



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 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]

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:

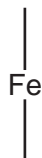
$[\text{Fe}(\text{CN})_6]^{4-}$ $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ [1]

- (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 Fe^{2+} with a coordination number of 6.

(i) Define the term *coordination number*.

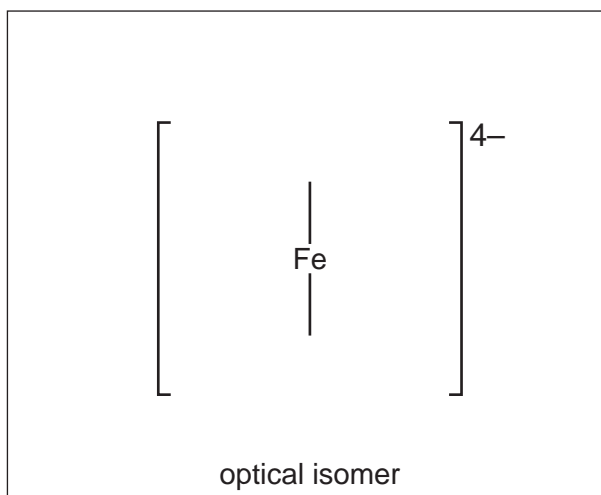
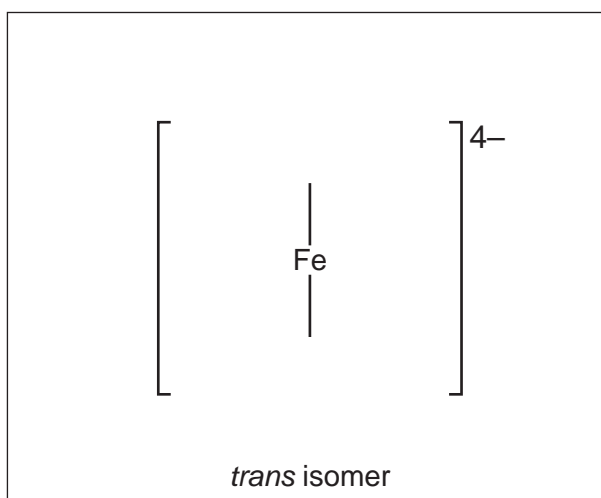
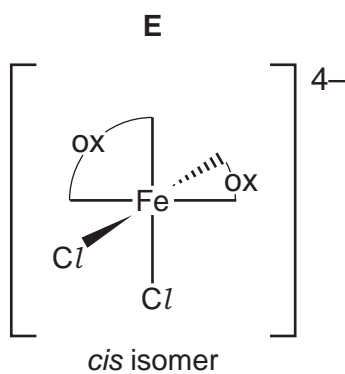
.....
 [1]

(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 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 3.5×10^5 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]

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_{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_{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 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 | $[\text{AuCl}_3]$ / mol dm^{-3} | $[\text{H}_2\text{O}_2]$ / mol dm^{-3} | rate of production of $\text{O}_2(\text{g})$ / $\text{dm}^3 \text{ minute}^{-1}$ |
|------------|---|--|---|
| 1 | 0.05 | 0.50 | 7.66×10^{-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 .

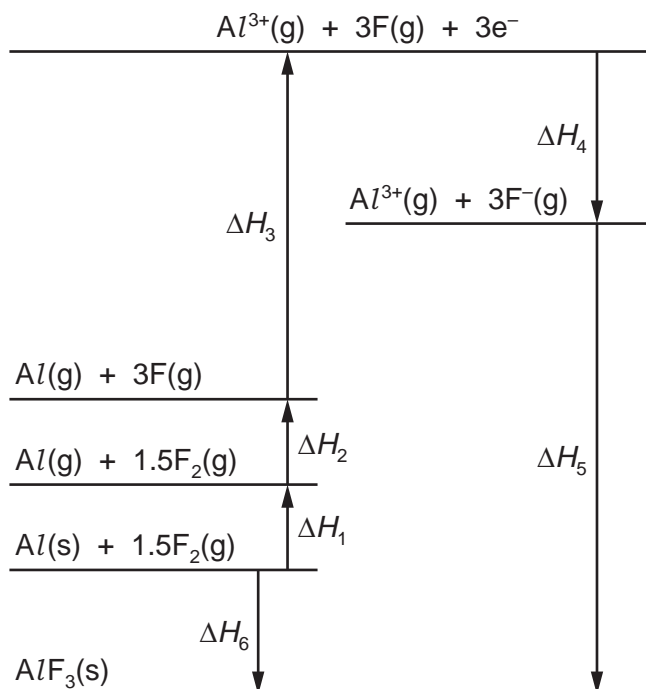
rate constant, $k =$

units =

[2]

(c) AlF_3 is an ionic compound.

