Cambridge Assessment
International Education

Cambridge International AS & A Level

CANDIDATE NAME	

CENTRE NUMBER		CANDIDATE NUMBER	

6430441026

CHEMISTRY **9701/42**

Paper 4 A Level Structured Questions **February/March 2021**

2 hours

You must answer on the question paper.

You will need: Data booklet

INSTRUCTIONS

- Answer **all** questions.
- Use a black or dark blue pen. You may use an HB pencil for any diagrams or graphs.
- Write your name, centre number and candidate number in the boxes at the top of the page.
- Write your answer to each question in the space provided.
- Do **not** use an erasable pen or correction fluid.
- Do **not** write on any bar codes.
- You may use a calculator.
- You should show all your working, use appropriate units and use an appropriate number of significant figures.

INFORMATION

- The total mark for this paper is 100.
- The number of marks for each question or part question is shown in brackets [ ].

This document has **28** pages. Any blank pages are indicated.

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

1 **(a)** The most common oxidation states of cobalt are +2 and +3.

Complete the electronic configurations of the following free ions.

- Co^{2+} [Ar] ....
- Co^{3+} [Ar] ....

[1]

(b) Co^{2+} and Co^{3+} both form complexes with $edta^{4-}$.

half-equation	$E^{\ominus}/V$
$Co^{3+} + e^- \rightleftharpoons Co^{2+}$	+1.82
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23
$[Co(edta)]^- + e^- \rightleftharpoons [Co(edta)]^{2-}$	+0.38
$Co^{2+} + 2e^- \rightleftharpoons Co$	–0.28

Use the data in the table to predict what happens, if anything, when separate aqueous solutions of Co^{3+} and $[Co(edta)]^-$ are left to stand in the air.

aqueous solution of Co^{3+}

....

....

aqueous solution of $[Co(edta)]^-$

....

....

[3]

(c) Hydrated cobalt(II) nitrate, $Co(NO_3)_2•6H_2O$, is a red solid that behaves like hydrated magnesium nitrate, $Mg(NO_3)_2•6H_2O$, when heated.

Describe in detail what you would expect to observe when crystals of $Co(NO_3)_2•6H_2O$ are heated in a boiling tube, gently at first and then more strongly.

....

....

....

.... [2]

(d) Explain why the thermal stability of the Group 2 nitrates increases down the group.

....

....

....

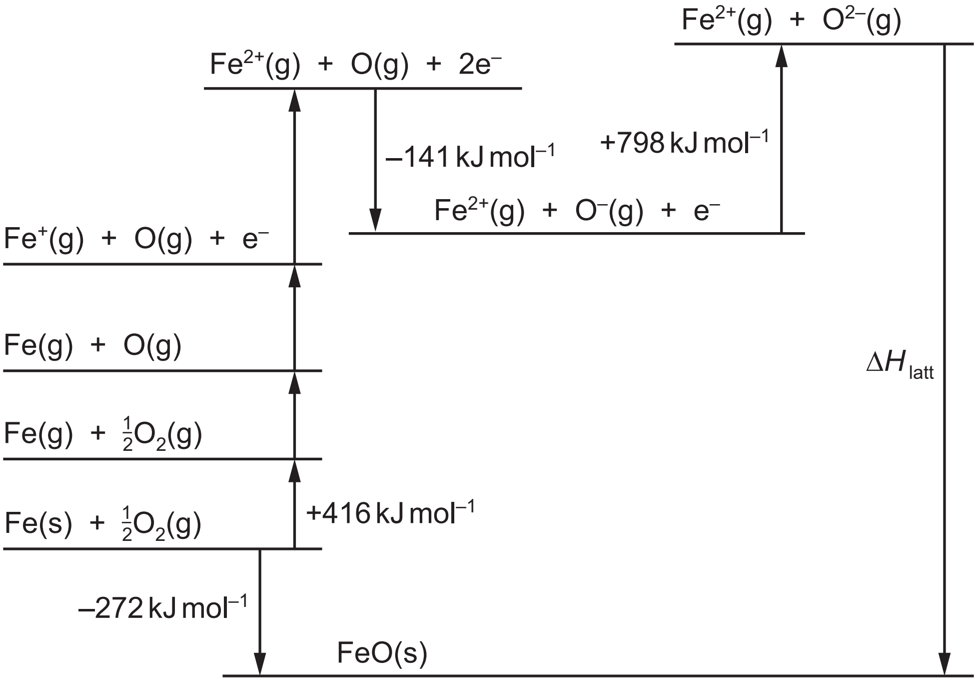
.... [2]

[Total: 8]

2 **(a)** Iron(II) compounds are generally only stable in neutral, non-oxidising conditions.

