



## Cambridge International AS & A Level

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**CHEMISTRY**

**9701/42**

Paper 4 A Level Structured Questions

**February/March 2020**

**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 **24** pages. Blank pages are indicated.



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

- 1 Iron is a transition element in the fourth period. Iron forms compounds containing the ions  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ .

(a) (i) Define the term *transition element*.

.....  
.....  
..... [1]

(ii) Compare the melting point and density of iron with those of calcium, an s-block element in the fourth period.

melting point .....

density ..... [1]

(iii) Complete the electronic configuration of an isolated gaseous  $\text{Fe}^{2+}$  ion.

$1s^2$  ..... [1]

(iv) Aqueous  $\text{Fe}^{3+}$  ions form coloured complexes.

Explain the origin of the colour in transition element complexes.

.....  
.....  
.....  
.....  
.....  
..... [4]

## 3

- (b) When an excess of  $\text{CN}^-(\text{aq})$  ions is added to green  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$  ions, yellow  $[\text{Fe}(\text{CN})_6]^{4-}$  complex ions are formed.

Heating  $[\text{Fe}(\text{CN})_6]^{4-}$  with dilute nitric acid and then neutralising the product with  $\text{Na}_2\text{CO}_3(\text{aq})$  produces red crystals, containing the  $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$  complex ion.

NO is a neutral, monodentate ligand.

- (i) State the shape of the  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$  complex ion.

..... [1]

- (ii) Write the equation for the reaction between  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$  ions and an excess of  $\text{CN}^-(\text{aq})$  ions.

..... [1]

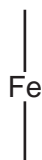
- (iii) Deduce the oxidation states of iron in:

$[\text{Fe}(\text{CN})_6]^{4-}$  .....  $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$  ..... [1]

- (iv) Define the term *monodentate ligand*.

.....  
 ..... [2]

- (v) Complete the diagram to show the three-dimensional structure of the  $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$  complex ion.



[1]

- (vi) The two complex ions  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$  are different colours.

Explain why the colours of the two complex ions are different.

.....  
 .....  
 ..... [2]

(c) **E** is a complex ion,  $[\text{Fe}(\text{C}_2\text{O}_4)_2\text{Cl}_2]^{4-}$ , containing  $\text{Fe}^{2+}$  with a coordination number of 6.

(i) Define the term *coordination number*.

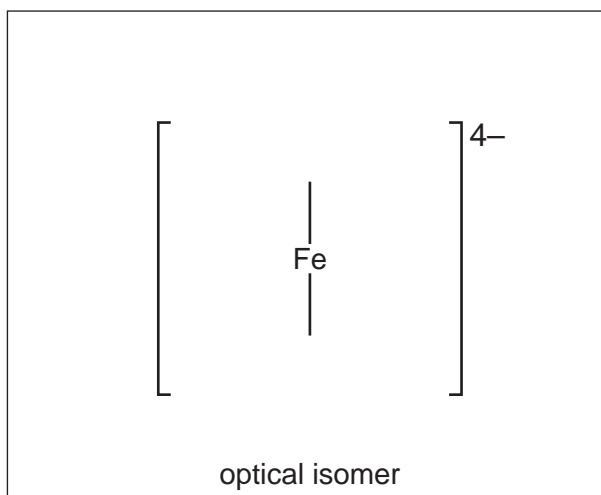
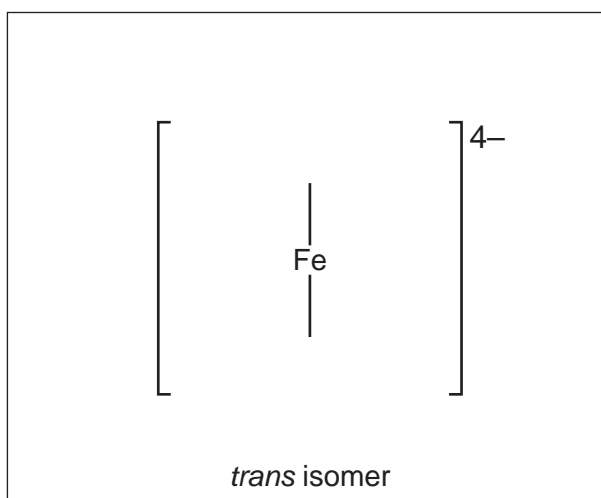
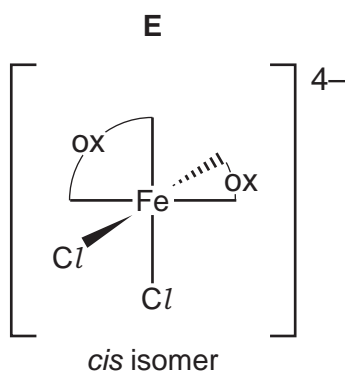
.....  
 ..... [1]

(ii) **E** shows both optical isomerism and *cis-trans* isomerism.