The Born–Haber cycle for the formation of AlF_3 is shown.



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

$\Delta H_4 =$

$\Delta H_6 =$

[2]

(ii) Use the data in the table and data from the *Data Booklet* to calculate the lattice energy of AlF_3 .

| process | enthalpy change / 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 $\text{AlF}_3 =$ 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 AlF_3 compares with the lattice energy of ScF_3 .

Explain your answer.

.....

 [2]

- (d) 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_{sp} , of AlF_3 .

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

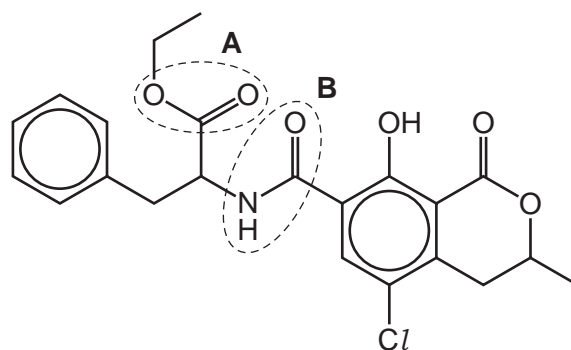
- (ii) Calculate the numerical value of K_{sp} for AlF_3 at 298 K.

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

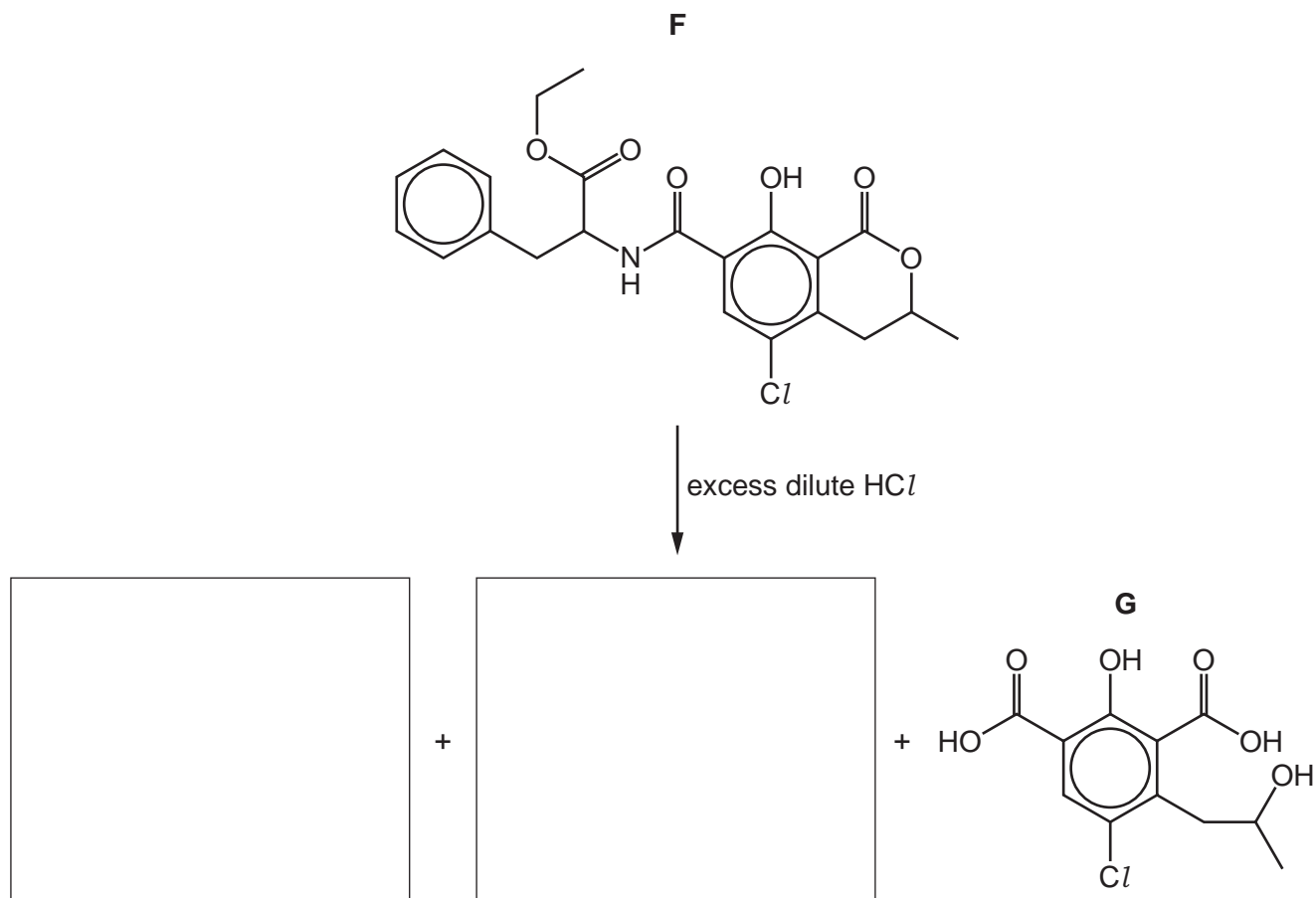
(ii) State the number of chiral carbon atoms in one molecule of **F**.