It is difficult to determine the lattice energy of FeO experimentally.

(i) Use data from the *Data Booklet* and this Born–Haber cycle to calculate the lattice energy, ΔH_{latt}, of FeO(s) in kJ mol^{-1}.



ΔH_{latt}FeO(s) = ... kJ mol^{-1} [2]

(ii) Most naturally occurring samples of iron(II) oxide are found as the mineral wüstite.

Wüstite has formula $Fe_{20}O_x$. It contains both Fe^{2+} and Fe^{3+} ions.

90% of the iron is present as Fe^{2+} and 10% is present as Fe^{3+}.

Deduce the value of *x*.

x = ... [1]

(iii) State and explain how the lattice energy of FeO(s) compares to the lattice energy of CaO(s).

....

....

....

....

.... [2]

(b) Heating of FeO results in the formation of Fe_3O_4, as shown.

reaction 1 $4FeO \rightarrow Fe + Fe_3O_4$

Each formula unit of Fe_3O_4 contains one Fe^{2+} and two Fe^{3+} ions.

(i) Show how reaction 1 can be described as a disproportionation reaction.

....

....

.... [1]

Fe_3O_4(l) can be electrolysed using inert electrodes to form Fe.

(ii) Write the half-equation for the reaction that occurs at the anode during the electrolysis of Fe_3O_4(l).

.... [1]

(iii) Calculate the maximum mass of iron metal formed when Fe_3O_4(l) is electrolysed for six hours using a current of 50 A.

Assume the one Fe^{2+} and two Fe^{3+} ions are discharged at the same rate.

mass of iron = ... g [3]

(c) $LiFePO_4$ can be used in lithium-ion rechargeable batteries.

When the cell is charging, lithium reacts with a graphite electrode to form LiC_6.

When the cell is discharging, the half-equations for the two processes that occur are as follows.

anode half-equation $LiC_6 \rightarrow 6C + Li^+ + e^-$

cathode half-equation $Li^+ + FePO_4 + e^- \rightarrow LiFePO_4$

(i) State one possible advantage of developing cells such as lithium-ion rechargeable batteries.

.... [1]

(ii) Use the cathode half-equation to determine the change, if any, in oxidation states of lithium and iron at the **cathode** during discharging.

metal	change in oxidation state during discharging	
	from	to
lithium		
iron		

[1]

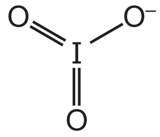
(iii) Write the equation for the overall reaction that occurs when this cell is discharging.

.... [1]

[Total: 13]

3 Iodates are compounds that contain the IO_3^- anion.

(a) The IO_3^- anion is shown.



Explain, with reference to the qualitative model of electron-pair repulsion, why the IO_3^- anion has a pyramidal shape.

....

....

.... [1]

(b) The reaction of iodine and hot aqueous sodium hydroxide is similar to that of chlorine and hot aqueous sodium hydroxide. Sodium iodate, $NaIO_3$, is formed as one of the products.

Suggest an equation for the reaction of iodine and hot aqueous sodium hydroxide.

.... [1]

(c) The decomposition of hydrogen peroxide, H_2O_2, is catalysed by acidified IO_3^-.

H_2O_2 reduces acidified IO_3^- as shown.

$$5H_2O_2 + 2H^+ + 2IO_3^- \rightarrow I_2 + 5O_2 + 6H_2O$$

This reaction is followed by the oxidation of I_2 by H_2O_2.

half-equation	$E^\ominus$/V
$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	+1.77
$IO_3^- + 6H^+ + 5e^- \rightleftharpoons \frac{1}{2}I_2 + 3H_2O$	+1.19
$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2$	+0.68

(i) Use the data to show that the separate reactions of H_2O_2 with IO_3^- and with I_2 are both feasible under standard conditions.

In your answer, give the equation for the reaction of H_2O_2 with I_2.

....

....

....

....

....