One isomer of **E** is shown. The  $\text{C}_2\text{O}_4^{2-}$  ion is represented as  $\text{ox}^-$ .

In the boxes, draw three-dimensional diagrams to show:

- the *trans* isomer of **E**
- the optical isomer of **E**.



[2]

5

(iii)  $[\text{Fe}(\text{C}_2\text{O}_4)_2\text{Cl}_2]^{4-}$  contains ligands which are anions of ethanedioic acid,  $\text{HO}_2\text{CCO}_2\text{H}$ .

Complete the table to show any observations for the reactions of  $\text{HO}_2\text{CCO}_2\text{H}$  with the named reagents.

Where no change is observed, write 'none'.

reagent	observations with $\text{HO}_2\text{CCO}_2\text{H}$
warm acidified manganate(VII)	
2,4-dinitrophenylhydrazine	
warm Tollens' reagent	

[2]

[Total: 20]

2 (a) Group 2 metals form stable carbonates and sulfates.

(i) State and explain the trend in the thermal stability of the Group 2 carbonates down the group.

.....  
.....  
.....  
.....  
.....  
..... [3]

(ii) The sulfates of Group 2 elements become less soluble down the group.

Explain this trend.

.....  
.....  
.....  
.....  
..... [3]

(b) Aluminium is extracted from  $Al_2O_3$  by electrolysis.  $Al_2O_3$  is dissolved in cryolite in this process.

(i) The half-equation for the reaction at the anode is shown.



Use this half-equation to write the ionic equation for the electrolysis of  $Al_2O_3$ .

..... [1]

(ii) Aluminium oxide is electrolysed for 3.0 hours using carbon electrodes and a current of  $3.5 \times 10^5$  A.

Calculate the mass of aluminium that is formed.

mass of aluminium = ..... g [3]

(iii) Cryolite can be made from  $SiF_4$ .

The first step in this conversion is the reaction of  $SiF_4$  with  $H_2O$ , forming  $H_2SiF_6$  and  $SiO_2$ .

Write an equation for this reaction.

..... [1]

[Total: 11]

## 8

3 Gold is an unreactive metal that can only be oxidised under specific conditions.

(a) The standard electrode potential,  $E^\ominus$ , of  $\text{Au}^{3+}(\text{aq})/\text{Au}(\text{s})$  is +1.50 V.

(i) Define the term *standard electrode potential*.

.....  
.....  
..... [2]

(ii) Draw a fully labelled diagram of the apparatus that should be used to measure the standard cell potential,  $E^\ominus_{\text{cell}}$ , of  $\text{Au}^{3+}(\text{aq})/\text{Au}(\text{s})$  and  $\text{HNO}_3(\text{aq})/\text{NO}(\text{g})$ .

Include all necessary chemicals.

[4]



Some relevant half-equations and their standard electrode potentials are given.

	half-equation	$E^\ominus/V$
1	$\text{Au}^{3+}(\text{aq}) + 3\text{e}^- \rightleftharpoons \text{Au}(\text{s})$	+1.50
2	$[\text{AuCl}_4]^- (\text{aq}) + 3\text{e}^- \rightleftharpoons \text{Au}(\text{s}) + 4\text{Cl}^- (\text{aq})$	+1.00
3	$\text{NO}_3^- (\text{aq}) + 4\text{H}^+ (\text{aq}) + 3\text{e}^- \rightleftharpoons \text{NO}(\text{g}) + 2\text{H}_2\text{O}(\text{l})$	+0.96

- (iii) Write an ionic equation to show the spontaneous reaction that occurs when an electric current is drawn from the cell in (a)(ii).

..... [1]

- (iv) Calculate the  $E^\ominus_{\text{cell}}$  of the reaction in (a)(iii).

$$E^\ominus_{\text{cell}} = \dots\dots\dots \text{ V [1]}$$

- (v) Gold can be oxidised by a mixture of concentrated hydrochloric acid and concentrated nitric acid, known as *aqua regia*. Concentrated hydrochloric acid is  $12 \text{ mol dm}^{-3}$ . Concentrated nitric acid is  $16 \text{ mol dm}^{-3}$ .

Explain why *aqua regia* is able to dissolve gold.

In your answer, state and explain what effect the use of concentrated hydrochloric acid and concentrated nitric acid have on the  $E$  values of half-equations 2 and 3.

.....  
 .....  
 .....  
 .....  
 .....  
 .....  
 ..... [3]

- (b) Aqueous gold(III) chloride,  $\text{AuCl}_3$ , reacts with aqueous hydrogen peroxide,  $\text{H}_2\text{O}_2$ , under certain conditions, forming Au,  $\text{O}_2$  and  $\text{HCl}$ .