..... [1]

14

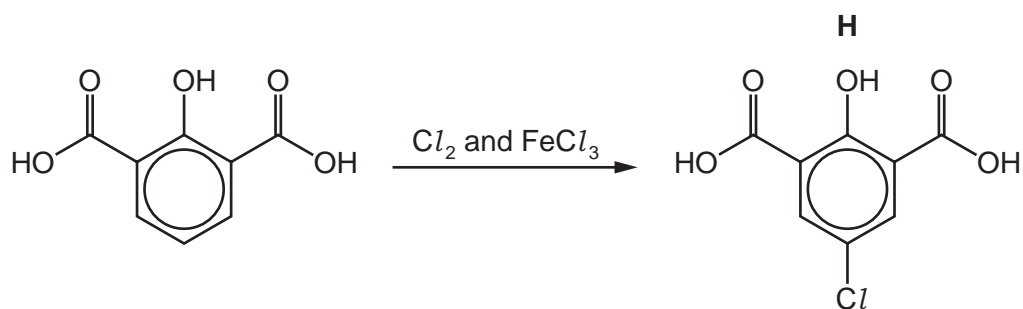
(b) **F** can be hydrolysed by heating with an excess of dilute hydrochloric acid, as shown.

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 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

.....

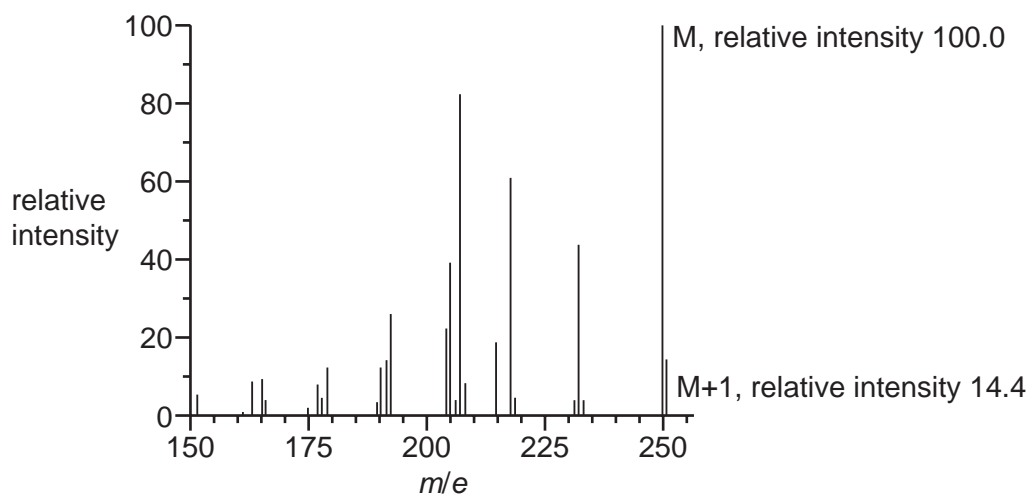
2

.....

