Cambridge Assessment International Education

Cambridge International AS & A Level

CANDIDATE NAME

CENTRE NUMBER

CANDIDATE NUMBER

4320996227

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.

[Turn over

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

1 Iron is a transition element in the fourth period. Iron forms compounds containing the ions Fe^{2+} and 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 Fe^{2+} ion.

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

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

Explain the origin of the colour in transition element complexes.

.....

.....

.....

.....

.....

..... [4]

(b) When an excess of $CN^-(aq)$ ions is added to green $[Fe(H_2O)_6]^{2+}(aq)$ ions, yellow $[Fe(CN)_6]^{4-}$ complex ions are formed.

Heating $[Fe(CN)_6]^{4-}$ with dilute nitric acid and then neutralising the product with $Na_2CO_3(aq)$ produces red crystals, containing the $[Fe(CN)_5NO]^{2-}$ complex ion.

NO is a neutral, monodentate ligand.

(i) State the shape of the $[Fe(H_2O)_6]^{2+}(aq)$ complex ion.

..... [1]

(ii) Write the equation for the reaction between $[Fe(H_2O)_6]^{2+}(aq)$ ions and an excess of $CN^-(aq)$ ions.

..... [1]

(iii) Deduce the oxidation states of iron in:

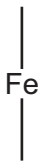
$[Fe(CN)_6]^{4-}$ ..... $[Fe(CN)_5NO]^{2-}$. .....
[1]

(iv) Define the term *monodentate ligand*.

.....

..... [2]

(v) Complete the diagram to show the three-dimensional structure of the $[Fe(CN)_5NO]^{2-}$ complex ion.



[1]

(vi) The two complex ions $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_5NO]^{2-}$ are different colours.

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

.....

.....

..... [2]

(c) **E** is a complex ion, $[Fe(C_2O_4)_2Cl_2]^{4-}$, containing Fe^{2+} with a coordination number of 6.

(i) Define the term *coordination number*.

.....

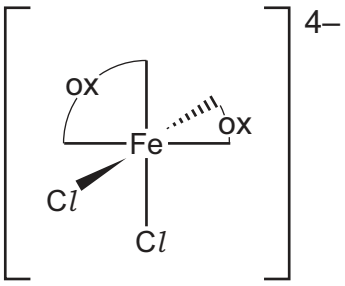
..... [1]

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

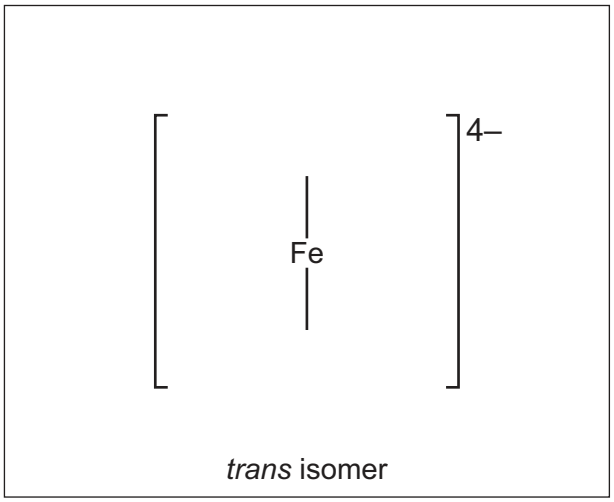
One isomer of **E** is shown. The $C_2O_4^{2-}$ ion is represented as ox.

In the boxes, draw three-dimensional diagrams to show:
- the *trans* isomer of **E**
- the optical isomer of **E**.