A student carries out separate experiments using different initial concentrations of  $\text{AuCl}_3$  and  $\text{H}_2\text{O}_2$ . The initial rate of each reaction is measured.

The table shows the results that are obtained.

experiment	$[\text{AuCl}_3]$ / $\text{mol dm}^{-3}$	$[\text{H}_2\text{O}_2]$ / $\text{mol dm}^{-3}$	rate of production of $\text{O}_2(\text{g})$ / $\text{dm}^3 \text{ minute}^{-1}$
1	0.05	0.50	$7.66 \times 10^{-2}$
2	0.10	0.50	$1.53 \times 10^{-1}$
3	0.15	1.00	$4.60 \times 10^{-1}$

- (i) Write an equation for the reaction of  $\text{AuCl}_3$  with  $\text{H}_2\text{O}_2$ .

..... [1]

- (ii) Determine the rate equation of the reaction.

Show your reasoning, quoting data from the table.

.....  
 .....  
 .....  
 .....  
 ..... [3]

- (iii) Use the results of experiment 2 to calculate the value of the rate constant,  $k$ , for this reaction.

Include the units of  $k$ .

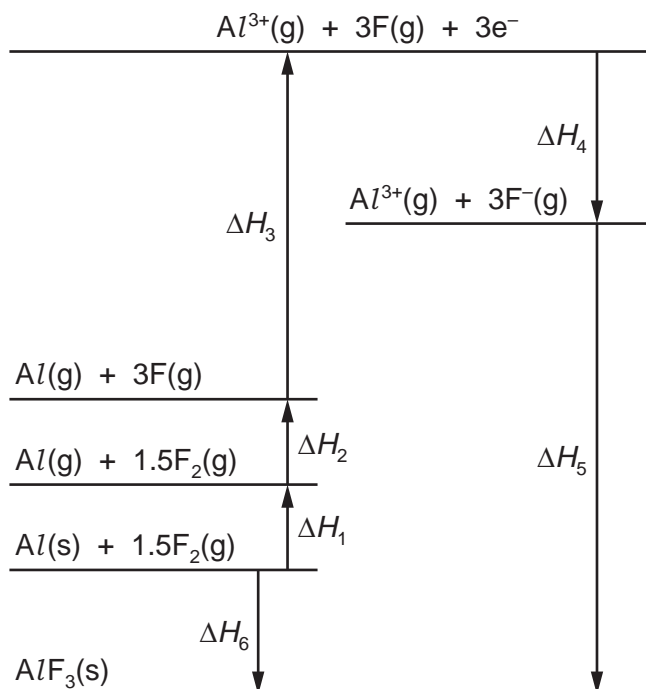
rate constant,  $k =$  .....

units = .....

[2]

(c)  $\text{AlF}_3$  is an ionic compound.

The Born–Haber cycle for the formation of  $\text{AlF}_3$  is shown.



(i) Name the enthalpy changes labelled  $\Delta H_4$  and  $\Delta H_6$ .

$\Delta H_4 = \dots\dots\dots$

$\Delta H_6 = \dots\dots\dots$

[2]

(ii) Use the data in the table and data from the *Data Booklet* to calculate the lattice energy of  $\text{AlF}_3$ .

process	enthalpy change / $\text{kJ mol}^{-1}$
$\text{Al(s)} \rightarrow \text{Al(g)}$	+326
$\text{Al(g)} \rightarrow \text{Al}^{3+}(\text{g})$	+5137
$\text{F(g)} \rightarrow \text{F}^{-}(\text{g})$	-328
$\text{Al(s)} + 1.5\text{F}_2(\text{g}) \rightarrow \text{AlF}_3(\text{s})$	-1504

lattice energy of  $\text{AlF}_3 = \dots\dots\dots \text{kJ mol}^{-1}$  [2]

- (iii) Scandium fluoride,  $\text{ScF}_3$ , is an ionic compound.

Use data from the *Data Booklet* to suggest how the lattice energy of  $\text{AlF}_3$  compares with the lattice energy of  $\text{ScF}_3$ .

Explain your answer.

.....  
 .....  
 ..... [2]

- (d)  $\text{AlF}_3$  is sparingly soluble in water. The concentration of its saturated solution at 298 K is  $6.5 \times 10^{-2} \text{ mol dm}^{-3}$ .

- (i) Write an expression for the solubility product,  $K_{\text{sp}}$ , of  $\text{AlF}_3$ .