[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]

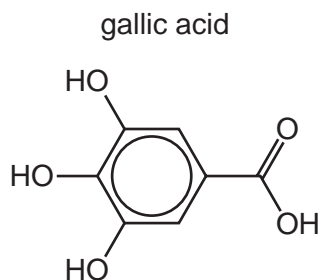
- (ii) The mass spectrum has a peak at $m/e = 205$.

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 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]

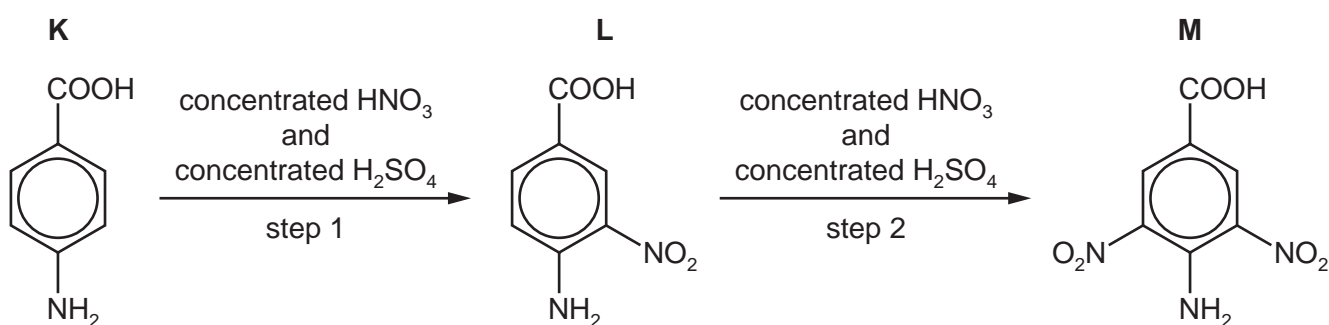
- (iii) Write **two** equations to show how a solution containing gallic acid, $C_7H_6O_5$, and gallate ions, $C_7H_5O_5^-$, acts as a buffer.

.....

 [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.



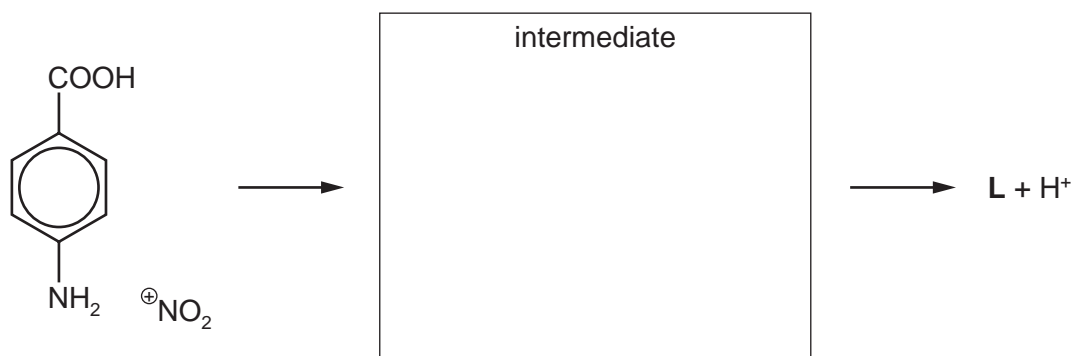
Nitronium ions, NO_2^+ , are generated by the reaction between concentrated sulfuric acid and concentrated nitric acid.

- (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.



