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CHEMISTRY

9701/41

Paper 4 A Level Structured Questions

October/November 2017

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, candidate number and name on all the work you hand in.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

DO **NOT** WRITE IN ANY BARCODES.

Answer **all** questions.

Electronic calculators may be used.

You may lose marks if you do not show your working or if you do not use appropriate units.

A Data Booklet is provided.

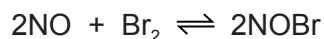
At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [] at the end of each question or part question.

This document consists of **17** printed pages and **3** blank pages.

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

- 1 The compound nitrosyl bromide, NOBr, can be formed by the reaction shown.



- (a) Using oxidation numbers, explain why this reaction is a redox reaction.

.....

 [2]

- (b) Nitrosyl bromide contains a trivalent nitrogen atom.

Draw the 'dot-and-cross' diagram for NOBr. Show outer electrons only.

[2]

- (c) The rate of the reaction was measured at various concentrations of the two reactants, NO and Br₂, and the following results were obtained.

experiment	[NO]/mol dm ⁻³	[Br ₂]/mol dm ⁻³	initial rate /mol dm ⁻³ s ⁻¹
1	0.03	0.02	3.4×10^{-3}
2	0.03	0.04	6.8×10^{-3}
3	0.09	0.04	6.1×10^{-2}
4	0.12	0.06	to be calculated

The general form of the rate equation for this reaction is as follows.

$$\text{rate} = k[\text{NO}]^a[\text{Br}_2]^b$$

- (i) What is meant by the term *order of reaction* with respect to a particular reagent?

.....
 [1]

- (ii) Use the data in the table to deduce the values of a and b in the rate equation. Show your reasoning.

.....

 [2]

- (iii) Use the data in the table to calculate the initial rate for experiment 4.

initial rate = ... $\text{mol dm}^{-3} \text{s}^{-1}$ [1]

- (iv) Use the results of experiment 1 to calculate the rate constant, k , for this reaction. Include the units of k .

rate constant, k = ... units [2]

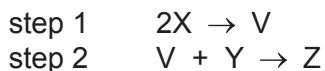
- (v) By considering the rate equation, explain why the rate decreases with decreasing temperature.

.....
 [1]

- (d) The reaction between X and Y was studied.



The following sequence of steps is a proposed mechanism for the reaction.



The general form of the rate equation for this reaction is as follows.

$$\text{rate} = k[\text{X}]^m[\text{Y}]^n$$

Step 1 is the slower step in the mechanism.

Deduce the values of m and n in the rate equation.

m = ... n = ... [1]

[Total: 12]

- 2 (a) The table lists values of solubility products, K_{sp} , of some Group 2 carbonates.

	solubility product in water at 298 K, $K_{sp} / \text{mol}^2 \text{dm}^{-6}$
MgCO_3	1.0×10^{-5}
CaCO_3	5.0×10^{-9}
SrCO_3	1.1×10^{-10}

Use the data in the table to describe the trend in the solubility of the Group 2 carbonates down the group.

.....
 [1]

- (b) (i) Write an equation to show the equilibrium for the solubility product for MgCO_3 .
 Include state symbols.

$\rightleftharpoons$

..... [1]

- (ii) With reference to your equation in (i), suggest what is observed when a few cm^3 of concentrated $\text{Na}_2\text{CO}_3(\text{aq})$ are added to a saturated solution of MgCO_3 . Explain your answer.

.....

 [2]

- (c) Use the data in the table to calculate the solubility of MgCO_3 in water at 298 K, in g dm^{-3} .

solubility of MgCO_3 = ... g dm^{-3} [2]

- (d) (i) Magnesium nitrate decomposes at a **lower** temperature than barium nitrate.

Explain why.

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

- (ii) A sample of barium nitrate was heated strongly until no further change occurred. A white solid was formed.

Write an equation for the action of heat on barium nitrate.

..... [1]

- (iii) When water was added to the white solid produced in (d)(ii), an alkaline solution was produced. Adding sulfuric acid to this solution produced a white precipitate.

Write equations to explain these observations.

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

[Total: 11]

3 (a) Define the term *standard cell potential*.

.....

.....

..... [2]

(b) (i) Draw a fully labelled diagram of the experimental set-up you could use to measure the standard electrode potential of the $\text{Pb}^{2+}(\text{aq})/\text{Pb}(\text{s})$ electrode. Include the necessary chemicals.

[4]

(ii) The $E^\ominus$ for a $\text{Pb}^{2+}(\text{aq})/\text{Pb}(\text{s})$ electrode is -0.13 V .