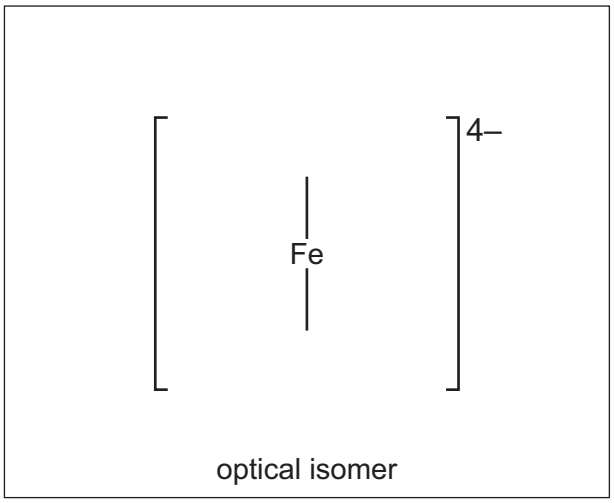
E



cis isomer



trans isomer



optical isomer

[2]

(iii) $[Fe(C_2O_4)_2Cl_2]^{4-}$ contains ligands which are anions of ethanedioic acid, HO_2CCO_2H.

Complete the table to show any observations for the reactions of HO_2CCO_2H with the named reagents.

Where no change is observed, write 'none'.

reagent	observations with HO_2CCO_2H
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.

$$O^{2-} + C \rightarrow CO + 2e^-$$

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 3.5×10^5 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]

[Turn over

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

(a) The standard electrode potential, $E^{\ominus}$, of $Au^{3+}(aq)/Au(s)$ 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, $E^{\ominus}_{cell}$, of $Au^{3+}(aq)/Au(s)$ and $HNO_3(aq)/NO(g)$.

Include all necessary chemicals.

[4]

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

	half-equation	$E^{\ominus}$/V
1	$Au^{3+}(aq) + 3e^- \rightleftharpoons Au(s)$	+1.50
2	$[AuCl_4]^-(aq) + 3e^- \rightleftharpoons Au(s) + 4Cl^-(aq)$	+1.00
3	$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O(l)$	+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 $E^{\ominus}_{cell}$ of the reaction in **(a)(iii)**.

$E^{\ominus}_{cell}$ = ... 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 mol dm^{-3}. Concentrated nitric acid is 16 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, $AuCl_3$, reacts with aqueous hydrogen peroxide, H_2O_2, under certain conditions, forming Au, O_2 and HCl.

A student carries out separate experiments using different initial concentrations of $AuCl_3$ and H_2O_2. The initial rate of each reaction is measured.

The table shows the results that are obtained.

experiment	$[AuCl_3]$ / mol dm^{-3}	$[H_2O_2]$ / mol dm^{-3}	rate of production of $O_2(g)$ / dm^3 minute^{-1}
1	0.05	0.50	7.66×10^{-2}
2	0.10	0.50	1.53×10^{-1}
3	0.15	1.00	4.60×10^{-1}

(i) Write an equation for the reaction of $AuCl_3$ with H_2O_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.

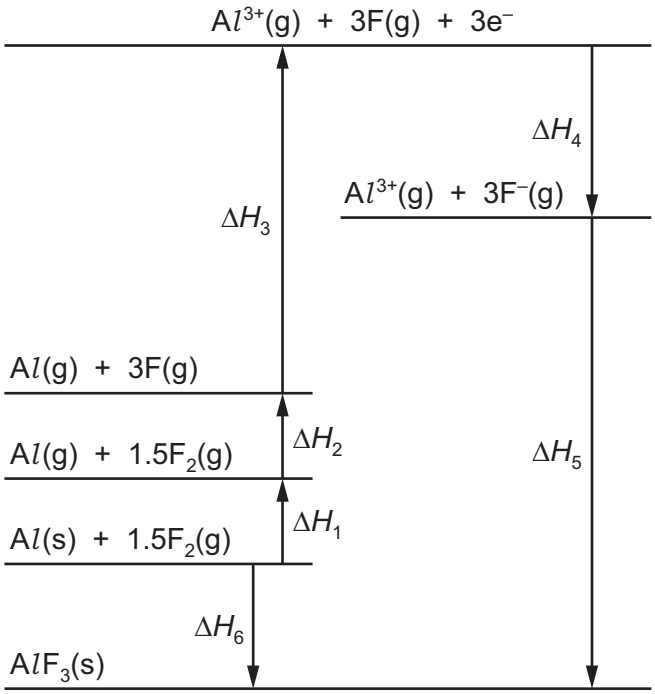
Include the units of *k*.

rate constant, *k* = ...

units = ...
[2]

(c) $Al F_3$ is an ionic compound.

