_3CH(NH_2)CO_2H$, can polymerise under suitable conditions. No other monomer is involved in this reaction.

(i) Draw a section of the polymer chain formed including **three** monomer residues. Clearly identify **one** repeat unit on your diagram.

[3]

4 **(a)** The molecular formulae of three nitrogen-containing compounds are given.

S $C_6H_5CONH_2$

T $C_6H_5NH_2$

U $C_6H_5CH_2NH_2$

Describe and explain the relative basicities of **S**, **T** and **U**.

..... > ..... > .....

most basic least basic

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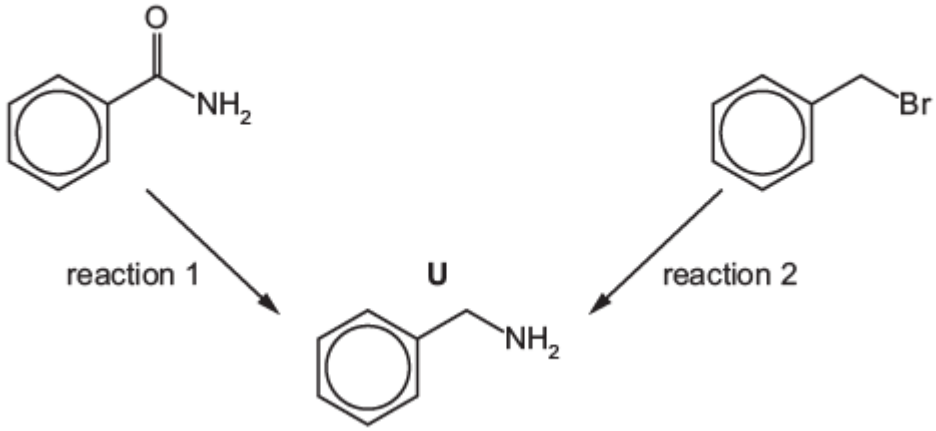
[3]

(b) Compound **U** can be prepared by two different methods as shown.



(i) Suggest reagents and conditions for reaction 1 and for reaction 2.

reaction 1 .....

reaction 2 .....

[2]

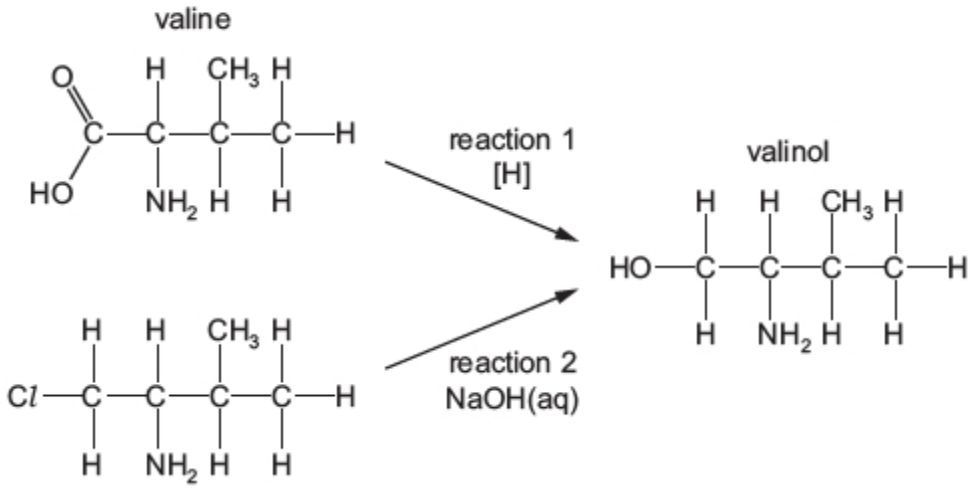
(ii) State the type of reaction in reaction 1 and name the mechanism in reaction 2.

type of reaction in reaction 1 .....

mechanism of reaction 2 .....

[2]

6 Valinol can be synthesised by the following reactions. Reaction 1 uses valine as the starting material.



(b) Valine and glycine, H_2NCH_2COOH, form the tripeptide Gly–Val–Gly.

Draw the structure of this tripeptide. Show the peptide bonds fully displayed.

[2]

(c) (i) Valine exists as two stereoisomers.

Draw three-dimensional diagrams to show the two stereoisomers of valine. In your diagrams, the $–CH(CH_3)_2$ group can be represented by –R.

State the type of stereoisomerism shown.

type of stereoisomerism .....

[2]

(ii) Valine is an amino acid.

Draw the zwitterion of valine.

[1]

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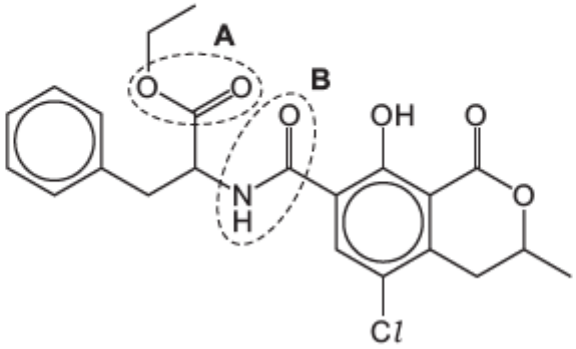
4 Compound **F** has been found in small quantities in some cereals and dried fruit.

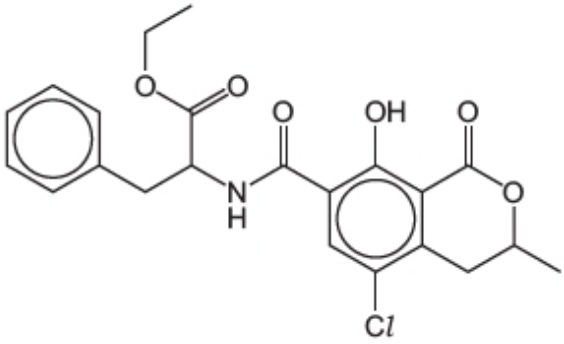
F



(b) **F** can be hydrolysed by heating with an excess of dilute hydrochloric acid, as shown.

Three products are formed: **G** and two others.

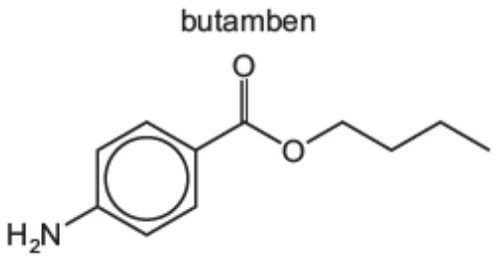
F



excess dilute HCl

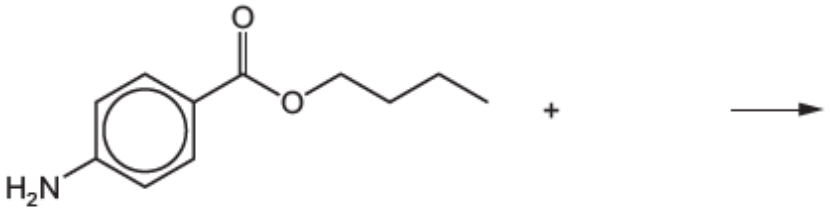
Draw the structures of the other products of the reaction in the boxes provided. [3]

9 The structure of butamben is shown.



(a) Butamben can act as a base.

(i) Complete the equation for a reaction in which butamben acts as a base.



[1]

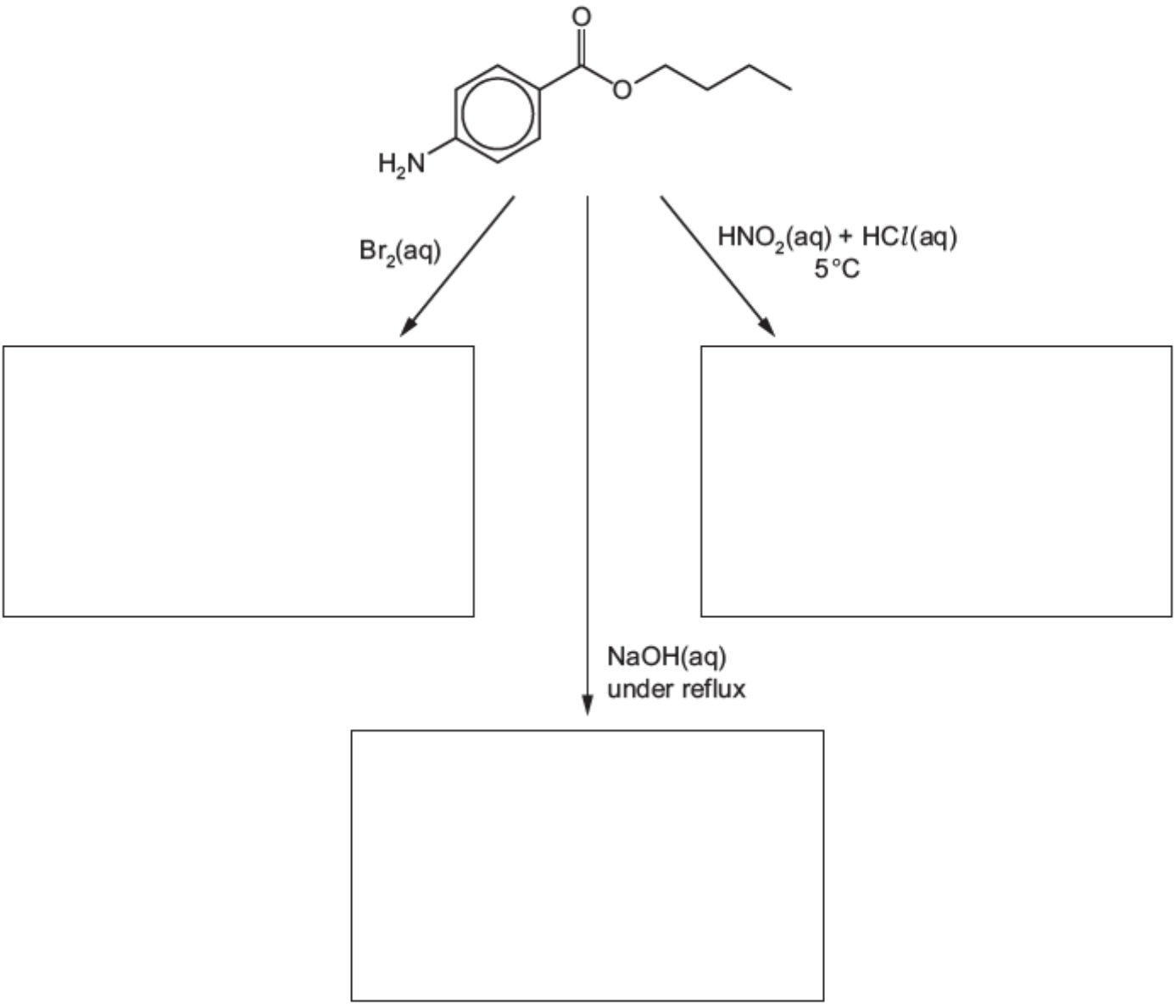
(ii) Predict whether butamben is a stronger or weaker base than ammonia. Give a reason for your answer.

.....

.....

..... [1]

(b) Complete the reaction scheme below to show the structural formulae of the products formed when butamben is treated separately with the stated reagent.



[3]

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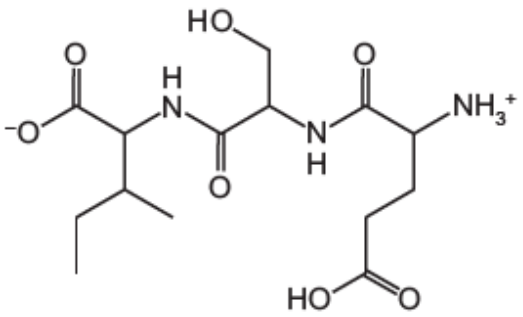
8 Proteins are natural polymers. When one particular protein is partially hydrolysed the product mixture includes tripeptide **E**.

tripeptide **E**



(a) (i) Describe the conditions that could be used to hydrolyse **E** to produce a mixture of three amino acids.

..... [1]

(ii) Draw the structures of the three amino acids produced by this hydrolysis reaction.

The three amino acids should be shown in the correct form for the conditions you have chosen in **(a)(i)**.