.... [3]

(ii) Write the overall equation for the decomposition of H_2O_2 catalysed by acidified IO_3^-.

.... [1]

(d) A student collects some data for the reaction of H_2O_2 with acidified IO_3^-, as shown in the table.

experiment	$[H_2O_2]$ / mol dm^{-3}	$[IO_3^-]$ / mol dm^{-3}	$[H^+]$ / mol dm^{-3}	initial rate of reaction / mol dm^{-3} s^{-1}
1	0.0500	0.0700	0.025	1.47×10^{-5}
2	0.100	0.0700	0.050	2.94×10^{-5}
3	0.100	0.140	0.025	5.88×10^{-5}
4	0.150	0.140	0.025	8.82×10^{-5}

(i) Use the data to determine the order of reaction with respect to $[H_2O_2]$, $[IO_3^-]$ and $[H^+]$.

Show your reasoning.

order with respect to $[H_2O_2]$ = ...

....

....

....

order with respect to $[IO_3^-]$ = ...

....

....

....

order with respect to $[H^+]$ = ...

....

....

....

[3]

(ii) Use your answer to **(d)(i)** to write the rate equation for this reaction.

rate = ... [1]

(iii) Calculate the value of the rate constant, k, using data from experiment 4 and your answer to **(d)(ii)**.

Give the units of k.

k = ...

units = ...
[2]

(e) $Pb(IO_3)_2$ is only sparingly soluble in water at 25 °C.

The solubility product, K_{sp}, of $Pb(IO_3)_2$ is $3.69 \times 10^{-13}\,mol^3\,dm^{-9}$ at 25 °C.

(i) Write an expression for the solubility product of $Pb(IO_3)_2$.

K_{sp} =

[1]

(ii) Calculate the solubility, in $mol\,dm^{-3}$, of $Pb(IO_3)_2$ at 25 °C.

solubility = ... $mol\,dm^{-3}$ [2]

(f) NH_4IO_3 is an unstable compound that readily decomposes when warmed. The decomposition reaction is shown.

$$NH_4IO_3(s) \rightarrow \tfrac{1}{2}N_2(g) + \tfrac{1}{2}O_2(g) + \tfrac{1}{2}I_2(g) + 2H_2O(l) \qquad \Delta H = -154.6\,kJ\,mol^{-1}$$

(i) Use the data in the table to calculate the entropy change of reaction, ΔS, of the decomposition of $NH_4IO_3(s)$.

compound	S / J K^{-1} mol^{-1}
$NH_4IO_3(s)$	42
$N_2(g)$	192
$O_2(g)$	205
$I_2(g)$	261
$H_2O(l)$	70

ΔS = ... J K^{-1} mol^{-1} [2]

(ii) This reaction is feasible at all temperatures.

Explain why, using the data in **(f)** and your answer to **(f)(i)**.

....

....

.... [1]

[Total: 18]

4 The transition elements are able to form stable complexes with a wide range of molecules and ions.

(a) State the meaning of *transition element*.

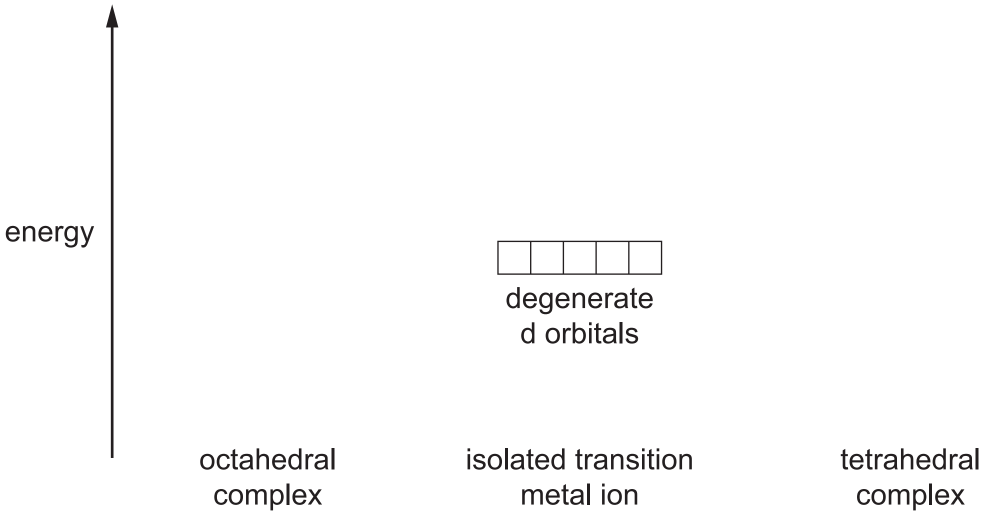
....