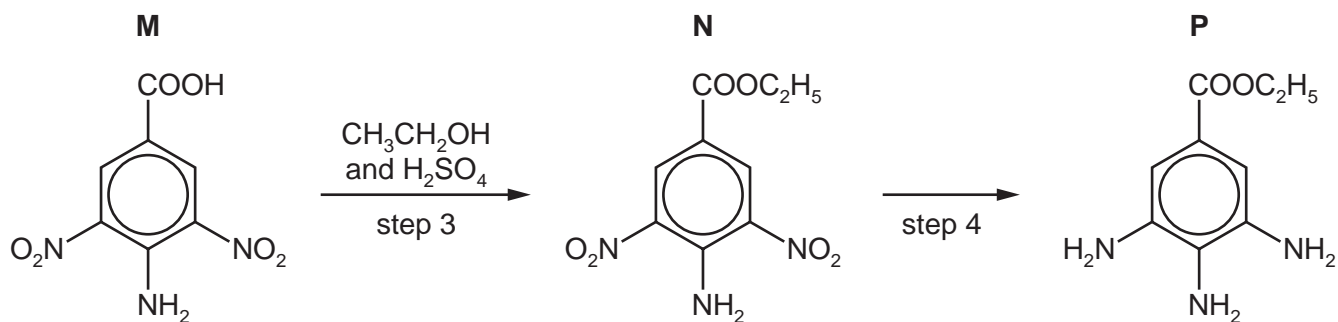
[2]

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

..... [1]

18

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

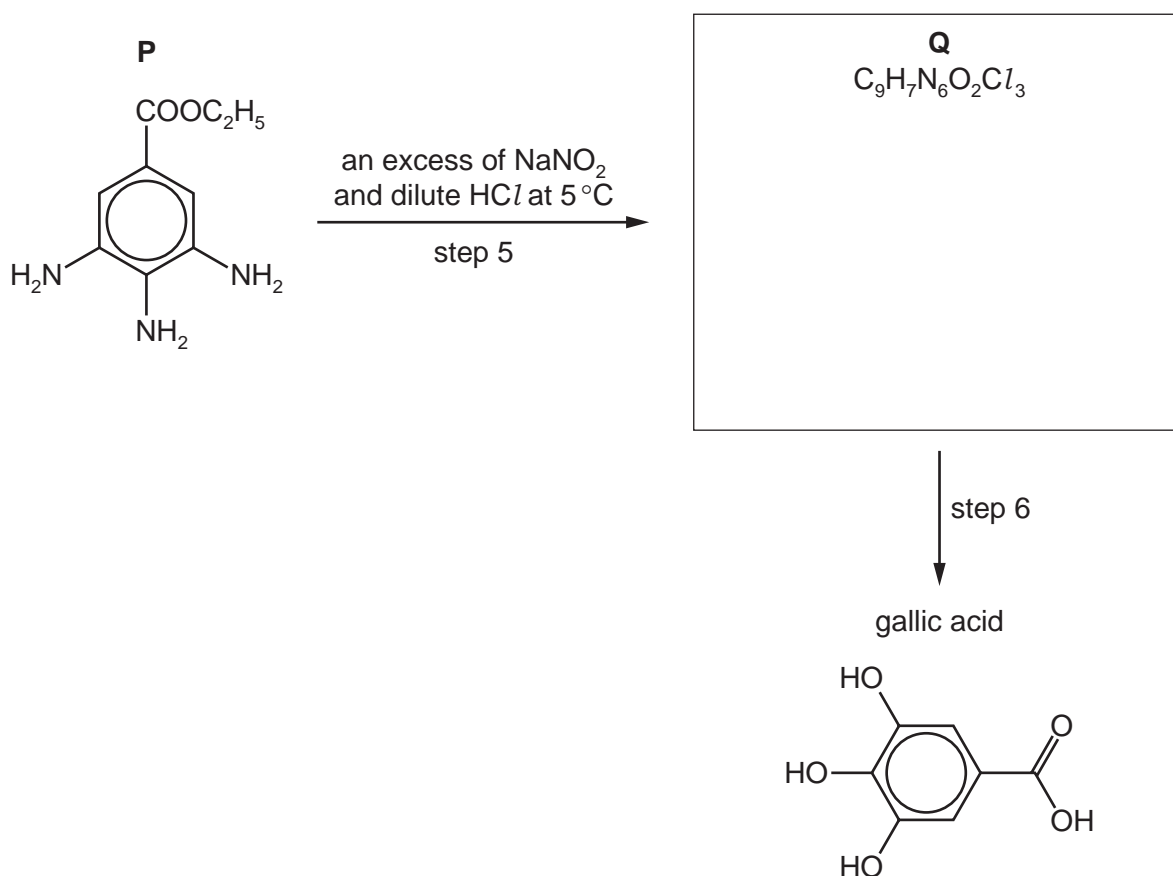


(iv) State the reagents and conditions for step 4.