[2]

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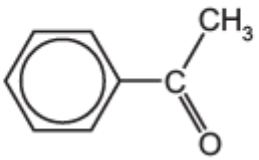
4 Phenylethanone is an important chemical with many uses.

phenylethanone



(c) Phenylethanone reacts with HCN in the presence of a small amount of NaCN.

(i) Name the mechanism of this reaction.

..... [1]

(ii) Draw the mechanism of this reaction below. Include all relevant charges, dipoles, lone pairs and curly arrows. Your mechanism should show the catalytic role of CN^- ions.

phenylethanone intermediate product

[4]

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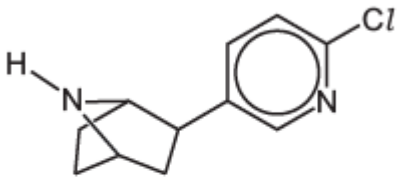
9 **(a)** Organochlorine compounds can undergo hydrolysis.

$$R\text{–}Cl + H_2O \rightarrow R\text{–}OH + HCl$$

(b) Epibatidine is a naturally occurring organochlorine compound.

epibatidine



(i) Epibatidine is a weak base.

State what is meant by the term *weak base*.

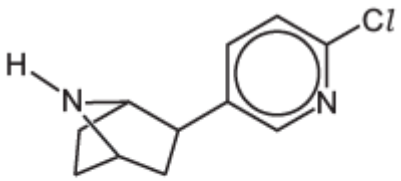
.....

..... [1]

A molecule of epibatidine contains two nitrogen atoms, both of which can act as a base.

(ii) Epibatidine reacts with HC*l*(aq).

Complete the structure to suggest the product formed in this reaction.



[1]

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(c) Methylamine, CH_3NH_2, is a monodentate ligand.

In the presence of aqueous methylamine, $[Cd(H_2O)_6]^{2+}$ reacts to form a mixture of two isomeric octahedral complexes.

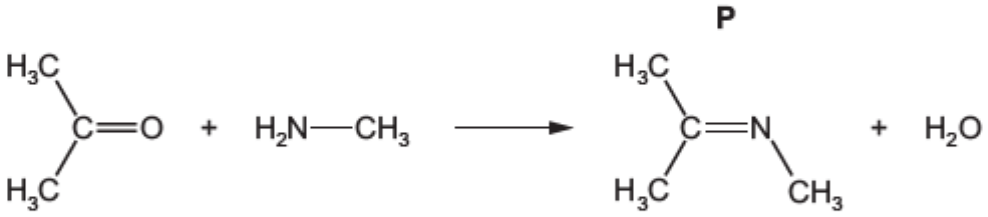
equilibrium **1** $[Cd(H_2O)_6]^{2+} + 4CH_3NH_2 \rightleftharpoons [Cd(CH_3NH_2)_4(H_2O)_2]^{2+} + 4H_2O \quad \Delta H_r^{\ominus} = -57\,kJ\,mol^{-1}$

(f) Methylamine is a useful reagent in organic chemistry.

(i) Write an equation for the reaction of ethanoyl chloride with methylamine.

..... [2]

(ii) Methylamine also reacts with propanone to form compound **P** as shown.



Deduce the *type of reaction* shown here.

..... [1]

[Total: 13]

Q# 402/ ALvl Chemistry/2018/w/TZ 1/Paper 4/Q# 6 /www.SmashingScience.org :o)

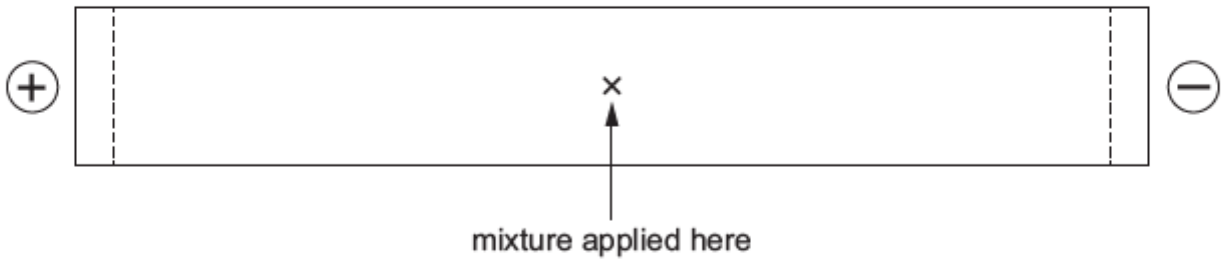
6 **(a)** Use the *Data Booklet* to draw the structure of the dipeptide val-lys. The peptide bond should be shown displayed.

[2]

(b) The isoelectric point is the pH at which an amino acid exists as a zwitterion. The isoelectric point of valine is 6.0 and of lysine is 9.8.

A mixture of the dipeptide, val-lys, and its two constituent amino acids, valine and lysine, was analysed by electrophoresis using a buffer at pH 6.0.

Draw and label **three** spots on the diagram of the electrophoresis paper to indicate the likely position of each of these three species after electrophoresis. Explain your answer.



explanation .....

.....

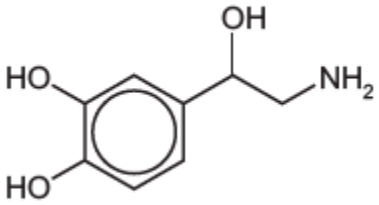
.....

[5]

[Total: 7]

Q# 403/ ALvl Chemistry/2018/s/TZ 1/Paper 4/Q# 9 /www.SmashingScience.org :o)

9 Noradrenaline is a hormone found in humans.



noradrenaline

(c) $HNO_2(aq)$ is reacted at 5 °C with separate samples of noradrenaline and phenylamine.
The reaction with phenylamine produces a stable diazonium ion.
The reaction with noradrenaline produces an unstable diazonium ion.

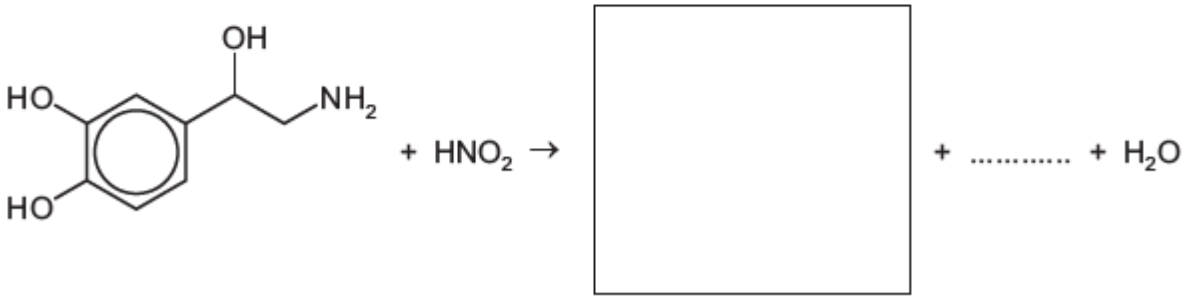
(i) Suggest why the diazonium ion produced with phenylamine is stable.

.....

..... [1]

(ii) When one noradrenaline molecule reacts with one HNO_2 molecule, the products are one water molecule, one molecule of an unreactive gas, and one molecule of an organic compound made up of carbon, hydrogen and oxygen only.

Complete the chemical equation for this reaction.



[2]

Q# 404/ ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 7 /www.SmashingScience.org :o)

(b) An amide bond forms when a carboxylic acid reacts with an amine.

(i) Complete the equation by writing the products in the box.

[1]

(ii) Use your answer to **(i)** to work out the bonds that are broken and the bonds that are formed during the reaction between a carboxylic acid and an amine.

- bonds that are broken

.....

- bonds that are formed

.....

[2]

(iii) Use bond energy values from the *Data Booklet* to calculate the enthalpy change, $\Delta H^{\ominus}$, when **one** mole of amide bonds is formed in the reaction in **(i)**.

$\Delta H^{\ominus}$ = ... kJ [2]

(c) Amide bonds can also be formed by reacting acyl chlorides with amines.

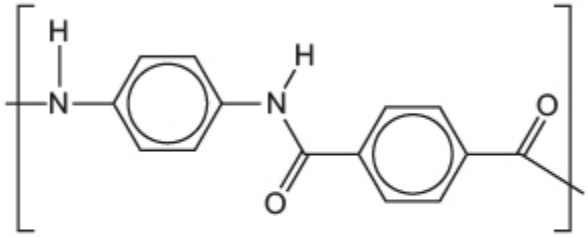
The enthalpy change for this process, $\Delta H^{\ominus}$, is $-6.00\,kJ\,mol^{-1}$.

Calculate the minimum entropy change, $\Delta S^{\ominus}$, for this reaction to be spontaneous (feasible) at 298 K.

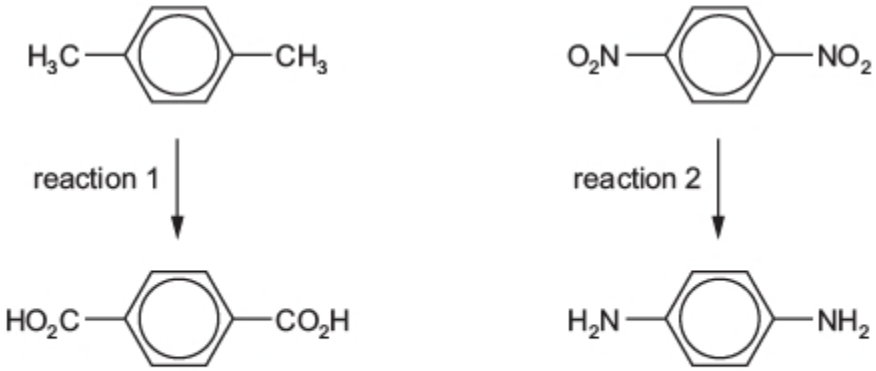
$\Delta S^{\ominus}$ = ... $JK^{-1}\,mol^{-1}$ [2]

Q# 405/ ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 7 /www.SmashingScience.org :o)

The repeat unit of the polyamide *Kevlar* is shown.



(d) The monomers of *Kevlar*, benzene-1,4-dioic acid and 1,4-diaminobenzene, can be synthesised as follows.



benzene-1,4-dioic acid

1,4-diaminobenzene

State the reagents and conditions needed for:

(ii) reaction 2

.....

..... [2]

Q# 406/ ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 4 /www.SmashingScience.org :o)

(b) (i) Explain why butylamine is basic.

.....

..... [1]

(ii) Write an equation to show butylamine reacting as a base.

..... [1]

(iii) State how the basicity of butanamide, $C_3H_7CONH_2$, compares to that of butylamine.

..... [1]

(iv) State a reagent for the conversion of butanamide into butylamine.