....

.... [1]

(b) The d orbitals in an isolated transition metal ion are degenerate. In complexes, the d orbitals occupy two energy levels.

(i) Complete the diagram to show the arrangement of d orbital energy levels in octahedral and in tetrahedral complexes.

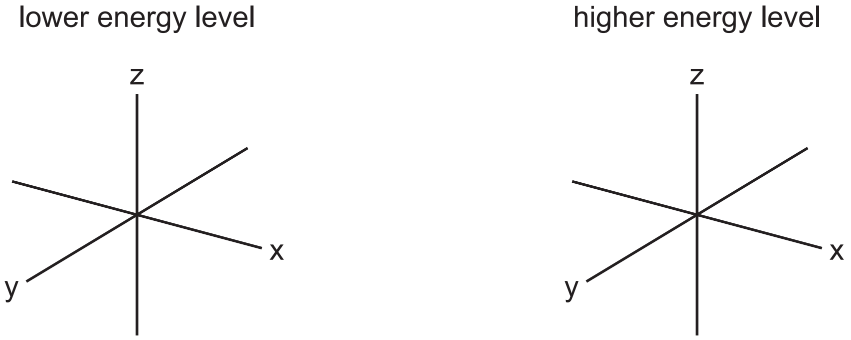


[1]

(ii) Sketch the shape of **two** d orbitals:

- one d orbital from the lower energy level in an octahedral complex
- one d orbital from the higher energy level in an octahedral complex.

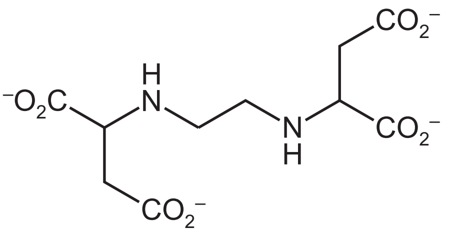
Use the axes below.



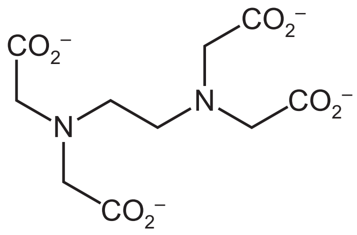
[2]

(c) Edds^{4-} and edta^{4-} are polydentate ligands that form octahedral complexes with Fe^{3+}(aq).

edds^{4-}



edta^{4-}



The formulae of the complexes are [Fe(edds)]$^-$ and [Fe(edta)]$^-$ respectively.

(i) On the diagram of edds^{4-}, circle each atom that forms a bond to the Fe^{3+} ion in [Fe(edds)]$^-$. [1]

(ii) [Fe(edds)]$^-$ is red and [Fe(edta)]$^-$ is yellow.

Explain why the two complexes have different colours.

....

....

....

....

.... [2]

(iii) When edds^{4-}(aq) is added to Fe^{3+}(aq), the following reaction occurs.

$$[Fe(H_2O)_6]^{3+}(aq) + edds^{4-}(aq) \rightleftharpoons [Fe(edds)]^{-}(aq) + 6H_2O(l)$$

State the type of reaction that occurs.

.... [1]

(iv) Write an expression for the stability constant, K_{stab}, of $[Fe(edds)]^-(aq)$.

K_{stab} =

[1]

(v) The table shows the values for the stability constants, K_{stab}, of both complexes.

complex	K_{stab} / $mol^{-1}\,dm^3$
$[Fe(edds)]^-$	3.98×10^{20}
$[Fe(edta)]^-$	1.26×10^{25}

Predict which of the $[Fe(edds)]^-$ and $[Fe(edta)]^-$ complexes is more stable.

Explain your answer with reference to the K_{stab} value for each complex.

....

....