$K_{\text{sp}} = \dots\dots\dots$  [1]

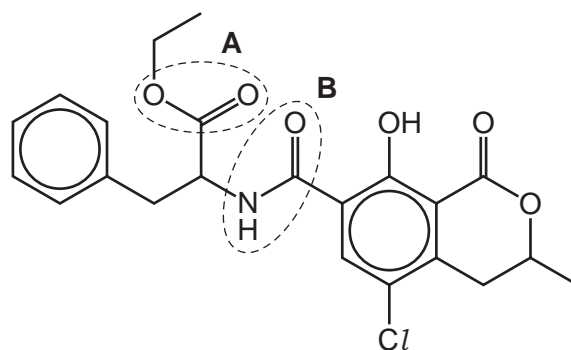
- (ii) Calculate the numerical value of  $K_{\text{sp}}$  for  $\text{AlF}_3$  at 298 K.

$K_{\text{sp}} = \dots\dots\dots$   
 [1]

[Total: 25]

13

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

**F**

(a) (i) Give the name of the functional groups labelled **A** and **B**.

**A** .....

**B** .....

[2]

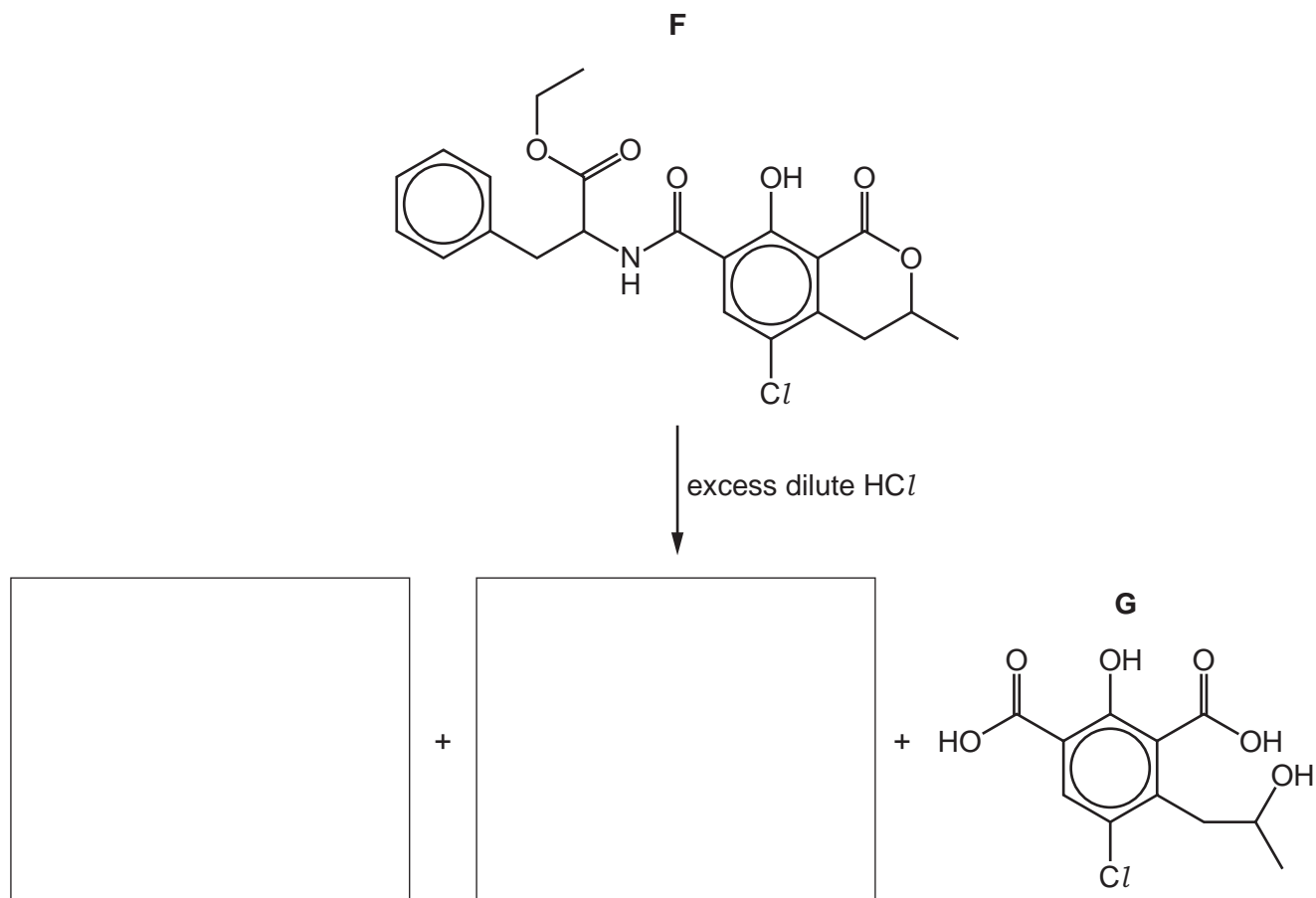
(ii) State the number of chiral carbon atoms in one molecule of **F**.