..... [1]

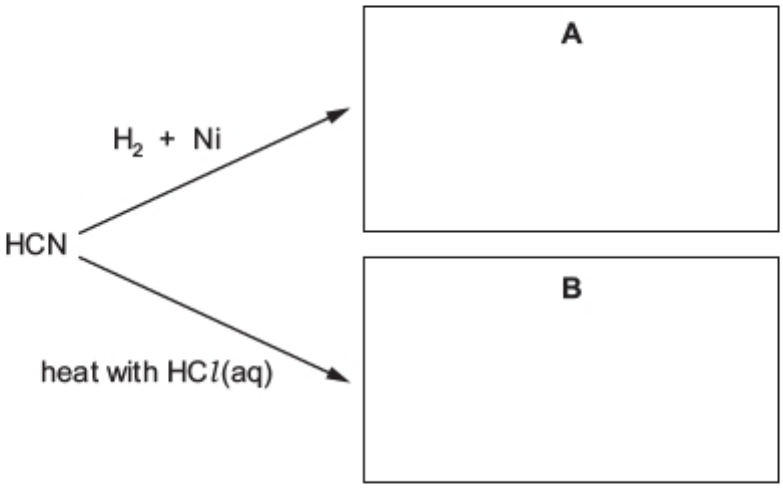
[Total: 9]

Q# 407/ ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 3 /www.SmashingScience.org :o)

3 (a) Hydrogen cyanide, HCN, is a weak acid in aqueous solution.

$$HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq) \qquad K_a = 6.2 \times 10^{-10}\,mol\,dm^{-3}$$

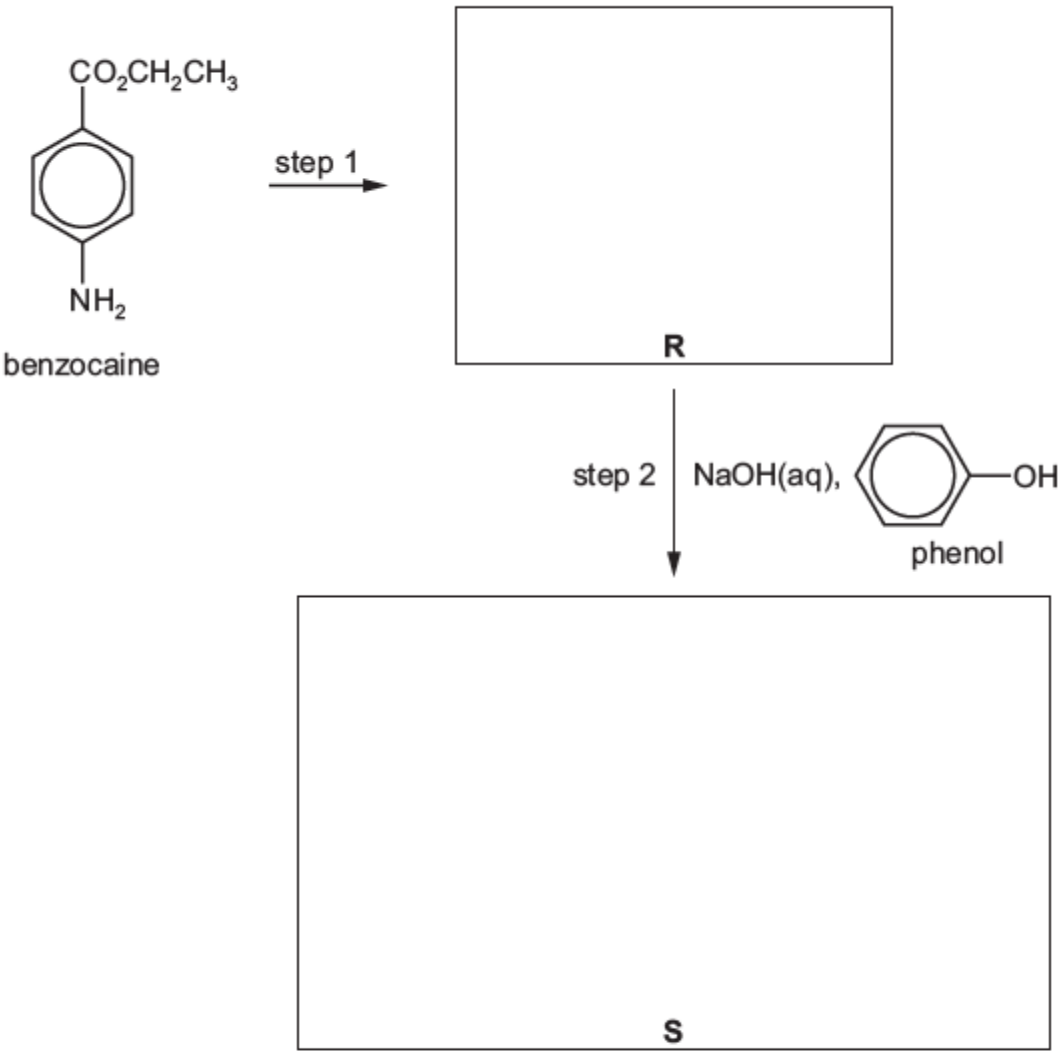
(iv) Suggest structures for the organic products **A** and **B** in the following reactions. Assume that HCN reacts in a similar way to RCN.



[2]

Q# 408/ ALvl Chemistry/2017/w/TZ 1/Paper 4/Q# 6 /www.SmashingScience.org :o)

(e) Benzocaine can also be used to synthesise the dyestuff **S** by the following route.



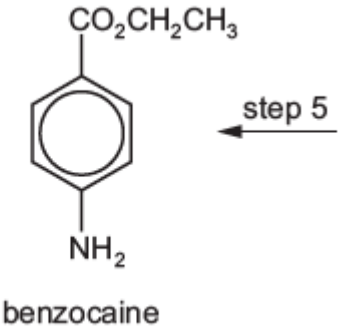
(i) Suggest the reagents used for step 1.

..... [1]

(ii) Suggest structures for compounds **R** and **S** and draw them in the boxes. [2]

[Total: 25]

Q# 409/ ALvl Chemistry/2017/w/TZ 1/Paper 4/Q# 6 /www.SmashingScience.org :o)



(c) Suggest how the basicity of benzocaine would compare to that of ethylamine.
Explain your answer.

.....

.....

..... [2]

Q# 410/ ALvl Chemistry/2017/s/TZ 1/Paper 4/Q# 2 /www.SmashingScience.org :o)

2 **(a)** One atom of each of the four elements H, C, N and O can bond together in different ways. Two examples are molecules of cyanic acid, HOCN, and isocyanic acid, HNCO. The atoms are bonded in the order they are written.

(e) When heated with HCl(aq), organic isocyanates, RNCO, are hydrolysed to the amine salt, RNH_3Cl, and CO_2.

$$RNCO + H_2O + HCl \rightarrow RNH_3Cl + CO_2$$

A 1.00 g sample of an organic isocyanate, RNCO, was treated in this way, and the CO_2 produced was absorbed in an excess of aqueous $Ba(OH)_2$ according to the equation shown. The solid $BaCO_3$ precipitated weighed 1.66 g.

$$Ba(OH)_2(aq) + CO_2(g) \rightarrow BaCO_3(s) + H_2O(l)$$

(i) Calculate the number of moles of $BaCO_3$ produced.

moles of $BaCO_3$ = ... [1]

(ii) Hence calculate the M_r of the organic isocyanate RNCO.

M_r of RNCO = ... [1]

The R group in RNCO and RNH_3Cl contains carbon and hydrogen only.

(iii) Use your M_r value calculated in **(ii)** to suggest the molecular formula of the organic isocyanate RNCO.

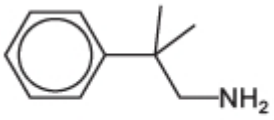
molecular formula of RNCO ..... [1]

(iv) Suggest a possible structure of the amine RNH_2, which forms the amine salt, RNH_3Cl.

[1]

Q# 411/ ALvl Chemistry/2017/m/TZ 2/Paper 4/Q# 5 /www.SmashingScience.org :o)

5 **(a)** Compound **H** can be synthesised from benzene



compound **H**

(b) Write an equation to show how compound **H**, $C_{10}H_{13}NH_2$, behaves as a base.

..... [1]

(c) Compare the relative basicities of ammonia, phenylamine and compound **H**. Explain your answer.

.....

.....

..... [2]

Q# 412/ ALvl Chemistry/2016/w/TZ 1/Paper 4/Q# 1 /www.SmashingScience.org :o)

1 Copper is a transition element and has atomic number 29.

(c) Copper also forms the complex ions $[Cu(NH_3)_2(H_2O)_4]^{2+}$ and $[Cu(en)(H_2O)_4]^{2+}$ where *en* is the bidentate ligand ethane-1,2-diamine, $H_2NCH_2CH_2NH_2$.

$$[Cu(H_2O)_6]^{2+} + 2NH_3 \rightleftharpoons [Cu(NH_3)_2(H_2O)_4]^{2+} + 2H_2O \qquad \text{equilibrium 1}$$

$$[Cu(H_2O)_6]^{2+} + en \rightleftharpoons [Cu(en)(H_2O)_4]^{2+} + 2H_2O \qquad \text{equilibrium 2}$$

(e) Ethane-1,2-diamine is a useful reagent in organic chemistry.

(i) Explain how the amino groups in ethane-1,2-diamine allow the molecule to act as a Brønsted-Lowry base.

.....

..... [2]

(ii) Write an equation for the reaction of ethane-1,2-diamine with an excess of hydrochloric acid.

..... [1]

(f) **(i)** Under certain conditions, ethane-1,2-diamine reacts with ethanedioic acid, HO_2CCO_2H, to form the polymer **Z**.

Draw the structure of this polymer, **Z**, showing **two** repeat units.

[2]

(ii) Name the *type of reaction* occurring during this polymerisation.

..... [1]

(iii) Polymer **Z** is an example of a biodegradable polymer.

Name a polymer that is non-biodegradable.

..... [1]

Q# 413/ ALvl Chemistry/2016/s/TZ 1/Paper 4/Q# 7 /www.SmashingScience.org :o)

7 **(a)** **(i)** Use the *Data Booklet* to draw the structure of the tripeptide Ala-Ser-Gly showing its peptide bonds in full.

Ala-Ser-Gly

[2]

(ii) Calculate the relative molecular mass, M_r, of Ala-Ser-Gly.

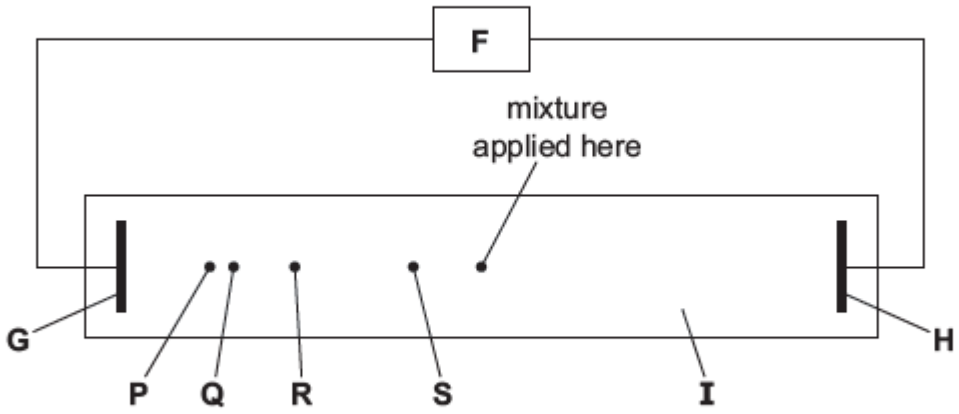
M_r = ... [1]

(b) Electrophoresis can be used to separate mixtures of amino acids and peptides.
A mixture of the tripeptide Ala-Ser-Gly and its three constituent amino acids was subjected to electrophoresis in a buffer at pH 11.

(i) Draw the structure of serine at pH 11.

[1]

At the end of the experiment the following results were seen.



(ii) Identify the components labelled **F**-**I** in the above diagram.

F .....

G .....

H .....

I .....

[4]

(iii) Suggest the identities of the species responsible for

spot **P**, ...

spot **S**. .....

Explain your answers.

.....

..... [3]

(c) (i) State the reagents and conditions needed for converting the tripeptide into its three constituent amino acids.

..... [1]

(ii) Name the *type of reaction* in **(i)**.

..... [1]

Q# 414/ ALvl Chemistry/2016/s/TZ 1/Paper 4/Q# 6 /www.SmashingScience.org :o)

6 Nitrobenzene, $C_6H_5NO_2$, can be reduced to phenylamine, $C_6H_5NH_2$, in acid solution in a two step process.

(a) (i) Balance the half-equation for this reaction to work out how many moles of electrons are needed to reduce one mole of nitrobenzene.

$$C_6H_5NO_2 + ...e^- + ...H^+ \rightarrow C_6H_5NH_2 + ...H_2O \quad [1]$$

(ii) The reducing agent normally used is granulated tin and concentrated hydrochloric acid. In the first step, the reduction of nitrobenzene to phenylammonium chloride can be represented by the equation shown.

Use oxidation numbers or electrons transferred to balance this equation. You might find your answer to **(i)** useful.

$$.....C_6H_5NO_2 + ...HCl + ...Sn \rightarrow .....C_6H_5NH_3Cl + ...SnCl_4 + ...H_2O \quad [2]$$

(b) When 5.0 g of nitrobenzene was reduced in this reaction, 4.2 g of phenylammonium chloride, $C_6H_5NH_3Cl$, was produced.

Calculate the percentage yield.

percentage yield of phenylammonium chloride = ... % [2]

(c) Following the reaction in **(b)**, an excess of NaOH(aq) was added to liberate phenylamine from phenylammonium chloride.

(i) Calculate the mass of phenylamine, $C_6H_5NH_2$, produced when 4.20 g of phenylammonium chloride reacts with an excess of NaOH(aq).

mass of phenylamine = ... g [1]

The final volume of the alkaline solution of phenylamine in **(i)** was 25.0 cm^3. The phenylamine was extracted by addition of 50 cm^3 of dichloromethane. After the extraction, the dichloromethane layer contained 2.68 g of phenylamine.