.... [1]

(vi) When an excess of $edta^{4-}(aq)$ is added to $[Fe(edds)]^-(aq)$, the following equilibrium is established.

$$[Fe(edds)]^-(aq) + edta^{4-}(aq) \rightleftharpoons [Fe(edta)]^-(aq) + edds^{4-}(aq)$$

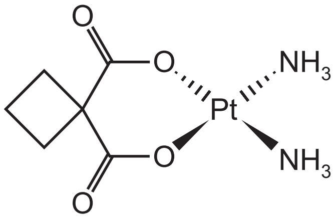
Calculate the equilibrium constant, K_c, for this equilibrium, using the K_{stab} values given in the table in **(c)(v)**.

K_c = ... [1]

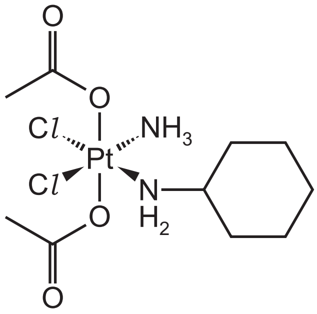
[Total: 11]

5 **(a)** Carboplatin and satraplatin are used as anticancer drugs instead of cisplatin.

carboplatin



satraplatin



(i) Describe the action of cisplatin as an anticancer drug.

....

....

.... [2]

(ii) Suggest the geometry of the platinum centre in the carboplatin complex.

.... [1]

(iii) Suggest why carboplatin does **not** show cis-trans isomerism.

....

....

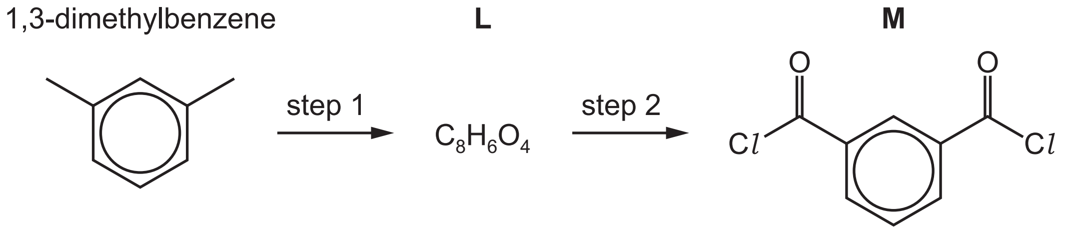
.... [1]

(iv) Satraplatin is a neutral complex, containing the ligands $CH_3CO_2^-$, $C_6H_{11}NH_2$, Cl^- and NH_3.

Deduce the oxidation state of platinum in satraplatin.

.... [1]

(b) Compound **M** is made from 1,3-dimethylbenzene in a two-step synthesis.



(i) Draw the structure of **L**.

[1]

(ii) Suggest reactants and conditions for each step of this synthesis.

step 1 ....

step 2 ....
[2]

(iii) Write an equation for step 2.

.... [1]

(iv) A student investigates a possible synthesis of **M** directly from benzene using $COCl_2$ in the presence of an $AlCl_3$ catalyst.

Benzene initially reacts with $COCl_2$ as shown.

reaction 1 $COCl_2 + AlCl_3 \rightarrow AlCl_4^- + Cl{-}\overset{+}{C}{=}O$

reaction 2 $C_6H_6 + Cl{-}\overset{+}{C}{=}O \rightarrow C_6H_5COCl + H^+$

Reaction 2 is the electrophilic substitution of $Cl{-}\overset{+}{C}{=}O$ for H^+ in benzene.

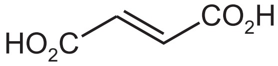
Suggest a mechanism for reaction 2.

[3]

[Total: 12]

6 Fumaric acid is a naturally occurring dicarboxylic acid.

fumaric acid



(a) Identify the products of the reaction between fumaric acid and an excess of hot, concentrated, acidified manganate(VII).

.... [1]

(b) Fumaric acid can form addition and condensation polymers.

(i) Draw the repeat unit of the addition polymer poly(fumaric acid).

[1]

(ii) Draw the repeat unit of the polyester formed when fumaric acid reacts with ethane-1,2-diol, $(CH_2OH)_2$.

The ester bond should be shown fully displayed.

[2]

(iii) Explain why polyesters normally biodegrade more readily than polyalkenes.

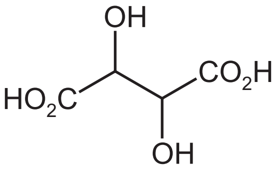
....