..... [1]

14

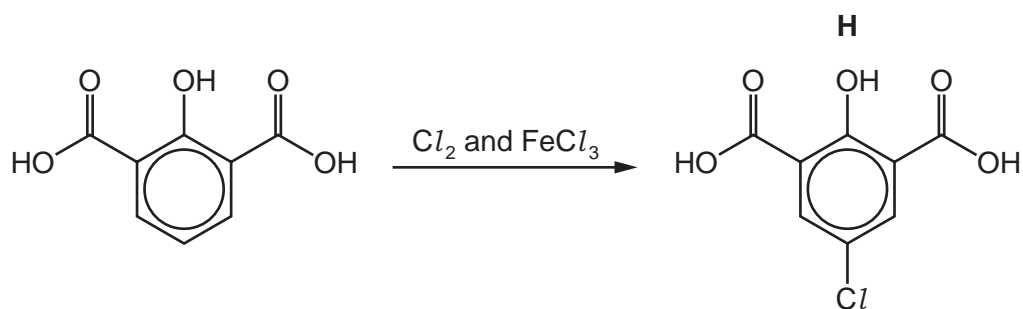
(b) **F** can be hydrolysed by heating with an excess of dilute hydrochloric acid, as shown.

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



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

(c) Compound **H** is formed in one step of a different synthesis, as shown.



(i) State the role of  $\text{FeCl}_3$  in this step.

..... [1]

- (ii) Use the *Data Booklet* to suggest **two** reasons why the chlorine atom in compound **H** substitutes into the ring at the position shown, instead of the other positions in the ring.

1 .....

.....

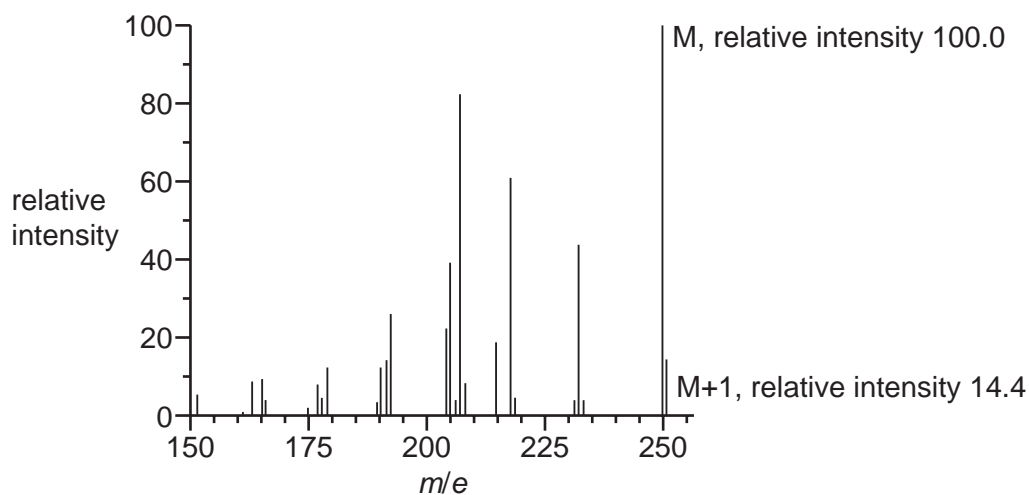
2 .....

.....

[2]

- (d) Compound **J**,  $C_xH_yO_z$ , is also found in some cereals.

Part of the mass spectrum of **J** is shown. The *M* and *M*+1 peaks are labelled, along with their relative intensities.



- (i) Calculate the number of carbon atoms, *x*, present in **J**.

$x = \dots\dots\dots$  [2]

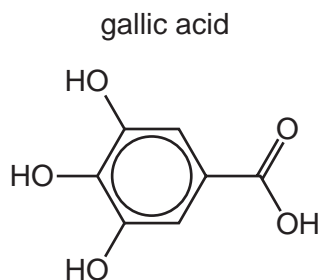
- (ii) The mass spectrum has a peak at  $m/e = 205$ .

Suggest the identity of the fragment lost from **J** to form this peak.

..... [1]

[Total: 12]

- 5 Gallic acid,  $C_7H_6O_5$ , is a naturally occurring aromatic molecule.



- (a) Gallic acid contains the carboxylic acid and phenol functional groups.

State and explain the relative acid strength of these two functional groups.

.....

.....

.....

..... [2]

- (b) A buffer solution was prepared by dissolving 2.04 g of gallic acid in  $250\text{ cm}^3$  of a solution containing  $0.0600\text{ mol dm}^{-3}$  of gallate ions,  $C_7H_5O_5^-$ .



- (i) Define the term *buffer solution*.

.....

.....