(ii) Use the data to calculate the partition coefficient, $K_{partition}$, of phenylamine between dichloromethane and water.

$K_{partition}$ = ... [2]

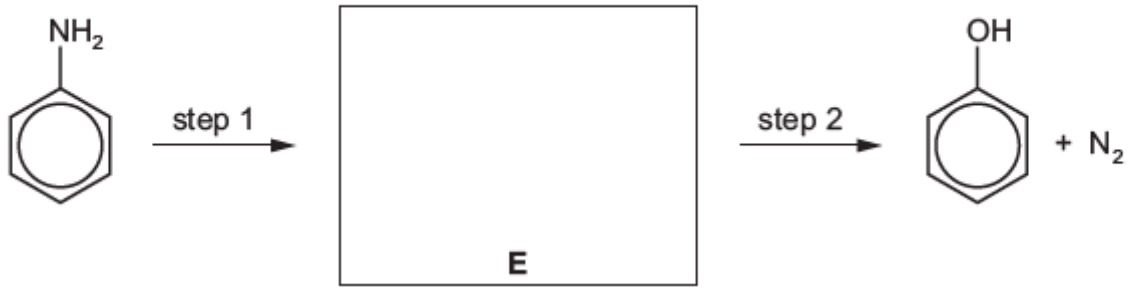
(d) How does the basicity of phenylamine compare to that of ethylamine? Explain your answer.

.....

.....

..... [2]

(e) Phenol can be synthesised from phenylamine in two steps.



(i) State the reagents and conditions for steps 1 and 2.

step 1 .....

step 2 .....

[2]

(ii) Draw the structure of the intermediate compound **E** in the box above. [1]

Q# 415/ ALvl Chemistry/2016/m/TZ 2/Paper 4/Q# 9 /www.SmashingScience.org :o)

(c) A section of polypeptide was hydrolysed and the following amino acids identified.

amino acid	formula
T	$CH_3CH(NH_2)CO_2H$
U	$C_6H_5CH_2CH(NH_2)CO_2H$
V	$H_2N(CH_2)_4CH(NH_2)CO_2H$

(i) Which of the amino acids **T**, **U** or **V** has the highest pH in aqueous solution? Explain why.

amino acid .....

.....

.....

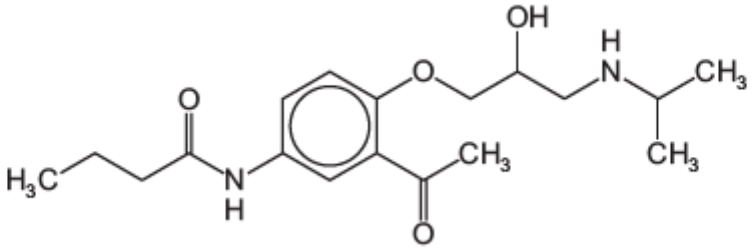
[1]

(ii) State how many different dipeptides could be formed from a reaction mixture consisting of amino acids **T** and **U**.

..... [1]

Q# 416/ ALvl Chemistry/2016/m/TZ 2/Paper 4/Q# 8 /www.SmashingScience.org :o)

8 Acebutolol is a drug that can be used to lower blood pressure.



(c) On warming with dilute hydrochloric acid, acebutolol splits to form two molecules.

(i) Draw a line through the bond broken by heating with dilute hydrochloric acid. [1]

(ii) Draw the structure of the **smaller** molecule produced by this reaction.

[1]

Q# 417/ ALvl Chemistry/2016/m/TZ 2/Paper 4/Q# 7 /www.SmashingScience.org :o)

(b) (i) Phenylamine reacts with aqueous bromine to give compound **F**.

Describe the appearance of compound **F**.

..... [1]

(ii) Phenylamine reacts with nitrous acid to form a diazonium salt.

State the conditions for this reaction.

..... [1]

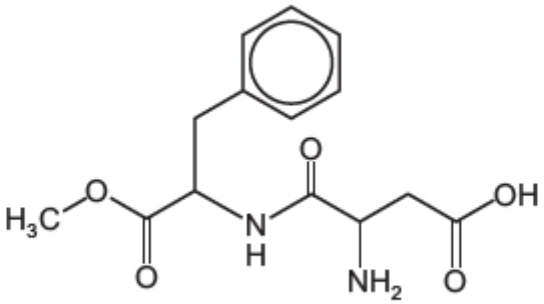
(iii) The diazonium salt in **(ii)** reacts with an alkaline solution of phenol to produce a coloured compound, **G**.

Draw the structure of **G**.

[2]

Q# 418/ ALvl Chemistry/2015/w/TZ 1/Paper 4/Q# 10 /www.SmashingScience.org :o)

10 (a) Aspartame is an artificial sweetener that has the structure shown below.



aspartame

In the stomach, aspartame is hydrolysed by acid to form three organic products.

(ii) On the diagram above, use arrows to indicate the **two** bonds that would be hydrolysed in the stomach. [2]

(iii) Draw the structures of the **three** products formed after complete acid hydrolysis of aspartame.

[3]

(b) Aspartame is soluble in water.

By referring to the structure of aspartame, explain why it is soluble in water.

.....

.....

..... [2]

Q# 419/ ALvl Chemistry/2015/s/TZ 1/Paper 4/Q# 8 /www.SmashingScience.org :o)

Section B

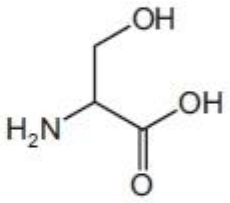
Answer **all** the questions in the spaces provided.

8 Proteins are formed by the polymerisation of amino acids.

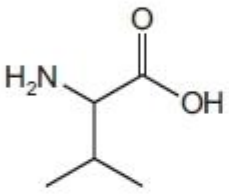
(a) (i) State the type of chemical reaction used to form these polymer chains.

..... [1]

(ii) The amino acids serine and valine can combine together to form a dipeptide.



serine, *ser*



valine, *val*

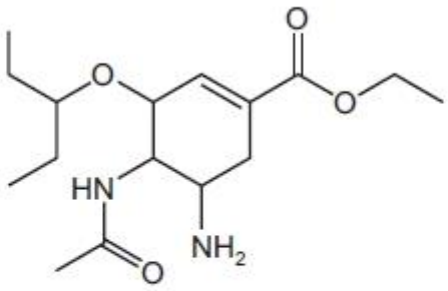
Draw the skeletal structure of the dipeptide '*val-ser*'.

[2]

Q# 420/ ALvl Chemistry/2014/w/TZ 1/Paper 4/Q# 7 /www.SmashingScience.org :o)

The human body includes organs like the stomach, which contain strong acids like HCl.

7 (a) Oseltamivir is an antiviral drug that slows the spread of the influenza (flu) virus.



oseltamivir

Circle **two** bonds, each in a different functional group, that could be easily hydrolysed in the body. [2]

Section B

Answer **all** the questions in the spaces provided.

6 **(a)** A mixture of amino acids can be separated by electrophoresis. During an electrophoresis experiment,

- different amino acids move in different directions,
- different amino acids move at different speeds,
- some amino acids do not move at all.

Explain these observations.

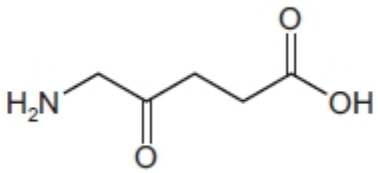
.....

.....

.....

..... [3]

(b) Aminolaevulinic acid is involved in the synthesis of haemoglobin and chlorophyll.



aminolaevulinic acid

(c) Aminolaevulinic acid reacts readily with bromoethane.

(i) Show the mechanism of the **first step** of this reaction on the diagram. Include all necessary curly arrows, lone pairs and relevant dipoles.

$H_3C—CH_2—Br$

(ii) Name the mechanism in **(c)(i)**.

.....

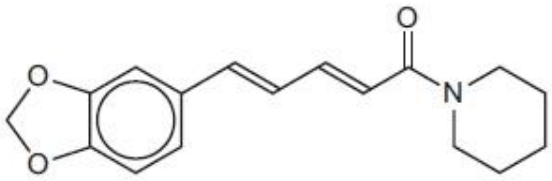
(iii) Identify the non-organic product formed in this reaction.

.....

[5]

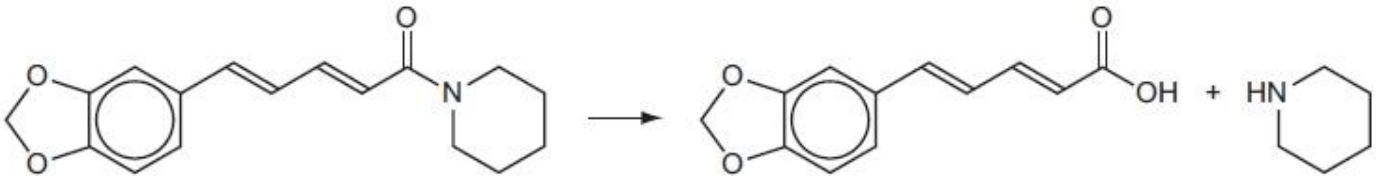
Q# 423/ ALvl Chemistry/2014/s/TZ 1/Paper 4/Q# 3 /www.SmashingScience.org :o)

3 Piperine is the compound responsible for the hot taste of black pepper.



piperine

Piperine is an amide and can be broken down as follows:



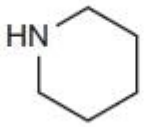
piperine piperic acid piperidine

(a) Suggest reagents and conditions for this reaction.

..... [1]

Q# 424/ ALvl Chemistry/2014/s/TZ 1/Paper 4/Q# 3 /www.SmashingScience.org :o)

(iii) The pH of a 0.150 mol dm^{-3} solution of piperidine is 11.9.



piperidine

(iv) How would you expect the basicity of piperidine to compare to that of ammonia? Explain your reasoning.

.....

..... [1]

Q# 425/ ALvl Chemistry/2013/w/TZ 1/Paper 4/Q# 7 /www.SmashingScience.org :o)

7 Electrophoresis is a technique which can be used to separate amino acids or peptide fragments present in a mixture.

(a) Draw a diagram to show the apparatus used to carry out electrophoresis. You should label each of the relevant parts of the apparatus.

[4]

(b) How far an amino acid will travel during electrophoresis depends on the pH of the solution. For a given potential difference, state **two other** factors that will affect how far a given amino acid travels in a fixed time during electrophoresis.

1. .....

.....

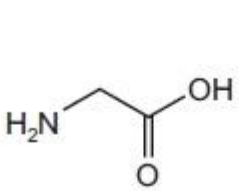
2. .....

.....

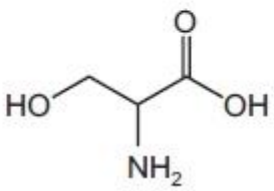
[2]

Q# 426/ ALvl Chemistry/2013/w/TZ 1/Paper 4/Q# 6 /www.SmashingScience.org :o)

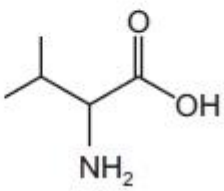
6 **(a)** Protein molecules are formed by the polymerisation of amino acids in the body. The structures of three amino acids are given.



glycine (*gly*)



serine (*ser*)



valine (*val*)

(i) How many different tripeptides can be made using **one** molecule of **each** of the amino acids shown?

.....

(ii) Draw the tripeptide *ser-gly-val*, showing the peptide bonds in displayed form.

(iii) Within the tripeptide, which amino acid provides a hydrophobic side chain?

..... [4]

Q# 427/ ALvl Chemistry/2013/s/TZ 1/Paper 4/Q# 4 /www.SmashingScience.org :o)

4 Because of the lack of reactivity of the nitrogen molecule, extreme conditions need to be used to synthesise ammonia from nitrogen in the Haber process.

(c) Describe and explain how the basicities of ethylamine and phenylamine compare to that of ammonia.

.....

.....

.....

.....

.....

[4]

Q# 428/ ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 8 /www.SmashingScience.org :o)

(c) Polymerisation can take place by two different methods depending on the monomers involved. The two methods are addition and condensation.
Give **two** differences between the methods.