The Born–Haber cycle for the formation of $Al F_3$ is shown.



(i) Name the enthalpy changes labelled ΔH_4 and ΔH_6.

ΔH_4 = ...

ΔH_6 = ...

[2]

(ii) Use the data in the table and data from the *Data Booklet* to calculate the lattice energy of $Al F_3$.

process	enthalpy change / kJ mol^{-1}
$Al(s) \rightarrow Al(g)$	+326
$Al(g) \rightarrow Al^{3+}(g)$	+5137
$F(g) \rightarrow F^-(g)$	–328
$Al(s) + 1.5F_2(g) \rightarrow AlF_3(s)$	–1504

lattice energy of $Al F_3$ = ... kJ mol^{-1} [2]

(iii) Scandium fluoride, ScF_3, is an ionic compound.

Use data from the *Data Booklet* to suggest how the lattice energy of $Al F_3$ compares with the lattice energy of ScF_3.

Explain your answer.

.....

.....

..... [2]

(d) $Al F_3$ is sparingly soluble in water. The concentration of its saturated solution at 298 K is 6.5×10^{-2} mol dm^{-3}.

(i) Write an expression for the solubility product, K_{sp}, of $Al F_3$.

K_{sp} = ... [1]

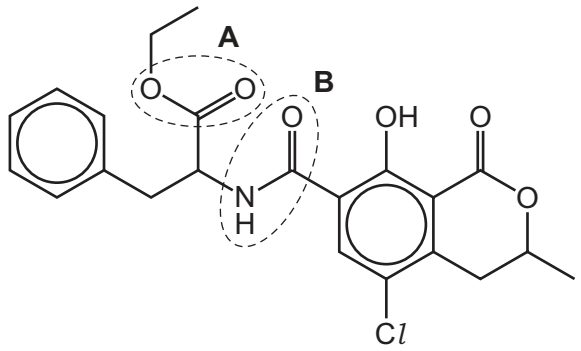
(ii) Calculate the numerical value of K_{sp} for $Al F_3$ at 298 K.

K_{sp} = ...
[1]

[Total: 25]

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]

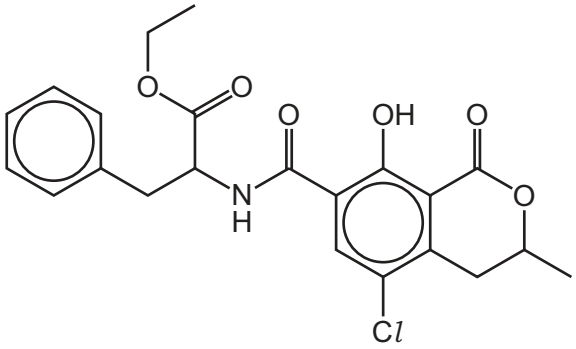
(ii) State the number of chiral carbon atoms in one molecule of **F**.