..... [2]

- (ii) Calculate the pH of this buffer solution.

pH = ..... [3]

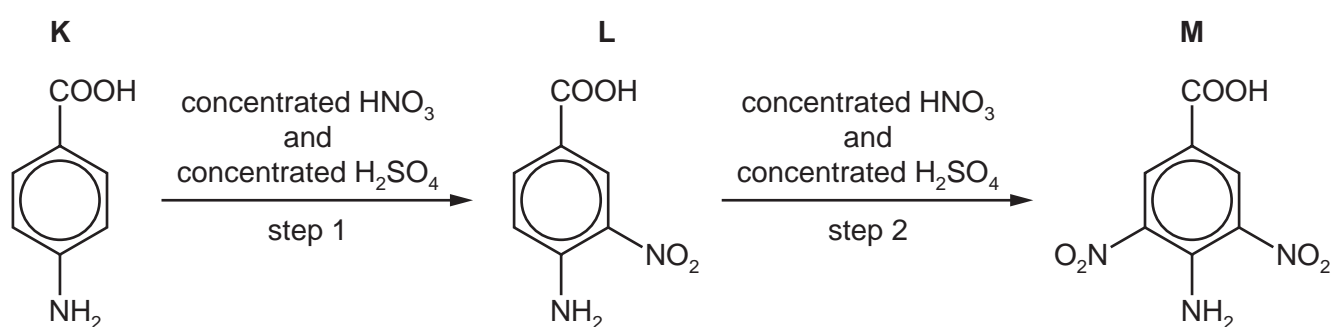


- (iii) Write **two** equations to show how a solution containing gallic acid,  $C_7H_6O_5$ , and gallate ions,  $C_7H_5O_5^-$ , acts as a buffer.

.....  
 .....  
 .....  
 ..... [2]

- (c) Compound **K** is used as the starting material in a synthesis of gallic acid.

A student suggested the first two steps of the synthesis could be as shown.



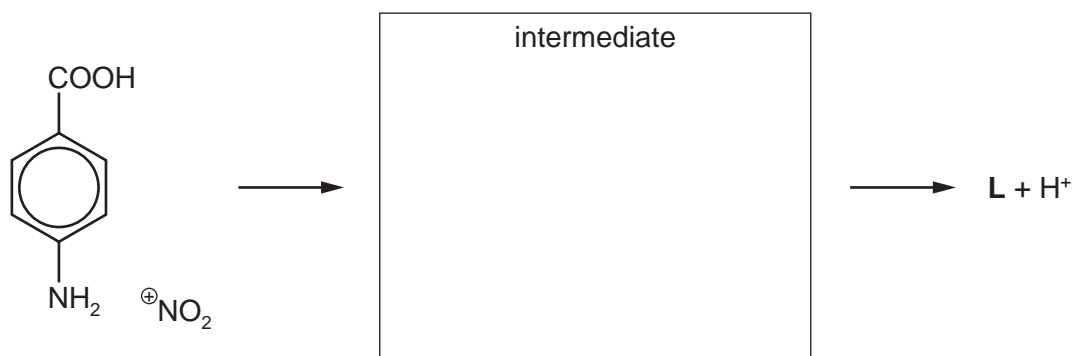
Nitronium ions,  $\text{NO}_2^+$ , are generated by the reaction between concentrated sulfuric acid and concentrated nitric acid.

- (i) Construct an equation for the formation of  $\text{NO}_2^+$  by this method.

..... [1]

- (ii) Complete the mechanism and draw the intermediate of step 1.

Include all relevant charges and curly arrows to show the movement of electron pairs.



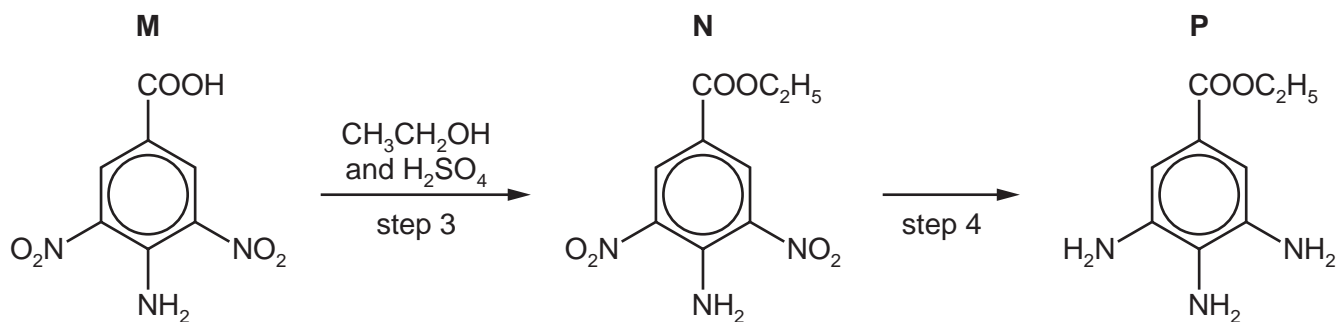
[2]

- (iii) State the name of the mechanism in (c)(ii).