1. .....

.....

2. .....

.....

[2]

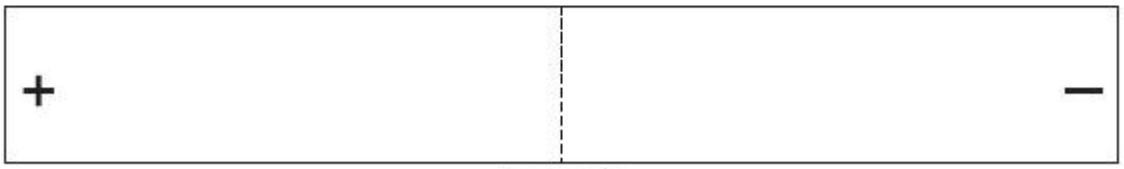
Q# 429/ ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 7 /www.SmashingScience.org :o)

7 The analysis of a protein may be carried out by breaking it down into its amino acids. These can then be separated by a process called electrophoresis.

(a) The structures of glycine, lysine and glutamic acid at pH 7 are shown.

glycine	$H_3N^+CH_2CO_2^-$
lysine	$H_3N^+CH(CH_2CH_2CH_2CH_2NH_3^+)CO_2^-$
glutamic acid	$H_3N^+CH(CH_2CH_2CO_2^-)CO_2^-$

Draw and label three circles on the chart below to indicate the likely position of each of these amino acids after electrophoresis of a solution containing these amino acids in a buffer at pH 7.



[3]

Q# 430/ ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 6 /www.SmashingScience.org :o)

Section B

Answer **all** the questions in the spaces provided.

6 In key reactions responsible for growth and repair in the human body, amino acids react together to form polymers known as proteins.

(a) (i) What *type of reaction* is this polymerisation?

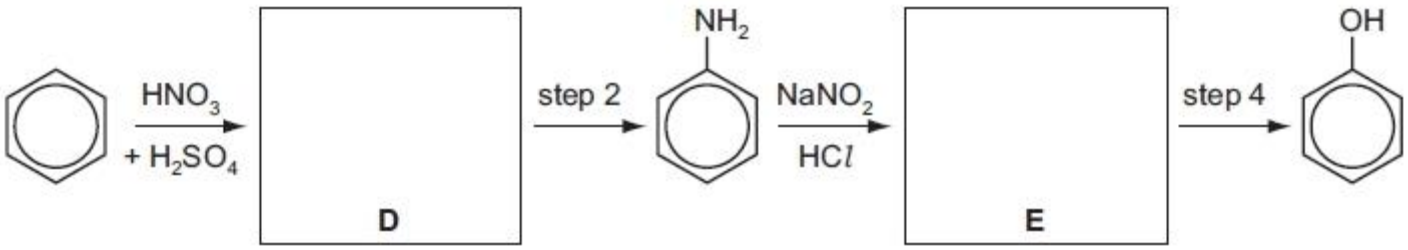
.....

(ii) From stocks of glycine and alanine, it is possible to make the dipeptide gly-ala. Using the same three-letter abbreviations for the amino acids, give the structures of all other possible dipeptides that can be made from these stocks of amino acids.

[3]

Q# 431/ ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 5 /www.SmashingScience.org :o)

(b) Phenol can be synthesised from benzene by the following route.



(i) Suggest structures for compounds **D** and **E** and draw them in the boxes above.

(ii) Suggest reagents and conditions for

step 2, ...

step 4. .....

[4]

Q# 432/ ALvl Chemistry/2011/w/TZ 1/Paper 4/Q# 7 /www.SmashingScience.org :o)

7 One of the key areas of investigation in understanding the structures of polypeptides and proteins is the sequence of amino acids that make up the polypeptide chains.

(a) One of the methods used to determine the amino acids present in a polypeptide chain is electrophoresis.

Sketch and label the apparatus used to carry out electrophoresis.

[4]

(b) In electrophoresis, different amino acids move in different directions and at different speeds.

(i) What factors determine the *direction of travel* of an amino acid?

.....

.....

.....

(ii) What factors determine the *speed of movement* of an amino acid?

.....

.....

[3]

Q# 433/ ALvl Chemistry/2011/w/TZ 1/Paper 4/Q# 4 /www.SmashingScience.org :o)

4 (a) (i) Write the equation for a reaction in which ethylamine, $C_2H_5NH_2$, acts as a Brønsted-Lowry base.

.....

(ii) Ammonia, ethylamine and phenylamine, $C_6H_5NH_2$, are three nitrogen-containing bases.

Place these three compounds in order of basicity, with the most basic first.

most basic		least basic

(iii) Explain why you have placed the three compounds in this order.

.....

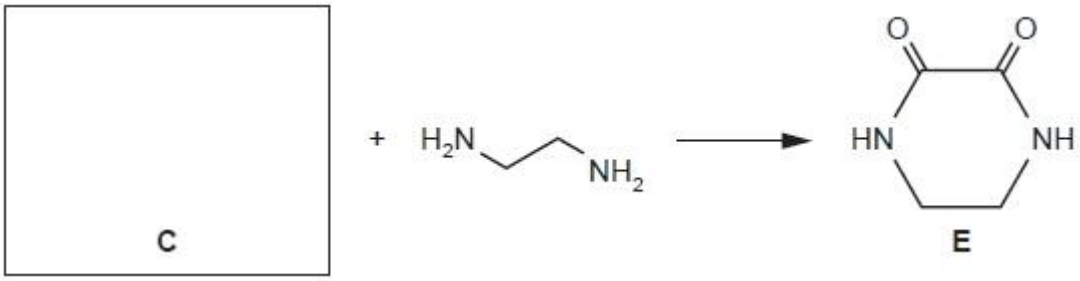
.....

.....

.....

[4]

Q# 434/ ALvl Chemistry/2010/s/TZ 1/Paper 4/Q# 6 /www.SmashingScience.org :o)



(ii) Suggest the major type of intermolecular interaction that occurs between **E** and water.

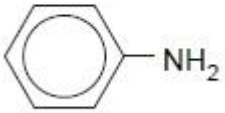
.....

(iii) A solution of the diamine $H_2NCH_2CH_2NH_2$ in water has pH = 11 but a solution of **E** in water has pH = 7. Suggest why this is the case.

.....

..... [2]

4 Ethanolamine and phenylamine are two organic bases that are industrially important. Ethanolamine is a useful solvent with basic properties, whilst phenylamine is an important starting material in the manufacture of dyes and pharmaceuticals.
The following table lists some of their properties, together with those of propylamine.

compound	formula	M_r	boiling point/°C	solubility in water
propylamine	$CH_3CH_2CH_2NH_2$	59	48	fairly soluble
ethanolamine	$HOCH_2CH_2NH_2$	61	170	very soluble
phenylamine		93	184	sparingly soluble

(a) Suggest why the boiling point of ethanolamine is much higher than that of propylamine. Draw a diagram to illustrate your answer.

.....

.....

[2]

(b) Describe and explain the relative basicities of propylamine and phenylamine.

.....

.....

.....[2]

(c) Write an equation showing ethanolamine acting as a Brønsted-Lowry base.

.....[1]

(e) Apart from their relative basicities, ethanolamine and phenylamine differ in many of their reactions.
For **each** of these two compounds, describe **one** test that would give a positive result with the stated compound, but a negative result with the other.

ethanolamine

test .....

observation .....

phenylamine

test .....

observation .....

[4]

[Total: 12]

Q# 436/ ALvl Chemistry/2009/w/TZ 1/Paper 4/Q# 5 /www.SmashingScience.org :o)

(e) 4-aminobenzoic acid, **E**, forms a zwitterion.

(i) What is meant by the term *zwitterion*?

.....

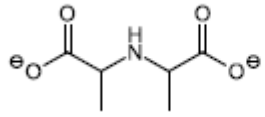
.....

(ii) Draw the structural formula of the zwitterion formed from 4-aminobenzoic acid.

[2]

Mark Scheme A Level Chem 34 EQ 22m to 09w **Paper 4** Nitrogen compounds 217marks

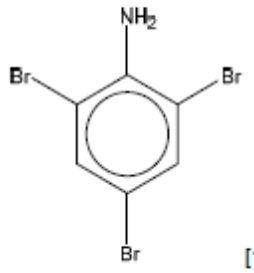
Q# 386/ ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 5 /www.SmashingScience.org :o)

5(c)(vi)		1

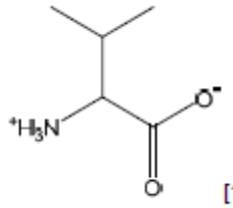
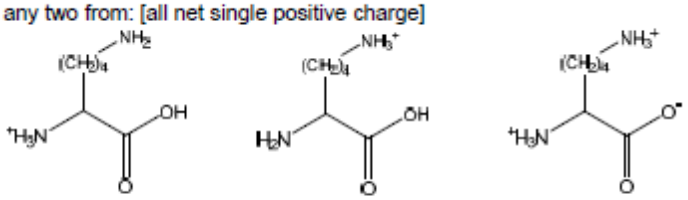
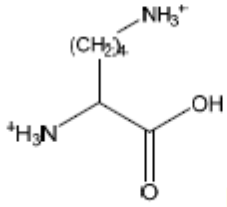
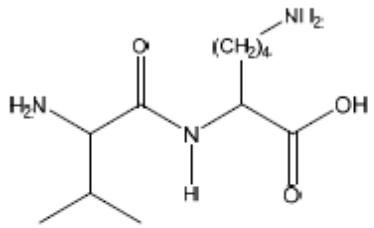
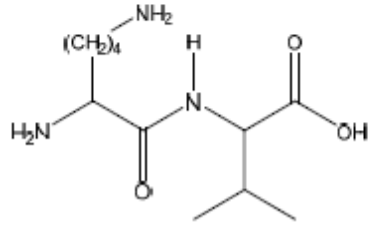
Q# 387/ ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 5 /www.SmashingScience.org :o)

5(a)(i)	$CH_3CHClCOOH + H_2O \rightleftharpoons CH_3CHClCOO^- + H_3O^+$ OR $CH_3CHClCOOH \rightleftharpoons CH_3CHClCOO^- + H^+$	1
5(a)(ii)	M1: $[H^+] = 10^{-1.51} = 0.0309$ (mol dm^{-3}) M2: $K_a = 0.0309^2/0.60 = 1.592 \times 10^{-3}$ ecf $pK_a = -\log 1.592 \times 10^{-3} = 2.80$ ecf	2

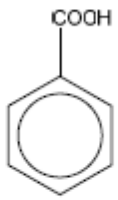
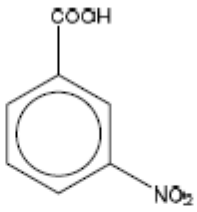
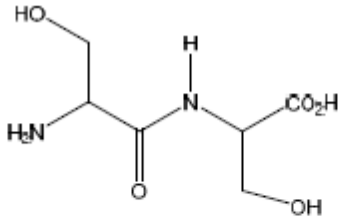
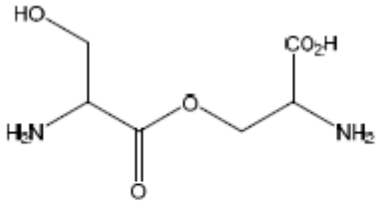
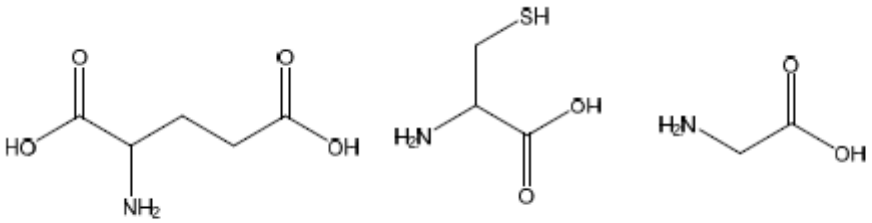
Q# 388/ ALvl Chemistry/2021/w/TZ 1/Paper 4/Q# 8 /www.SmashingScience.org :o)

8(a)	bromine decolourised OR orange / brown to colourless [1] white precipitate [1]	2
8(b)	no change [1]	1
8(c)	 [1]	1
8(d)	2,4,6-tribromophenylamine [1] ECF 8(c) for a bromophenylamine	1

Q# 389/ ALvl Chemistry/2021/w/TZ 1/Paper 4/Q# 10 /www.SmashingScience.org :o)