..... [1]

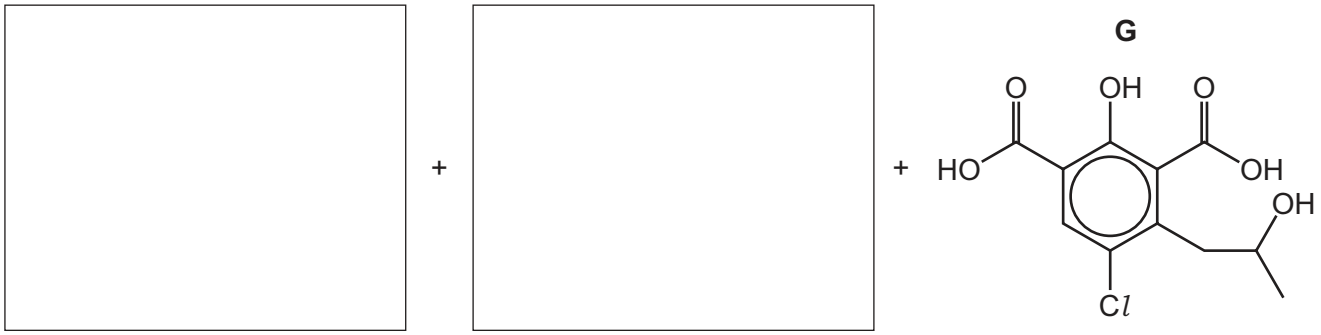
(b) **F** can be hydrolysed by heating with an excess of dilute hydrochloric acid, as shown.

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

F

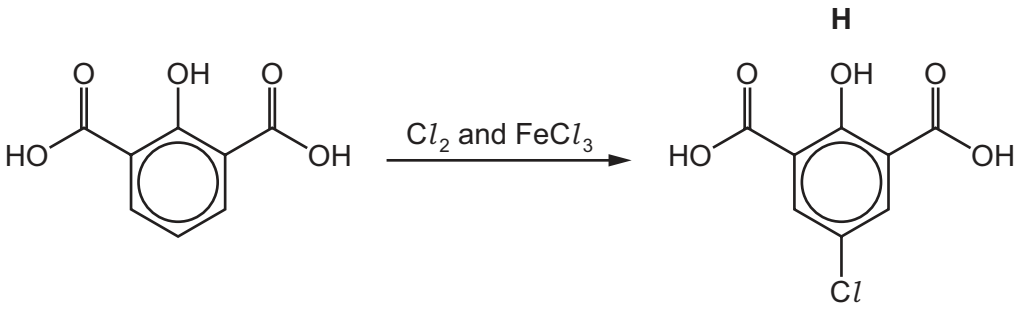


excess dilute HCl



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

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



(i) State the role of $FeCl_3$ 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 .....

.....

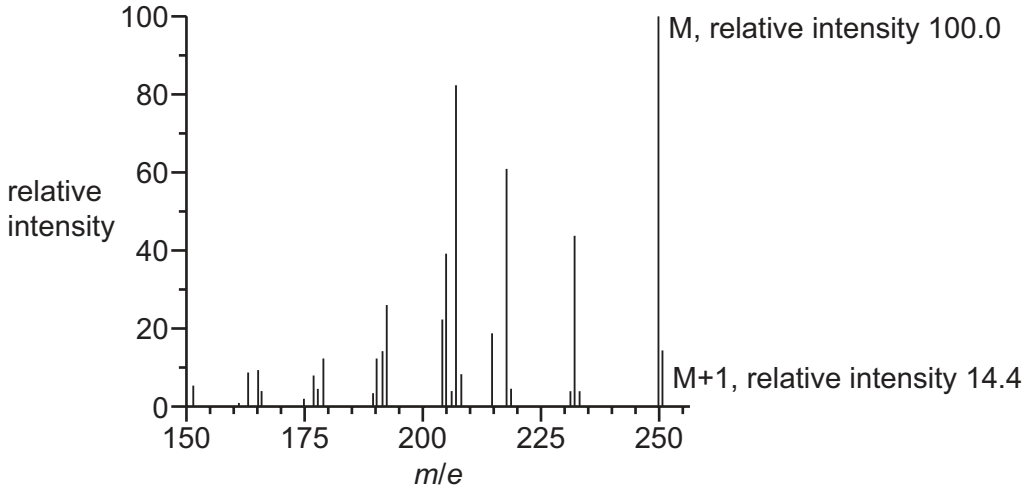
2 .....