..... [1]

18

Compound **M** is converted into compound **P** as shown.

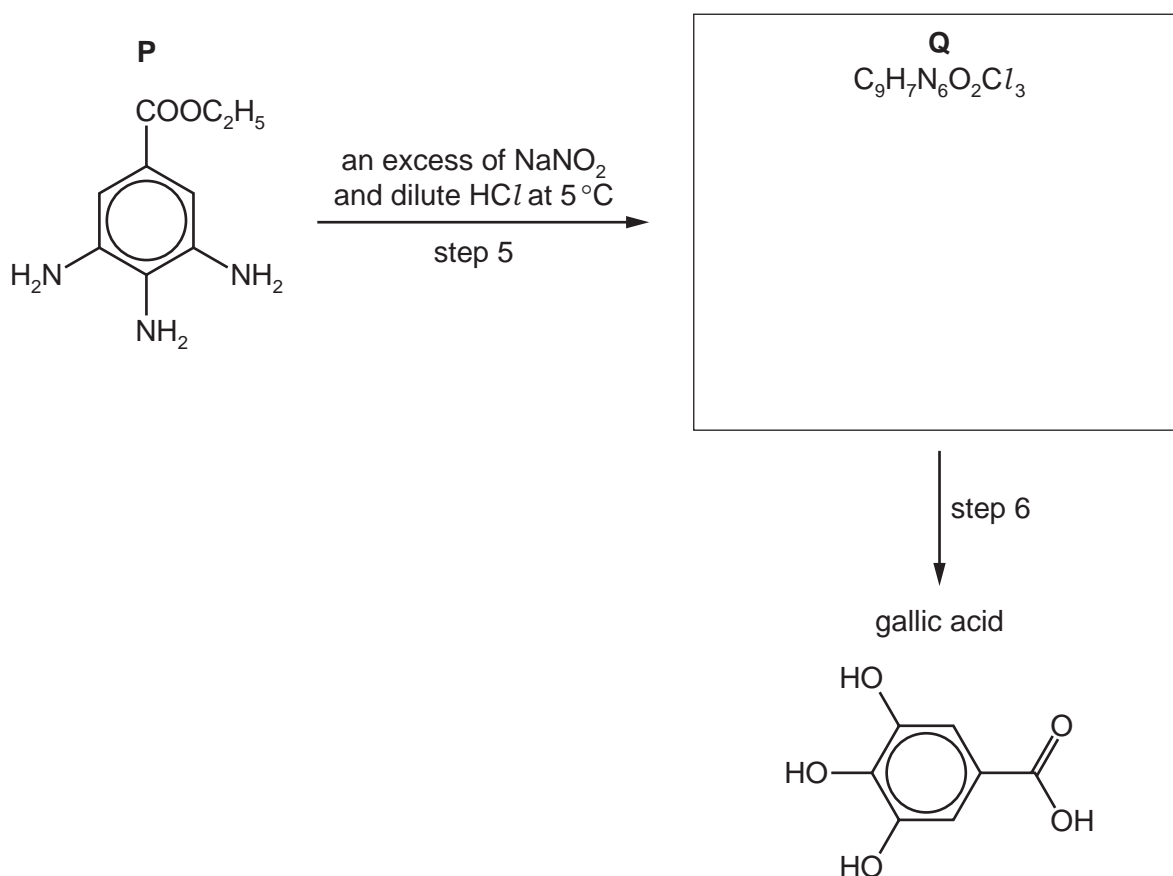


(iv) State the reagents and conditions for step 4.

..... [2]

**P** reacts with an excess of sodium nitrite,  $\text{NaNO}_2$ , and dilute  $\text{HCl}$  at  $5^\circ\text{C}$  to form compound **Q**,  $\text{C}_9\text{H}_7\text{N}_6\text{O}_2\text{Cl}_3$ .

Compound **Q** is then converted into gallic acid.

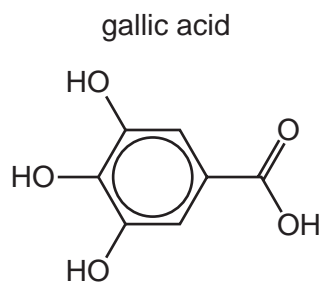


(v) Suggest the structure of compound **Q** in the box provided. [2]

(vi) State the reagents and conditions for step 6.

..... [1]

(d) (i) State the number of peaks that would be observed in the  $^{13}\text{C}$  NMR spectrum of gallic acid.



..... [1]

(ii) The proton NMR spectrum of gallic acid dissolved in  $\text{D}_2\text{O}$  is recorded.

- Predict the number of peaks observed and any expected splitting pattern.
- State the expected chemical shift range ( $\delta$ ) of each peak predicted.