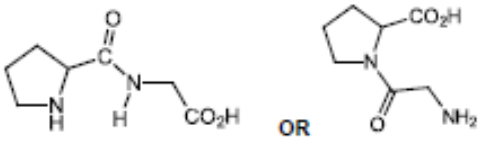
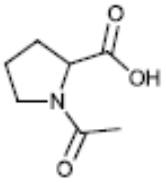
10(a)	 [1]	1
10(b)	A and B any two from: [all net single positive charge]  [1] × 2 C at pH 1.0 [2+ positive charge]  [1]	3
10(c)	M1: peptide link correct and displayed unit including C=O M2: everything else correct  OR  [2]	2

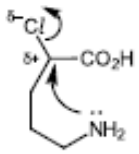
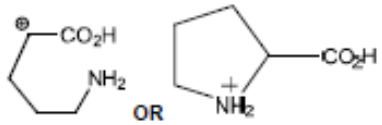
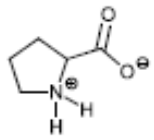
Q# 390/ ALvl Chemistry/2021/s/TZ 1/Paper 4/Q# 7 /www.SmashingScience.org :o)

7(a)(i)	M  N 	2
7(a)(ii)	**M1:** step 1 hot $KMnO_4$ / MnO_4^- **M2:** step 2 conc. H_2SO_4 and conc. HNO_3 **M3:** step 3 Sn and conc. HCl (heat)	3
7(b)(i)	  **M1 / M2:** each structure **M3:** both displayed linkage	3
7(b)(ii)	molecular formula: $C_9H_{19}N_3O_4$ — number of structural isomers formed: 4	1
7(c)(ii)	 one mark for two correct two marks for three correct	2

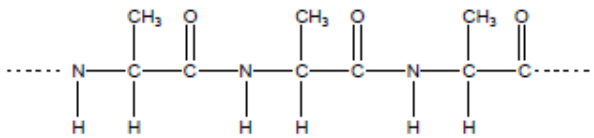
7(c)(iii) is [1] mark, but the mark scheme is not given in the published mark scheme. Only 12 marks for Q7 are accounted for in the mark scheme.

Q# 391/ ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 7 /www.SmashingScience.org :o)

7(a)(i)	 OR **M1:** peptide link shown **M2:** rest of Pro–Gly correct	2
7(a)(ii)	condensation **ALLOW** substitution / addition–elimination	1
7(b)(i)	$(C_4H_7NHCO_2H +)\ NaOH \rightarrow C_4H_7NHCO_2Na + H_2O$	1
7(b)(ii)	 skeletal only	1

7(b)(iii)	$LiAlH_4$	1
7(c)(i)	$CH_2(CO_2C_2H_5)_2$: • (di)ester CH_2=CHCN: • alkene • nitrile/cyanide All three correct for two marks	2
7(c)(ii)	addition	1
7(c)(iii)	H_2 / Ni **OR** H_2 / Pt **OR** H_2 / Pd	1
7(c)(iv)	condensation / (nucleophilic) substitution / elimination	1
7(c)(v)	ethanol / C_2H_5OH / CH_3CH_2OH	1
7(c)(vi)	 **M1/2**: All four correct: • lone pair on NH_2 • curly arrow from N: to C of C—Cl • correct dipole on C—Cl • curly arrow from C—Cl to Cl **M3**: intermediate = 	3
7(c)(vii)	Asterisk on *$CHCO_2H$	1
7(d)	9	1
7(e)(i)	**M1**:  **M2**: proton / H^+ transferred from carboxylic acid to amine	2
7(e)(ii)	 **M1**: glutamic acid towards + end (from the diagram) **M2**: proline and alanine towards – end (from the diagram) **M3**: Glu moves towards positive (pole) as negatively charged / contains a COO^- **OR** Pro/Ala move towards negative (pole) as positively charged / contains a NH_2^+ / contains a NH_3^+ **M4**: Ala moves farther than Pro because of lower M_r / size (with positive charge) ORA	4

Q# 392/ ALvl Chemistry/2020/w/TZ 1/Paper 4/Q# 10 /www.SmashingScience.org :o)

10(b)(i)	 • amide links displayed correct (NHCO OR CONH) • three monomers of Ala only • one repeat unit correctly identified • continuation bonds (with a polypeptide involving Ala only) mark as • ✓ ✓ ✓ [3]	3

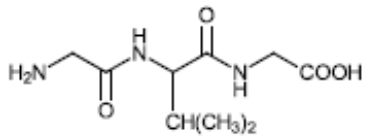
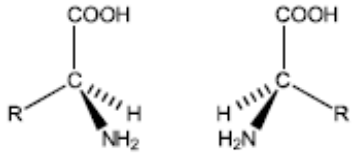
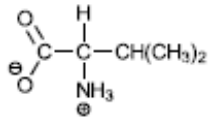
Q# 393/ ALvl Chemistry/2020/s/TZ 1/Paper 4/Q# 4 /www.SmashingScience.org :o)

4(a)	**M1** phenylmethanamine / **U** > phenylamine / **T** > benzamide / **S** [1] any two from: • alkyl group is electron donating so lone pair more able to accept a proton • lone pair on N overlaps with delocalised system so less able to accept a proton • presence of electron-withdrawing oxygen / carbonyl group means lone pair is not available to accept a proton OR amides are neutral	3

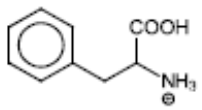
Q# 394/ ALvl Chemistry/2020/s/TZ 1/Paper 4/Q# 4 /www.SmashingScience.org :o)

4(b)(i)	reaction 1 $LiAlH_4$ reaction 2 heat NH_3 under pressure/ heat NH_3 in a sealed tube	2
4(b)(ii)	reaction 1 reduction reaction 2 nucleophilic substitution	2

Q# 395/ ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 6 /www.SmashingScience.org :o)

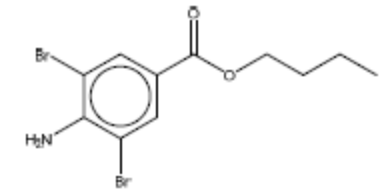
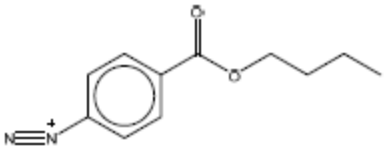
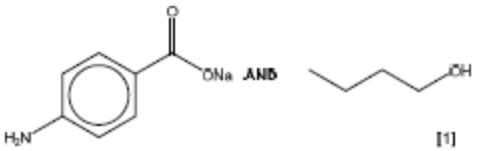
6(b)	 **M1** one peptide link fully displayed (but not contradicted by the other peptide link) **M2** rest of structure correct	2
6(c)(i)	**M1** optical isomerism **M2** 	2
6(c)(ii)		1

Q# 396/ ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 4 /www.SmashingScience.org :o)

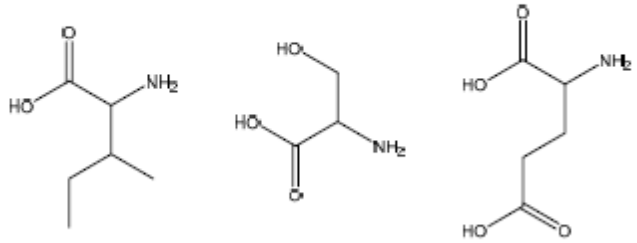
4(a)(i)	A = ester B = (2°) amide	2
4(a)(ii)	2	1
4(b)	 **M1** phenylalanine **M2** protonated amine **M3** (ethanol) CH_3CH_2OH	3
4(c)(i)	catalyst / halogen carrier	1
4(c)(ii)	**M1** —OH directs to 2,4 **AND** both 2 positions occupied / only position 4 is available **M2** —COOH directs to 3 position **AND** only position 3 is available / 5 is occupied	2
4(d)(i)	x = 14.4 / 100 × 100 / 1.1 = 13.1 13 carbon atoms (some working required)	1
4(d)(ii)	(250 – 205 = 45, so) CO_2H / C_2H_5O	1

Q# 397/ ALvl Chemistry/2019/w/TZ 1/Paper 4/Q# 9 /www.SmashingScience.org :o)

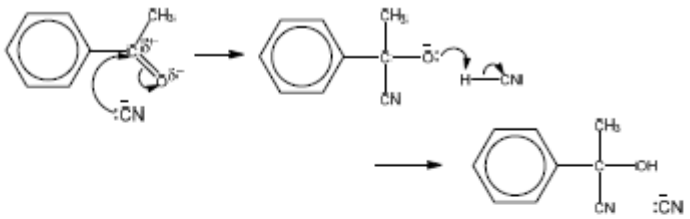
9(a)(i)	$RNH_2 + H^+ \rightarrow RNH_3^+$ OR $RNH_2 + HCl \rightarrow RNH_3Cl$ [1]	1
9(a)(ii)	weaker **AND** lone pair of N delocalised into benzene ring [1]	1

9(b)	 [1]  [1]  AND [1]	3

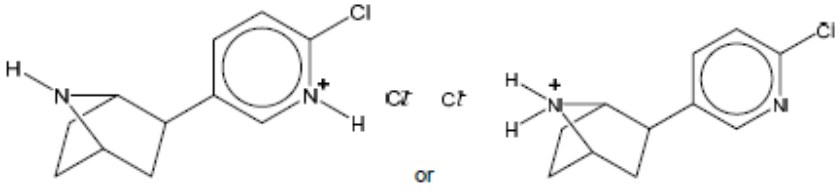
Q# 398/ ALvl Chemistry/2019/w/TZ 1/Paper 4/Q# 8 /www.SmashingScience.org :o)

8(a)(i)	any one from: • OH^- / NaOH; aqueous / dilute; heat under reflux • H^+ / HCl / H_2SO_4, aqueous / dilute; heat under reflux • protease or named protease; water; T = 30° – 40°C all three points in each bullet [1]	1
8(a)(ii)	 M1: three amino acids in any ionic / non-ionic states [1] M2: three amino acids in the correct ionic state for their conditions [1]	2

Q# 399/ ALvl Chemistry/2019/w/TZ 1/Paper 4/Q# 4 /www.SmashingScience.org :o)

4(c)(ii)	 **M1 and M2:** first structure – award one mark for two points correct, award two marks for four points correct. • correct polarity shown on C=O bond • curly arrow from double bond to O of the C=O • lone pair shown on C of CN^- ion • curly arrow from C (on CN^- ion) to C of C=O **M3:** middle structure • correct intermediate **AND** curly arrow from lone pair on O^- to H^+ or H of H_2O or HCN **M4**: third structure • correct product **AND** either CN^- reformed (if HCN seen in step 2) OR curly arrow on H-CN bond towards CN in step 2	4

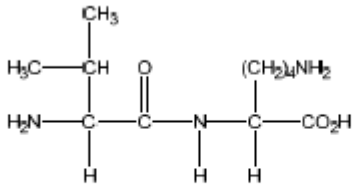
Q# 400/ ALvl Chemistry/2019/s/TZ 1/Paper 4/Q# 9 /www.SmashingScience.org :o)

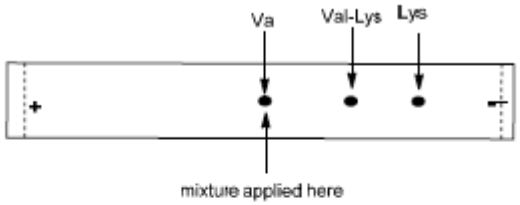
9(b)(i)	partially ionised **and** proton acceptor	1
9(b)(ii)		1

Q# 401/ ALvl Chemistry/2019/s/TZ 1/Paper 4/Q# 4 /www.SmashingScience.org :o)

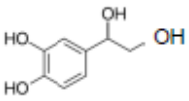
4(f)(i)	$CH_3COCl + CH_3NH_2 \rightarrow CH_3CONHCH_3 + HCl$ **M1** Correct formulae of CH_3COCl or $CH_3CONHCH_3$ **M2** rest of the equation	2
4(f)(ii)	condensation or addition-elimination	1

Q# 402/ ALvl Chemistry/2018/w/TZ 1/Paper 4/Q# 6 /www.SmashingScience.org :o)