.....

[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 = ... [2]

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

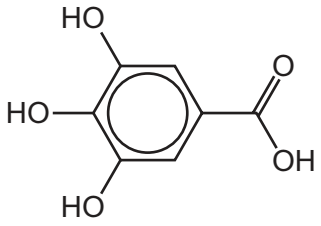
Suggest the identity of the fragment lost from **J** to form this peak.

..... [1]

[Total: 12]

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

gallic acid



(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 cm^3 of a solution containing 0.0600 mol dm^{-3} of gallate ions, $C_7H_5O_5^-$.

$$C_7H_6O_5 \rightleftharpoons C_7H_5O_5^- + H^+ \qquad K_a = 3.89 \times 10^{-5}\,\text{mol dm}^{-3} \text{ at } 298\,\text{K}$$

(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.

.....

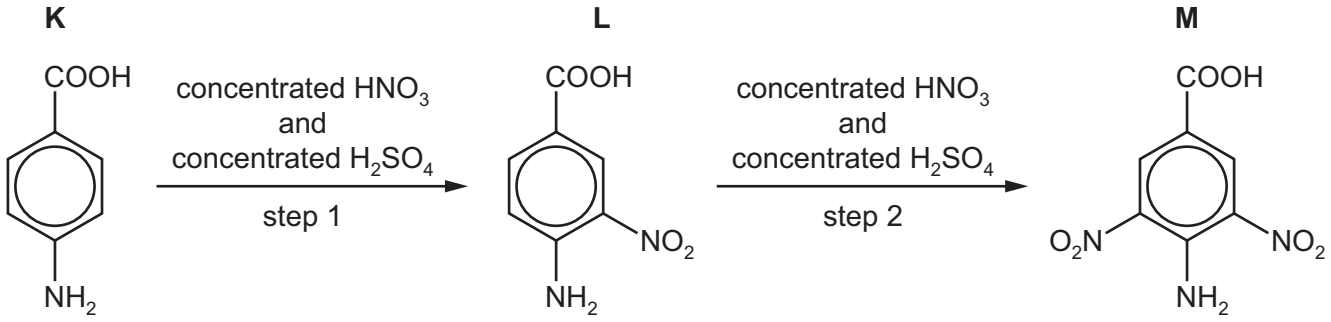
.....

.....

..... [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.



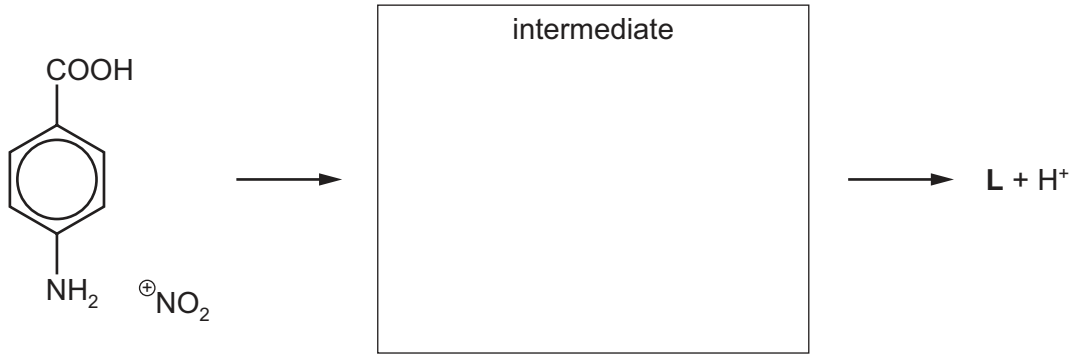
Nitronium ions, NO_2^+, are generated by the reaction between concentrated sulfuric acid and concentrated nitric acid.

(i) Construct an equation for the formation of 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.