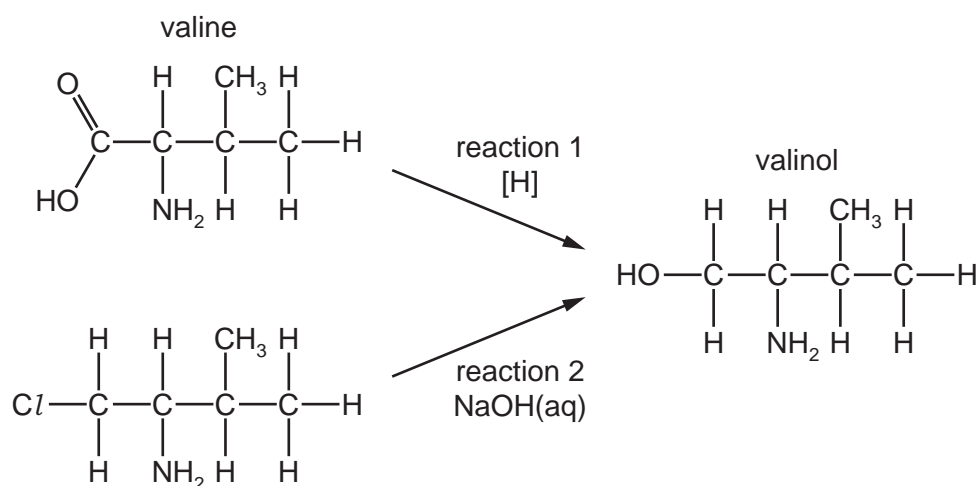
.....

.....

..... [2]

[Total: 21]

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



- (a) (i) Write an equation for reaction 1, using [H] to represent the reducing agent.

..... [1]

- (ii) Suggest a suitable reagent for reaction 1.

..... [1]

- (iii) Name the mechanism for reaction 2.

..... [1]

- (b) Valine and glycine,  $\text{H}_2\text{NCH}_2\text{COOH}$ , form the tripeptide Gly-Val-Gly.

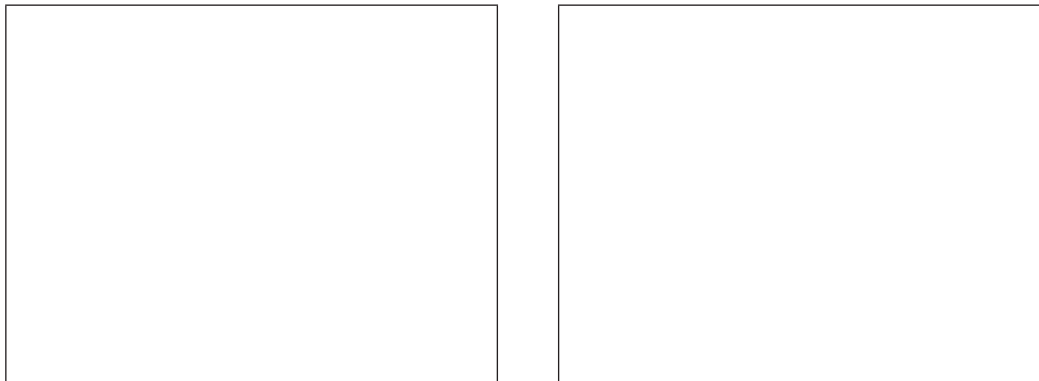
Draw the structure of this tripeptide. Show the peptide bonds fully displayed.

[2]

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

Draw three-dimensional diagrams to show the two stereoisomers of valine. In your diagrams, the  $-\text{CH}(\text{CH}_3)_2$  group can be represented by  $-\text{R}$ .

State the type of stereoisomerism shown.



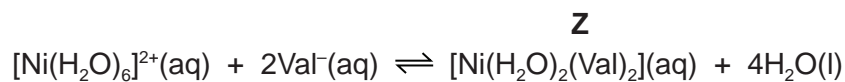
type of stereoisomerism ..... [2]

(ii) Valine is an amino acid.

Draw the zwitterion of valine.

[1]

- (iii) Valinate,  $\text{Val}^-$ , is the anion of valine. It takes part in a ligand substitution reaction with hexaaquanickel(II) ions. Complex **Z** is formed.



Write an expression for  $K_{\text{stab}}$  for this equilibrium.

$$K_{\text{stab}} =$$

[1]

- (iv) At room temperature, the numerical value of  $K_{\text{stab}}$  is  $2.34 \times 10^5$ .

Explain what this value indicates about the equilibrium and the stability of complex **Z**.

.....  
 .....  
 ..... [1]

- (v) **Z** is an octahedral complex with formula  $[\text{Ni}(\text{H}_2\text{O})_2(\text{Val})_2]$ .

Use this information to state the type of ligand that the valinate ion is acting as in this complex.

..... [1]

[Total: 11]



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