..... [2]

P reacts with an excess of sodium nitrite, NaNO_2 , and dilute HCl at 5°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.

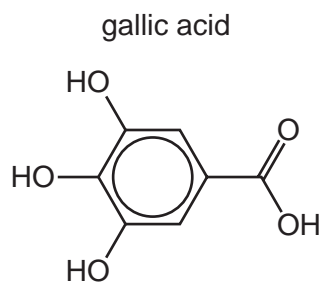


(v) Suggest the structure of compound **Q** in the box provided. [2]

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

..... [1]

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

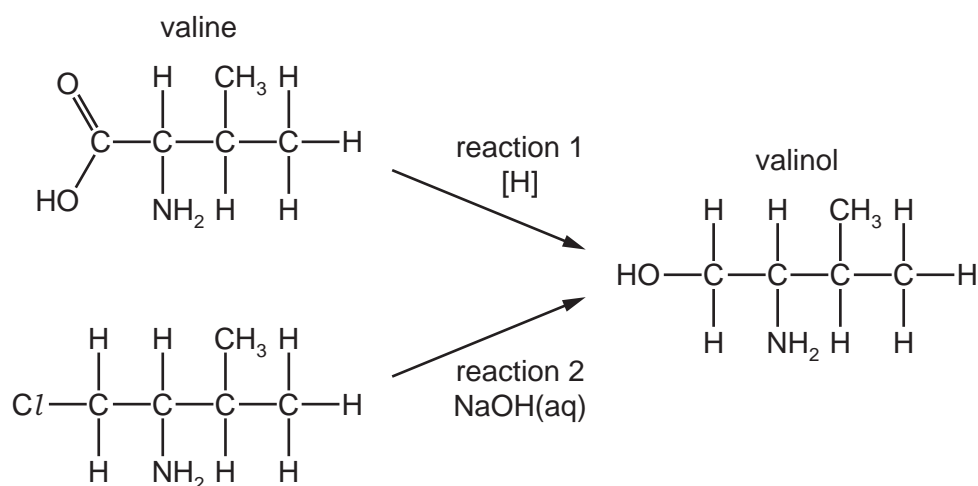
.....

.....

..... [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, $\text{H}_2\text{NCH}_2\text{COOH}$, form the tripeptide Gly-Val-Gly.

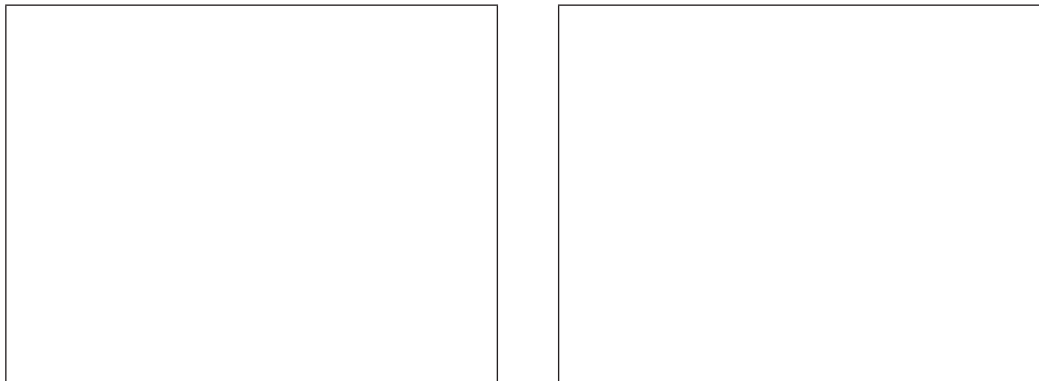
Draw the structure of this tripeptide. Show the peptide bonds fully displayed.

[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

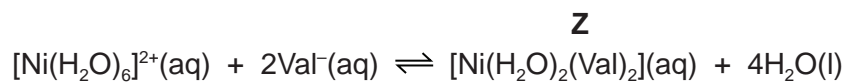
[2]

(ii) Valine is an amino acid.

Draw the zwitterion of valine.

[1]

- (iii) Valinate, 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_{stab} for this equilibrium.

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

[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 $[\text{Ni}(\text{H}_2\text{O})_2(\text{Val})_2]$.

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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