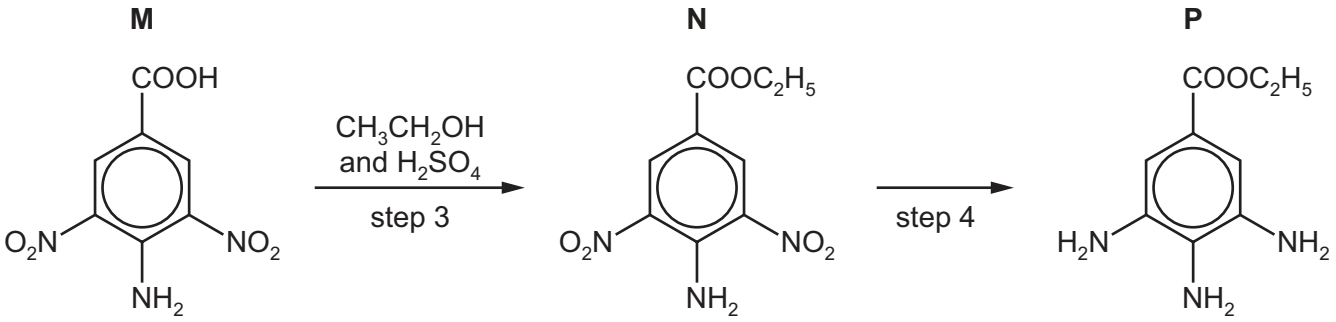


[2]

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

..... [1]