....

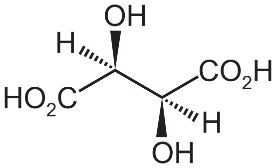
.... [1]

(c) Fumaric acid reacts with cold, dilute, acidified manganate(VII) to form compound **P**.

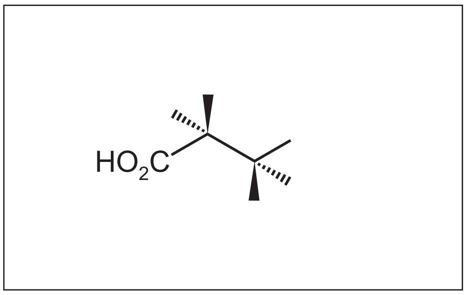
P

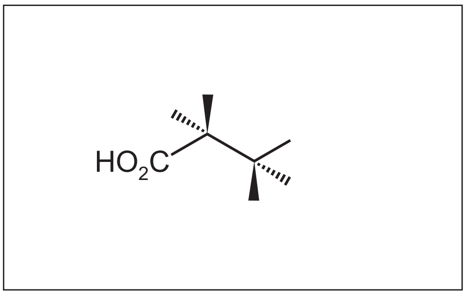


Only three stereoisomers of **P** exist. One of the stereoisomers is shown.



Complete the three-dimensional diagrams in the boxes to show the **other** two stereoisomers of **P**.





[2]

(d) The enzyme fumarase catalyses the reaction of fumarate ions, $C_4H_2O_4^{2-}$, with water to form malate ions, $C_4H_4O_5^{2-}$.

$$C_4H_2O_4^{2-} + H_2O \rightleftharpoons C_4H_4O_5^{2-}$$

Describe, with the aid of a suitably labelled diagram, how an enzyme such as fumarase can catalyse a reaction.

....

....

....

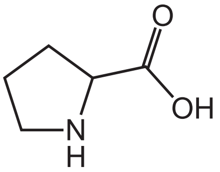
....

[3]

[Total: 10]

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.

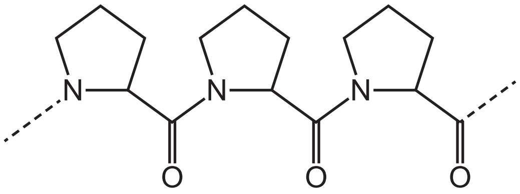
[2]

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

.... [1]

(iii) Proline is able to form a poly(proline) peptide chain.

A section of a poly(proline) chain is shown.

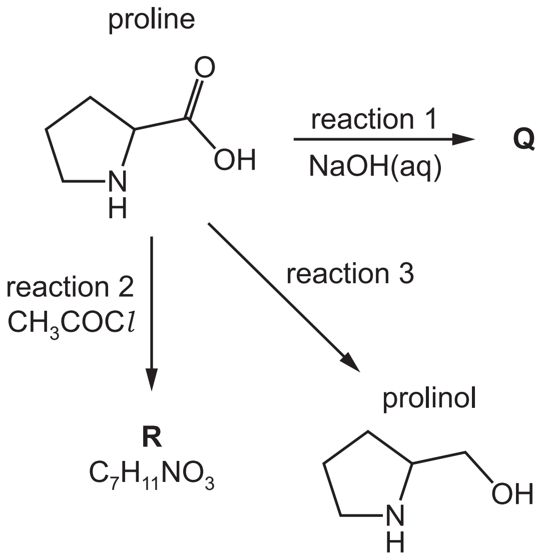


Suggest why the secondary structure of poly(proline) **cannot** be stabilised by hydrogen bonding.

....

.... [1]

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

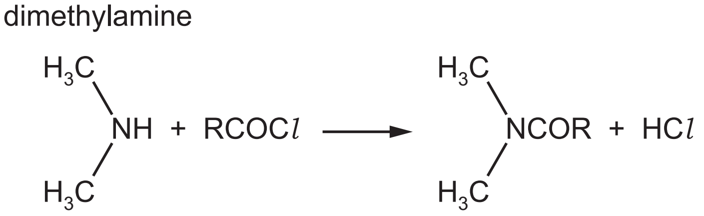


(i) Write an equation for the reaction of proline with NaOH(aq) in reaction 1.