6(a)	 **M1** amide bond displayed [1] **M2** rest of the structure [1]	2

6(b)	 **M1** valine on the cross [1] **M2** Val-Lys and Lys on the right of the cross (in any order) [1] **M3** relative order of Val-Lys and Lys (on the same side of the cross) [1] **Explanation** • Val does not move as it is a zwitterion / neutral (at pH6) OR Lys / Val-Lys move towards **negative** (pole) as they are **positively charged** • Lys moves the **furthest** as it has the **lowest** M_r (with the same positive charge) OR Val-Lys moves the **least** as it has the **largest** M_r (with the same positive charge) [1] × 2	5

Q# 403/ ALvl Chemistry/2018/s/TZ 1/Paper 4/Q# 9 /www.SmashingScience.org :o)

9(c)(i)	(phenyldiazonium ion is stabilised because) positive charge is delocalised by ring / positive charge is spread over ring	1
9(c)(ii)		1
	N_2	1

Q# 404/ ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 7 /www.SmashingScience.org :o)

7(b)(i)	$(RCO_2H + H_2NR' \longrightarrow) RCONHR' + H_2O$	1
7(b)(ii)	*broken:* C-O, N-H *formed:* C-N, O-H	2
7(b)(iii)	bonds formed: 305 + 460 or 765 bonds broken: 360 + 390 or 750 (both) $\Delta H = 750 - 765 = -15$ (kJ)	2
7(c)	(If $\Delta G = 0$, then) $\Delta H = T\Delta S$ $\Delta S = \Delta H / T = -6000 / 298 = -20.1$ ($J\ mol^{-1}\ K^{-1}$)	2

Q# 405/ ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 7 /www.SmashingScience.org :o)

7(d)(ii)	Sn and HCl heat + conc. (then add NaOH)	2

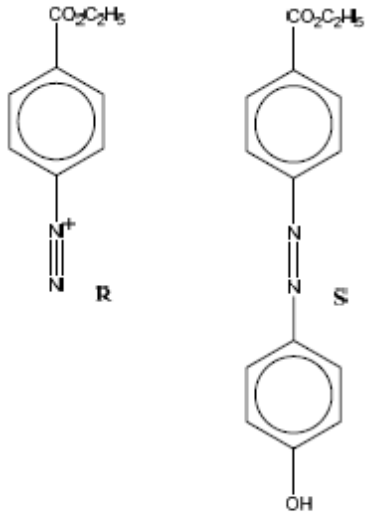
Q# 406/ ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 4 /www.SmashingScience.org :o)

4(b)(i)	nitrogen has a lone pair which can accept a proton or can be donated to a proton	1
4(b)(ii)	e.g. $C_4H_9NH_2 + HCl \rightleftharpoons C_4H_9NH_3^+ + Cl^-$ etc.	1
4(b)(iii)	butanamide is non-basic / neutral *or* (much) less basic than butylamine	1
4(b)(iv)	$LiAlH_4$ (in dry ether)	1

Q# 407/ ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 3 /www.SmashingScience.org :o)

3(a)(iv)	**A** is CH_3NH_2 **B** is HCO_2H	2

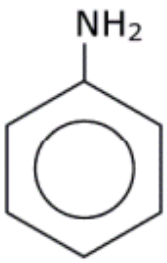
Q# 408/ ALvl Chemistry/2017/w/TZ 1/Paper 4/Q# 6 /www.SmashingScience.org :o)

6(e)(ii)		
	structure of diazonium salt **R**	1
	structure of azo dye **S**	1

Q# 409/ ALvl Chemistry/2017/w/TZ 1/Paper 4/Q# 6 /www.SmashingScience.org :o)

6(c)	(benzocaine) is less (basic than ethylamine) **AND** **lone pair** (on N) is less available to accept a proton / H^+ since (lone pair on N) is delocalised over the ring *or* phenyl ring is electron withdrawing group OR ethylamine is more basic (than benzocaine) **AND** **lone pair** (on N) is more available to accept a proton / H^+ since ethyl / alkyl group is electron-donating group	2

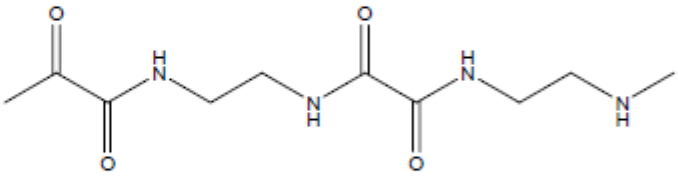
Q# 410/ ALvl Chemistry/2017/s/TZ 1/Paper 4/Q# 2 /www.SmashingScience.org :o)

2(e)(i)	$n(BaCO_3) = 1.66 / 197.3 = 8.4(1) \times 10^{-3}$ mol	1
2(e)(ii)	$n(RNCO) = 8.41 \times 10^{-3}$ mol, so $M_r = 1 / (8.41 \times 10^{-3}) = 119$	1
2(e)(iii)	molecular formula = C_7H_5NO	1
2(e)(iv)		1

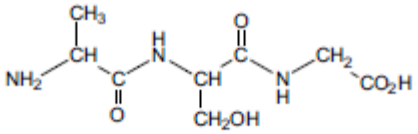
Q# 411/ ALvl Chemistry/2017/m/TZ 2/Paper 4/Q# 5 /www.SmashingScience.org :o)

5(b)	$C_{10}H_{13}NH_2 + H_3O^+ \rightleftharpoons C_{10}H_{13}NH_3^+ + H_2O$	1
5(c)	in compound **H**, the alkyl groups are electron donating / have a positive inductive effect, so it is more basic than NH_3	1
	in phenylamine, the lone pair (of N) is delocalised over the aryl group / benzene ring, so phenylamine is less basic than NH_3	1

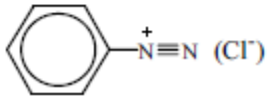
Q# 412/ ALvl Chemistry/2016/w/TZ 1/Paper 4/Q# 1 /www.SmashingScience.org :o)

1(e)(i)	lone pair receive / accepts a proton / H^+	1 1 2
1(e)(ii)	$H_2NCH_2CH_2NH_2 + 2HCl \rightarrow ClH_3NCH_2CH_2NH_3Cl$ OR $H_2NCH_2CH_2NH_2 + 2H^+ \rightarrow H_3N^+CH_2CH_2N^+H_3$	1 1
1(f)(i)	amide bond, displayed or –CONH– rest of the molecule with continuation bonds 	1 1 2
1(f)(ii)	condensation / addition – elimination	1 1
1(f)(iii)	any named polyalkene / eg polyethene, PVC allow Bakelite or Kevlar	1 1
	Total:	20

Q# 413/ ALvl Chemistry/2016/s/TZ 1/Paper 4/Q# 7 /www.SmashingScience.org :o)

7 (a) (i)		[2]
(ii)	$M_r = 233$	[1]
(b) (i)	$NH_2CH(CH_2OH)CO_2^-$	[1]
(ii)	**F** is a DC power supply **G** is the anode OR positive electrode **I** is the cathode OR negative electrode **H** is filter paper (OR gel) soaked in **buffer** solution	[4]
(iii)	**P** is $NH_2CH_2CO_2^-$ *or* $NH_2CH_2CO_2H$ *or* glycine **S** is [ala–ser–gly]$^{(-)}$ glycine is the smallest, so travels fastest; tripeptide is the largest, so travels slowest	[1] [1] [1]
(c) (i)	heat with H_3O^+ OR heat with $OH^-(aq)$	[1]
(ii)	hydrolysis	[1]
		[Total: 13]

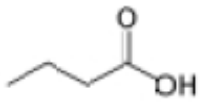
Q# 414/ ALvl Chemistry/2016/s/TZ 1/Paper 4/Q# 6 /www.SmashingScience.org :o)

6	(a) (i)	$C_6H_5NO_2 + 6e^- + 6H^+ \longrightarrow C_6H_5NH_2 + 2H_2O$	[1]
	(ii)	$2C_6H_5NO_2 + 14HCl + 3Sn \rightarrow 2C_6H_5NH_3Cl + 3SnCl_4 + 4H_2O$	[2]
	(b)	(M_r values: $C_6H_5NO_2$ = 123 $C_6H_5NH_3Cl$ = 129.5) theoretical yield = 5.0 × 129.5/123 = 5.26 g percentage yield = 100 × 4.2/5.26 = 79.8% (80%)	[1] [1]
	(c) (i)	$C_6H_5NH_2$ = 93 yield of phenylamine = 4.2 × 93/129.5 = 3.016 g	[1]
	(ii)	mass left in water = 3.016 – 2.68 = 0.336 g K_{part} = (2.68/50) / (0.336/25) = 3.99	[1] [1]
	(d)	phenylamine is less basic that ethylamine the lone pair on N is delocalised over the ring… …making it less available for reaction with a proton / δ+ H	[2]
	(e) (i)	step 1: HNO_2 OR ($NaNO_2$ + HCl) at $T \leqslant 10\,°C$ step 2: boil / heat in water	[1] [1]
	(ii)	**E** is 	[1]

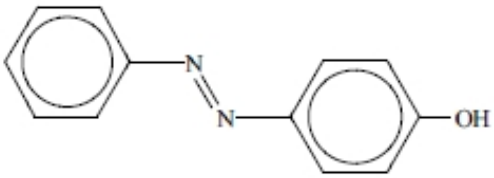
Q# 415/ ALvl Chemistry/2016/m/TZ 2/Paper 4/Q# 9 /www.SmashingScience.org :o)

(c) (i)	**V:** it has two amine / NH_2 groups (which can be protonated) *or* it has an amine / NH_2 group on its side chain / R group	**1**
(ii)	four (TT, TU, UT, UU)	**1**

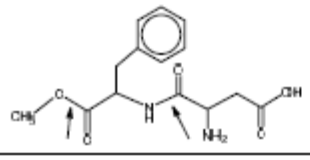
Q# 416/ ALvl Chemistry/2016/m/TZ 2/Paper 4/Q# 8 /www.SmashingScience.org :o)

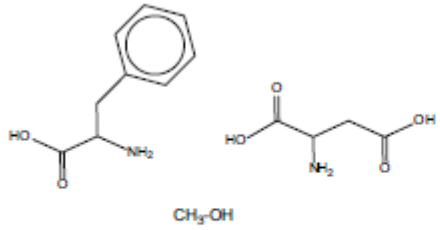
(c) (i)	see line on diagram in **(b)**	**1**
(ii)		**1**

Q# 417/ ALvl Chemistry/2016/m/TZ 2/Paper 4/Q# 7 /www.SmashingScience.org :o)

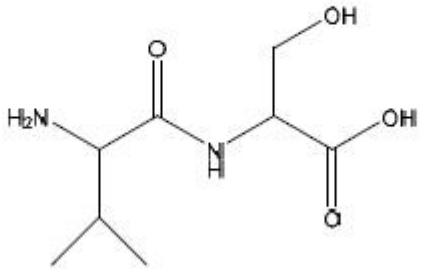
(b) (i)	white precipitate / solid	**1**
(ii)	between 0° C and 10 °C	**1**
(iii)	**M1**: double bond between nitrogen atoms **M2**: rest of molecule 	**1** **1**

Q# 418/ ALvl Chemistry/2015/w/TZ 1/Paper 4/Q# 10 /www.SmashingScience.org :o)

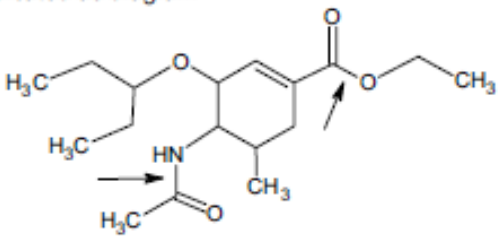
(ii)		**2**

(iii)		3
(b)	M1: hydrogen bonding M2: between the NH_2 groups and water **or** CO_2/C=O/–OH groups and water (allow names) **or** lone pair on N/O with water	2

Q# 419/ ALvl Chemistry/2015/s/TZ 1/Paper 4/Q# 8 /www.SmashingScience.org :o)

8 (a) (i)	condensation	1
(ii)		2

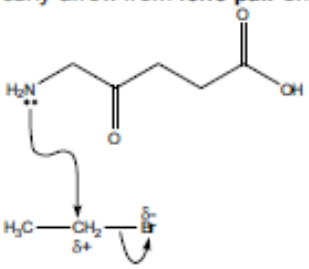
Q# 420/ ALvl Chemistry/2014/w/TZ 1/Paper 4/Q# 7 /www.SmashingScience.org :o)