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

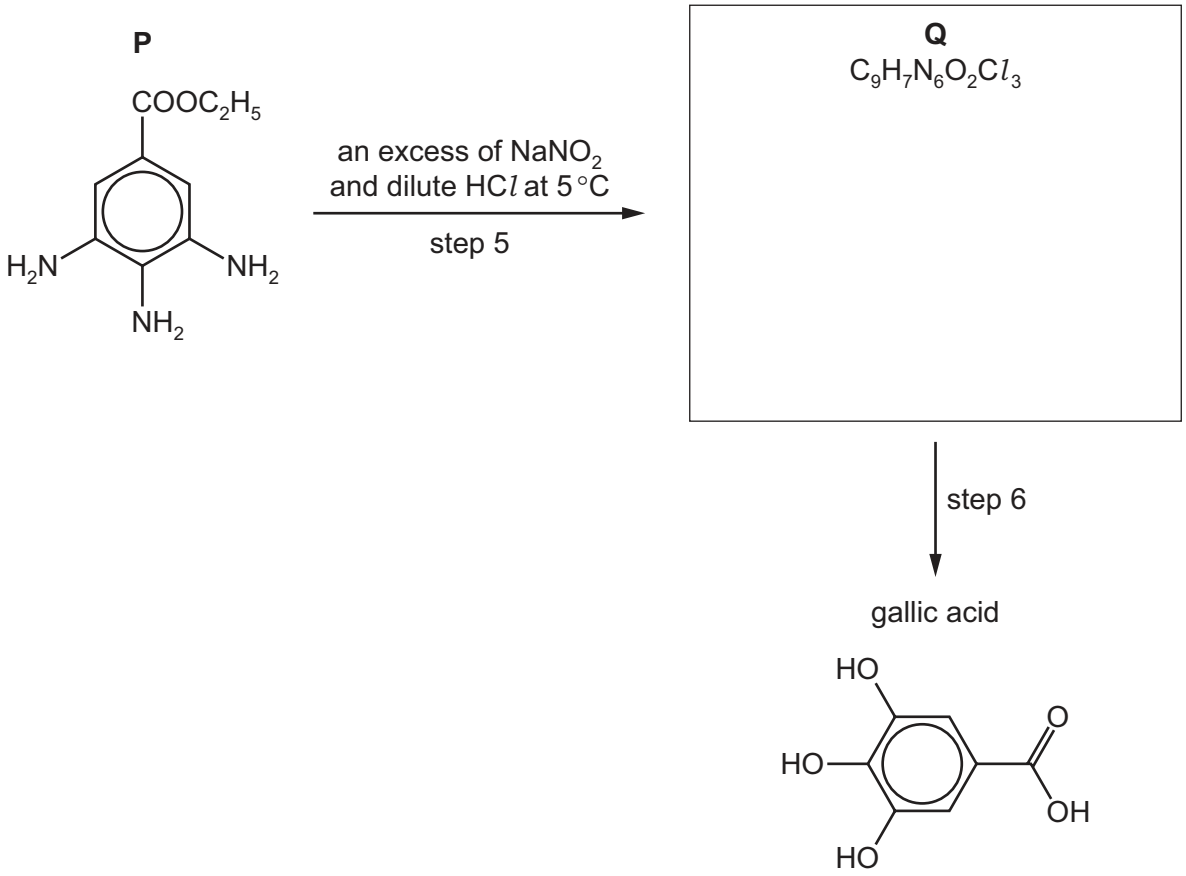


(iv) State the reagents and conditions for step 4.

..... [2]

P reacts with an excess of sodium nitrite, $NaNO_2$, and dilute HCl at 5 °C to form compound **Q**, $C_9H_7N_6O_2Cl_3$.

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



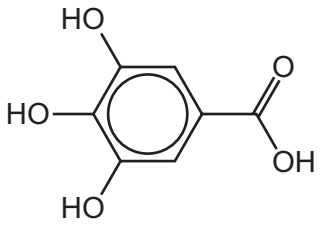
(v) Suggest the structure of compound **Q** in the box provided. [2]

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

..... [1]

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

gallic acid



..... [1]

(ii) The proton NMR spectrum of gallic acid dissolved in D_2O is recorded.

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

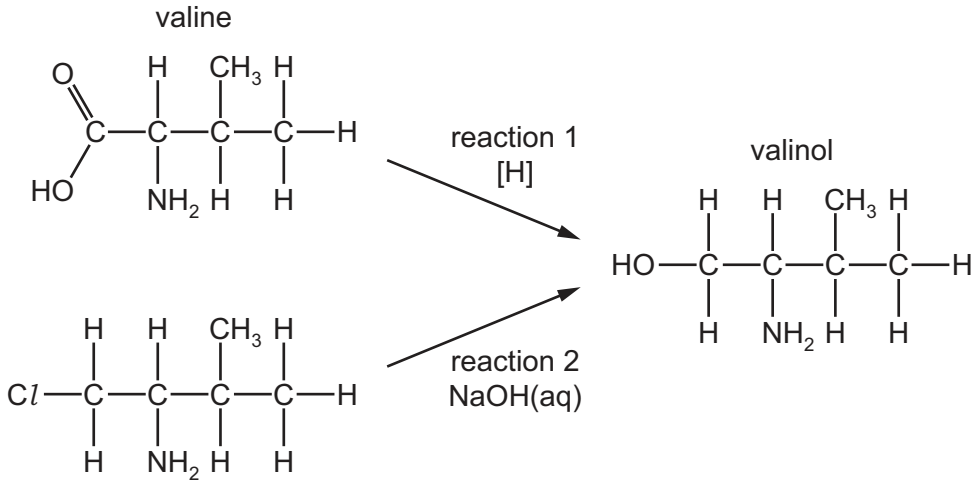
.....

.....

..... [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, 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]

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

$$[Ni(H_2O)_6]^{2+}(aq) + 2Val^-(aq) \rightleftharpoons [Ni(H_2O)_2(Val)_2](aq) + 4H_2O(l)$$

Z

Write an expression for K_{stab} for this equilibrium.

K_{stab} =

[1]

(iv) At room temperature, the numerical value of K_{stab} is 2.34×10^5.

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

.....

.....

..... [1]

(v) **Z** is an octahedral complex with formula $[Ni(H_2O)_2(Val)_2]$.

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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