$C_4H_7NHCO_2H$ + ... [1]

(ii) Proline has a secondary amine functional group.

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



$$(CH_3)_2NH + RCOCl \longrightarrow (CH_3)_2NCOR + HCl$$

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

[1]

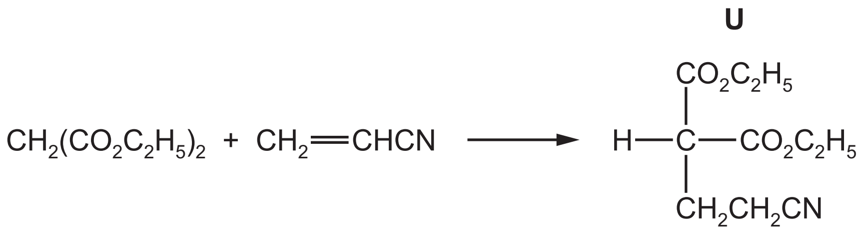
(iii) Suggest the reagent required for reaction 3.

.... [1]

(c) Proline was first synthesised in the laboratory using a multi-stage synthetic route.

In stage 1, $CH_2(CO_2C_2H_5)_2$ and CH_2=CHCN react to form a single product **U**.

stage 1



(i) Name **all** the functional groups present in the reactants of stage 1.

$CH_2(CO_2C_2H_5)_2$ ....

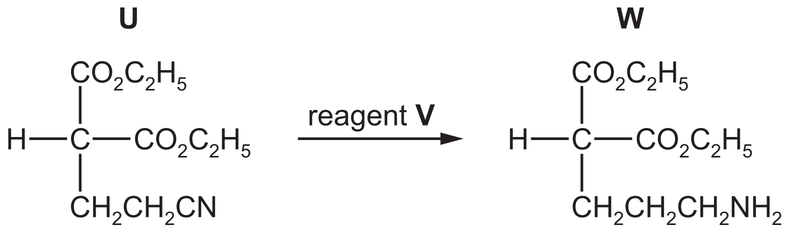
CH_2=CHCN .... [2]

(ii) Suggest the type of reaction that occurs in stage 1.

.... [1]

In stage 2, **U** reacts with reagent **V** to form **W**.

stage 2



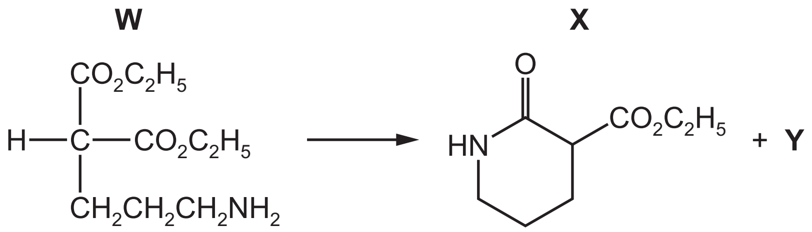
(iii) Suggest a suitable reagent **V**.

.... [1]

Stage 3 takes place in the presence of an acid catalyst.

X and **Y** are the only products of the reaction.

stage 3



(iv) Suggest the type of reaction that occurs in stage 3.

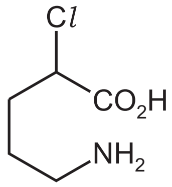
.... [1]

(v) Deduce the identity of **Y**.

.... [1]

After several further stages, **Z** is produced.

Z



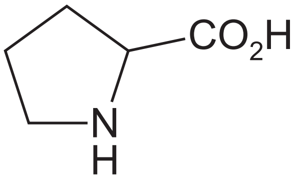
In the final stage of the synthesis, **Z** reacts via a nucleophilic substitution mechanism to form proline.

(vi) Complete the diagram to describe the reaction mechanism of the final stage. Draw curly arrows, ions and charges, partial charges and lone pairs of electrons, as appropriate.

Draw the structure of any organic intermediate ion.