Suggest how the E for this electrode would differ from its $E^\ominus$ value if the concentration of $\text{Pb}^{2+}(\text{aq})$ ions is reduced. Indicate this by placing a tick (✓) in the appropriate box in the table.

more negative	no change	less negative

Explain your answer.

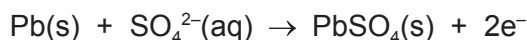
.....

.....

..... [2]

- (c) Car batteries are made up of rechargeable lead-acid cells. Each cell consists of a negative electrode made of Pb metal and a positive electrode made of PbO₂. The electrolyte is H₂SO₄(aq).

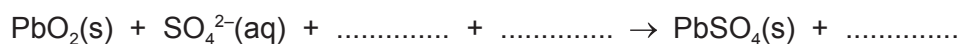
When a lead-acid cell is in use, Pb²⁺ ions are precipitated out as PbSO₄(s) at the negative electrode.



- (i) Calculate the mass of Pb that is converted to PbSO₄ when a current of 0.40A is delivered by the cell for 80 minutes.

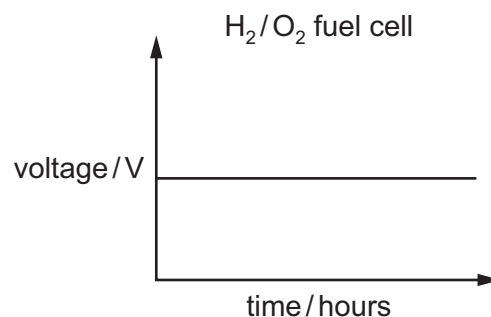
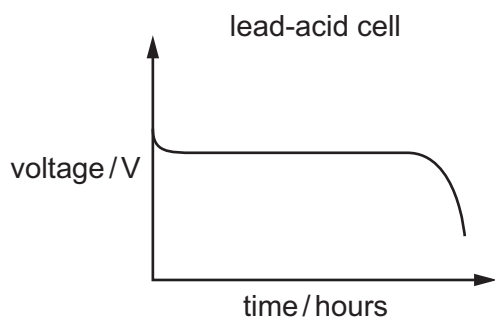
mass of Pb = ... g [2]

- (ii) Complete the half-equation for the reaction taking place at the positive electrode.



[1]

- (d) The diagrams show how the voltage across two different cells changes with time when each cell is used to provide an electric current.



Suggest a reason why

- the voltage of the lead-acid cell changes after several hours,

.....

- the voltage of the fuel cell remains constant.

.....

[2]

[Total: 13]

- 4 (a) Describe and explain how the density and melting point of cobalt compare to those of calcium.

density of cobalt

explanation

.....

melting point of cobalt

explanation

.....

[3]

- (b) Transition metals can form complexes.

What is meant by the term *transition metal complex*?

.....

..... [1]

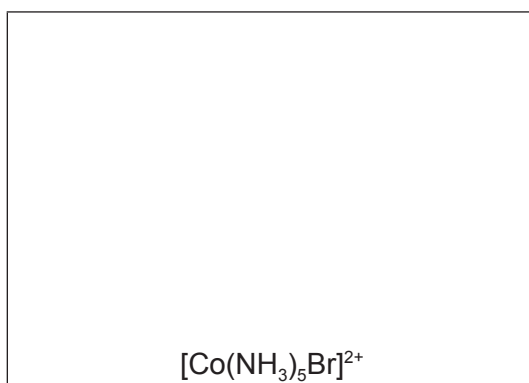
- (c) (i) Cobalt can form the compounds $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$.
These two compounds are structural isomers.

Define the term *structural isomer*.

.....

..... [1]

- (ii) Draw a three-dimensional diagram to show the structure of the ion $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+}$.
Name its shape.



shape [1]

- (iii) State the type of bonding between the cobalt ion and NH_3 groups in the $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+}$ ion.

..... [1]

(iv) State the oxidation number of cobalt in

- $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+}$ oxidation number of Co = ...
- $[\text{Co}(\text{NH}_3)_5\text{SO}_4]^+$ oxidation number of Co = ... [1]

(d) Solutions of the compounds $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ can be distinguished from each other by simple chemical tests.
Assume that any species bonded to the cobalt ion does not react in these tests.

Complete the table with two **different** tests that could be used to positively identify each compound. Give the expected observation with each compound.

test	observation with [Co(NH ₃) ₅ Br]SO ₄ (aq)	observation with [Co(NH ₃) ₅ SO ₄]Br(aq)

[2]

(e) The two compounds $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ are different colours.

Explain why the colours of the two compounds are different.

..... [2]

(f) Some transition metals and their compounds act as catalysts. The catalysis can be classified as heterogeneous or homogeneous.