7 (a)	amide group circled **OR** indicated as diagram ester group circled **OR** indicated as diagram 	1 1	[2]

Q# 421/ ALvl Chemistry/2014/w/TZ 1/Paper 4/Q# 6 /www.SmashingScience.org :o)

6 (a)	• (move in different directions) some amino acids have a different charge • (move at different speeds) some amino acids have a different size/different charge • (some amino acids do not move at all) some amino acids exist as a zwitterions/have no net(overall) charge/neutral/both NH_2/COOH are charged in amino acids	1 1 1	[3]

Q# 422/ ALvl Chemistry/2014/w/TZ 1/Paper 4/Q# 5 /www.SmashingScience.org :o)

(c) (i)	dipole on C-Br curly arrow breaking C-Br bond curly arrow from **lone pair** on N to carbon in C-Br bond 	1 1 1	
(ii)	nucleophilic substitution	1	
(iii)	HBr or hydrogen bromide	1	[5]

Q# 423/ ALvl Chemistry/2014/s/TZ 1/Paper 4/Q# 3 /www.SmashingScience.org :o)

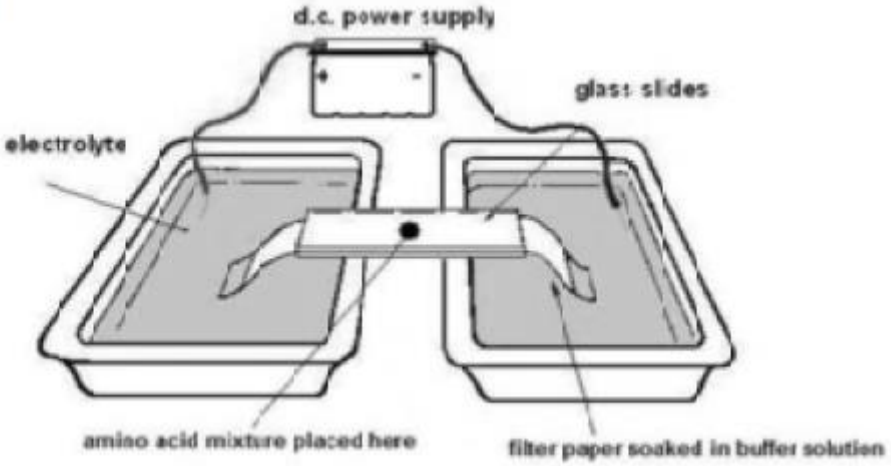
3 (a) heat in dilute HCl(aq) (or H_2SO_4(aq)) [1]

Q# 424/ ALvl Chemistry/2014/s/TZ 1/Paper 4/Q# 3 /www.SmashingScience.org :o)

(iv) piperidine should be a **stronger base/more basic** than ammonia because of the electron-donating (alkyl/CH_2) groups [1]

Q# 425/ ALvl Chemistry/2013/w/TZ 1/Paper 4/Q# 7 /www.SmashingScience.org :o)

7 (a)



power supply (idea of complete circuit)
electrolyte/buffer solution
gel/filter paper/absorbent paper
(amino acid) sample/mixture [centre of plate] 4 × [1]

[4]

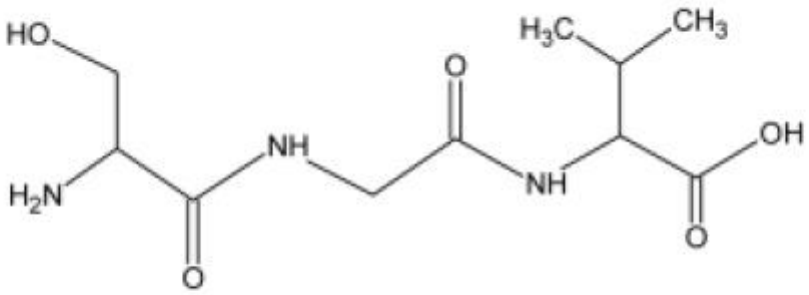
(b) *any two from:*
size/M_r (of the amino acid species)
charge (on the amino acid species)
temperature 2 × [1]

[2]

Q# 426/ ALvl Chemistry/2013/w/TZ 1/Paper 4/Q# 6 /www.SmashingScience.org :o)

6 (a) (i) **six/6** (gsv, sgv, gvs, vgs, svg,vsg) [1]

(ii)



two **displayed** peptide bonds [1]
correct formula of peptide [1]

(iii) valine (**allow** glycine) [1]

Q# 427/ ALvl Chemistry/2013/s/TZ 1/Paper 4/Q# 4 /www.SmashingScience.org :o)

(c) (base is a) proton acceptor [1]

basicities: ethylamine > NH_3 > phenylamine [1]

ethylamine (more basic) due to electron donating ethyl group [1]

phenylamine (less basic) due to lone pair being delocalised into the ring [1]
[4]

Q# 428/ ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 8 /www.SmashingScience.org :o)

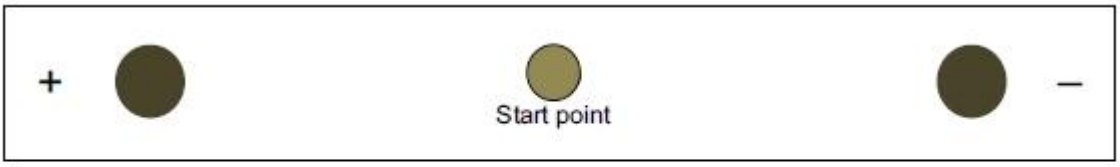
(c)

Addition OR	**condensation**
requires C=C/double bond	does not need C=C/double bond
uses the same functional group	needs two different functional groups
same general (empirical) formula as monomer	different formula
no loss of small molecule/H_2O/HCl	small molecule /H_2O/HCl is formed

Any two differences [1]
[2]

Q# 429/ ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 7 /www.SmashingScience.org :o)

7 (a)



Glutamic acid Glycine Lysine

Glutamic acid between + and start point [1]
Lysine between – and start point [1]
Glycine at, or *very* close to, start point [1]
[3]

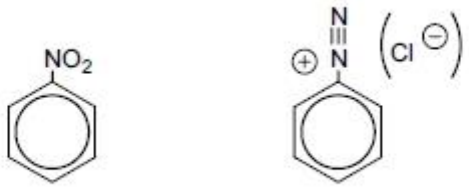
Q# 430/ ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 6 /www.SmashingScience.org :o)

6 (a) (i) Condensation [1]

(ii) ala-ala, gly-gly, ala-gly [2]
[3]

Q# 431/ ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 5 /www.SmashingScience.org :o)

(b) (i)



D **E**

[1] + [1]

(ii) step 2: Sn + HC*l* conc. + reflux **NOT** $LiAlH_4$, $NaBH_4$ *(warm is insufficient)* [1] [1]

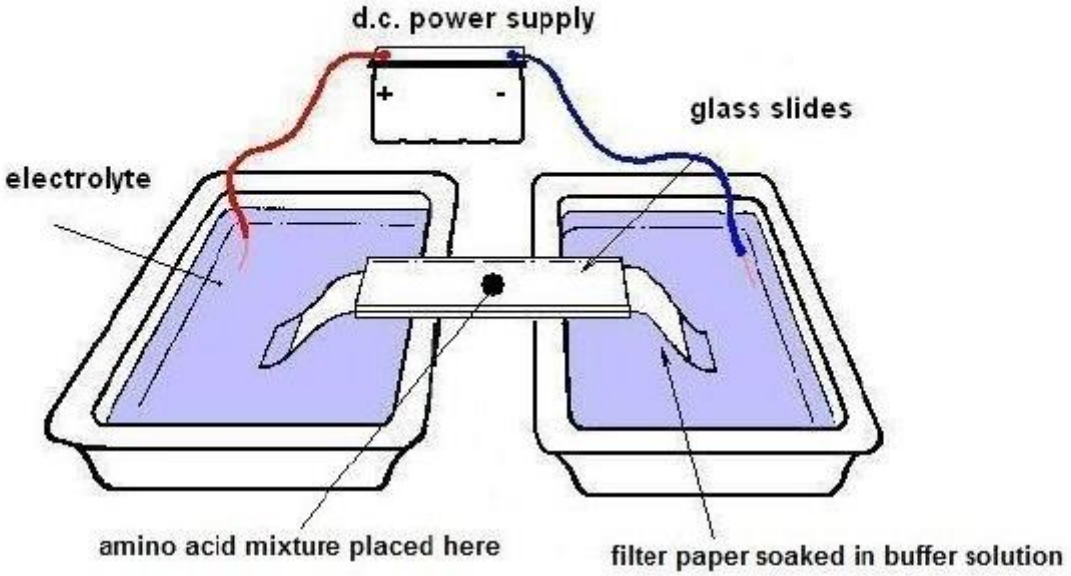
step 4 is conditional of structure E

step 4: warm + in H_2O [1]

[5 max 4]

Q# 432/ ALvl Chemistry/2011/w/TZ 1/Paper 4/Q# 7 /www.SmashingScience.org :o)

7 **(a)** Sketch and label the apparatus used to carry out electrophoresis e.g



Marks: power supply / electrolyte + filter paper / buffer / acid mixture central 4 × [1]

[4]

(b) (i) pH of the buffer [1]

Charge on the amino acid species [1]

(ii) Size of the amino acid species / M_r [1]

Voltage applied [1]

Magnitude of the charge (on the amino acid species) [1]

Temperature [1]

(max 3)

[max 3]

Q# 433/ ALvl Chemistry/2011/w/TZ 1/Paper 4/Q# 4 /www.SmashingScience.org :o)

4 (a) (i) $C_2H_5NH_2 + HA \rightarrow C_2H_5NH_3^+ + A^-$ (HA can be H_2O, HC*l* etc.) [1]
Allow $\rightleftharpoons$ instead of arrow

(ii)

most basic		least basic
ethylamine	**ammonia**	**phenylamine**

[1]

(iii) ethylamine > NH_3 due to electron-donating ethyl/alkyl group [1]
phenylamine < NH_3 due to delocalisation of lone pair over ring [1]
[4]

Q# 434/ ALvl Chemistry/2010/s/TZ 1/Paper 4/Q# 6 /www.SmashingScience.org :o)

(ii) hydrogen bonding (1)

(iii) because it's an amide *or* not an amine *or* its lone pair is delocalised (over C=O) or less
available due to electronegative oxygen [NOT: **E** is neutral, but the diamine is basic] (1)

Q# 435/ ALvl Chemistry/2010/s/TZ 1/Paper 4/Q# 4 /www.SmashingScience.org :o)

4 (a) hydrogen bonding (1)

diag: $NH_2CH_2CH_2OH$---$OHCH_2CH_2NH_2$ *or* $NH_2CH_2CH_2OH$---$NH_2CH_2CH_2OH$
(i.e. H-bond from OH group to either OH or NH_2) (1) [2]

(b) propylamine is more basic than phenylamine (1)
because lone pair on N is delocalised over ring in phenylamine (so less available for protonation)
or the propyl group is electron-donating, so the lone pair is more available (1) [2]

(c) $HOCH_2CH_2NH_2 + H^+ \longrightarrow HOCH_2CH_2NH_3^+$
or $HOCH_2CH_2NH_2 + HCl \longrightarrow HOCH_2CH_2NH_3^+Cl^-$
or $HOCH_2CH_2NH_2 + H_2O \longrightarrow HOCH_2CH_2NH_3^+OH^-$
(reaction with any acceptable Bronsted acid accepted) [1]

(e) ethanolamine:

	Na		effervescence / bubbles produced
or	$Cr_2O_7^{2-} / H^+$		colour turns from orange to green
or	MnO_4^- / H^+		purple colour disappears
or	PCl_3 / PCl_5 / $SOCl_2$	(1)	steamy fumes (1)

phenylamine:

	Br_2(aq)		decolourises / white ppt formed
or	HNO_2 / H^+ at T<10°C, then phenol in NaOH	(1)	coloured dye formed (1) [4]

Q# 436/ ALvl Chemistry/2009/w/TZ 1/Paper 4/Q# 5 /www.SmashingScience.org :o)

(e) (i) A species having positive and negative ionic centres / charges, with no overall charge [1]

(ii) $-O_2C-C_6H_4-NH_3^+$ [1]
[2]