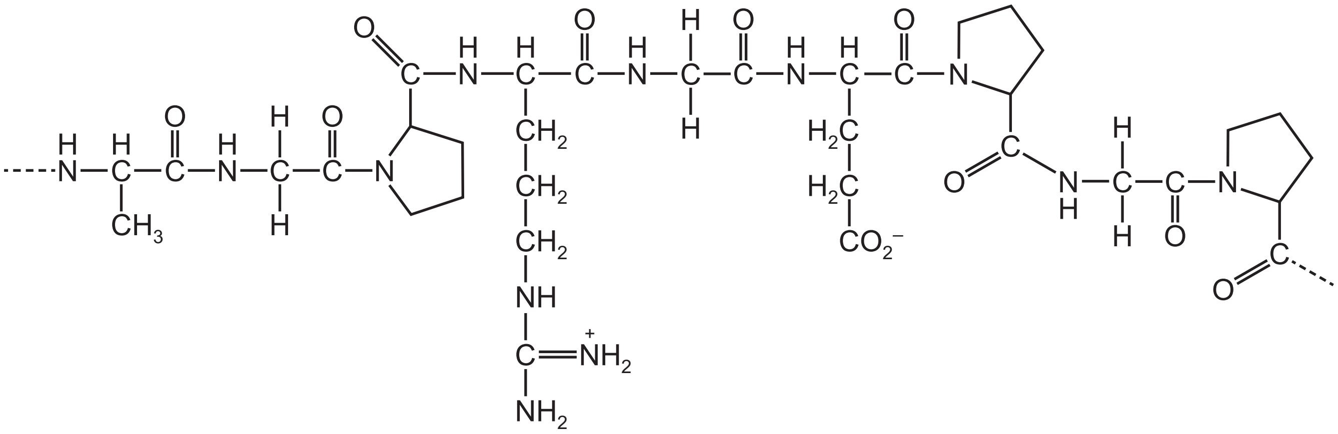
[3]

(vii) Identify with an asterisk (*) the chiral centre in proline.



[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.

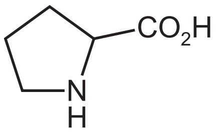
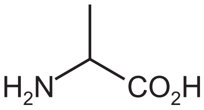
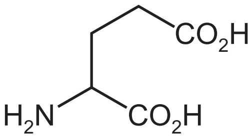
....

....

.... [2]

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

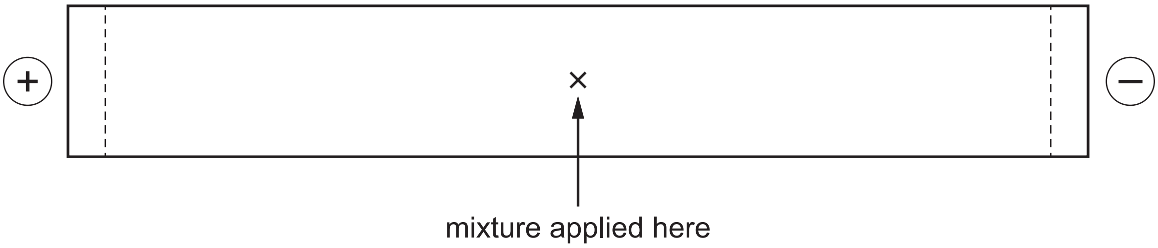
Three of the amino acids in gelatin are proline, alanine and glutamic acid. Their isoelectric points are shown.

	proline	alanine	glutamic acid
amino 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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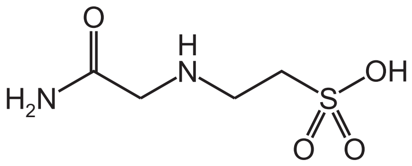
.... [4]

(f) The weak acid **ACES** is a compound that can be used to make a buffer solution for electrophoresis experiments.

ACES



The anion of the sodium salt of **ACES**, $C_4H_9N_2O_4SNa$, is a strong base.

A buffer solution is prepared by the following steps.

- 3.50 g of $C_4H_9N_2O_4SNa$ is dissolved in 100 cm^3 of distilled water.
- 50.0 cm^3 of 0.200 mol dm^{-3} dilute hydrochloric acid is added to the solution.
- The resulting mixture is transferred to a 250.0 cm^3 volumetric flask, and the solution made up to the mark.

$C_4H_9N_2O_4SNa$ reacts with HCl with a 1 : 1 stoichiometry.

The pK_a of **ACES** is 6.88 at 298 K.

Calculate the pH of the buffer solution formed at 298 K.

[M_r: $C_4H_9N_2O_4SNa$, 204.1]

pH = ... [4]

[Total: 28]

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