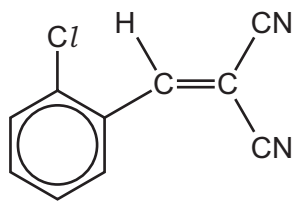
Complete the table by placing **one** tick (✓) in each row to indicate the type of catalysis in each reaction.

	heterogeneous	homogeneous
Fe in the Haber process		
Fe^{2+} in the $\text{I}^-/\text{S}_2\text{O}_8^{2-}$ reaction		
NO_2 in the oxidation of SO_2		
V_2O_5 in the Contact process		

[2]

[Total: 14]

- 5 Compound **P** contains several functional groups.



P

- (a) Name the functional groups present in **P**.

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

- (b) Compound **P** can be polymerised.

Draw a section of the polymer of **P** showing **two** repeat units.
Name the type of polymerisation.

type of polymerisation [2]

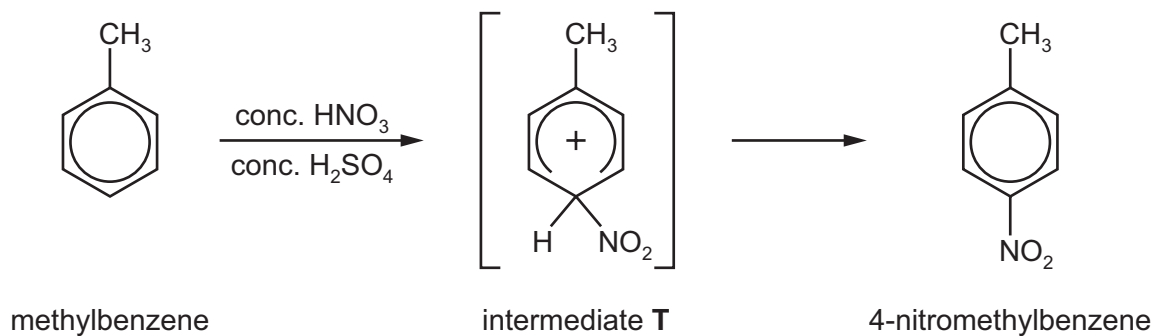
- (c) Complete the following table to show the structures of the products formed and the *type of organic reaction* when **P** reacts with the four reagents.

reagent	structure(s) of product(s)		<i>type of organic reaction</i>
excess Br ₂ (aq)			
excess hot, concentrated, acidified MnO ₄ ⁻ (aq)			
excess hot HCl(aq)			
excess H ₂ /Pt catalyst			

[8]

[Total: 12]

- 6 (a) 4-nitromethylbenzene can be prepared via an electrophilic substitution reaction as shown.



- (i) This reaction also forms an isomer of 4-nitromethylbenzene as a by-product.

Draw the structure of this by-product.

[1]

- (ii) Write an equation for the reaction between HNO_3 and H_2SO_4 that forms the electrophile for this reaction.

..... [1]

- (iii) Describe how the **structure and bonding** of the six-membered ring in intermediate T differs from that in methylbenzene.

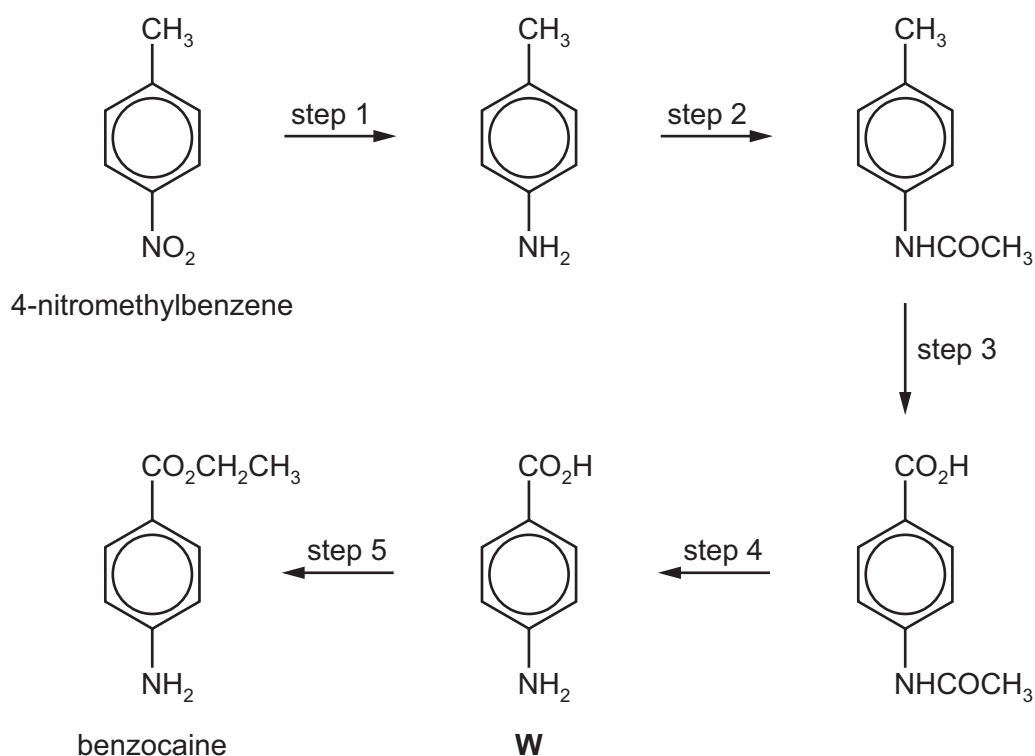
.....

.....

.....

..... [3]

- (b) Benzocaine is used as a local anaesthetic. It can be synthesised from 4-nitromethylbenzene by the route shown.



- (i) Give the systematic name of compound **W**.

..... [1]

- (ii) Suggest the reagents and conditions for steps 1–5.

step 1

step 2

step 3

step 4

step 5

[6]

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

.....

.....

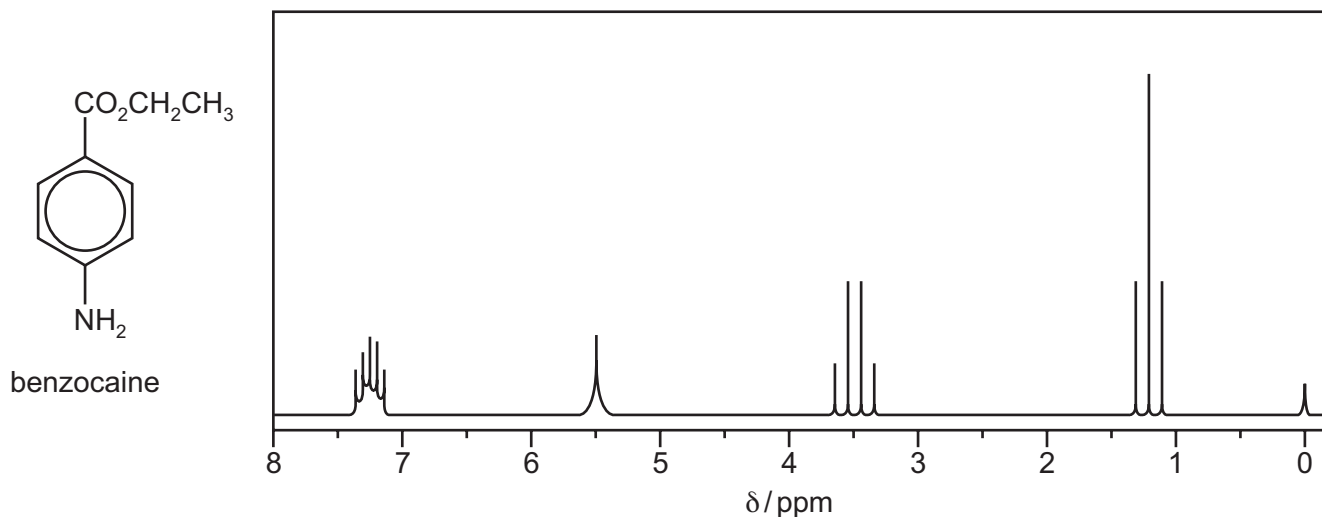
..... [2]

(d) A sample of benzocaine, shown below, was analysed by proton NMR and carbon-13 NMR spectroscopy.

(i) Predict the number of peaks that would be seen in the carbon-13 NMR spectrum.

..... [1]

(ii) Benzocaine was dissolved in CDCl_3 and the proton NMR spectrum of this solution was recorded.



Suggest why CDCl_3 and not CHCl_3 is used as the solvent when obtaining a proton NMR spectrum.

..... [1]

(iii) Use the *Data Booklet* and the spectrum in (d)(ii) to complete the table for the proton NMR spectrum of benzocaine. The actual chemical shifts, δ , for the four absorptions have been added.

δ/ppm	group responsible for the peak	number of ^1H atoms responsible for the peak	splitting pattern
1.2			
3.5			
5.5			
7.1–7.4			multiplet

[4]

(iv) Explain the splitting pattern for the absorption at $\delta 1.2\text{ ppm}$.

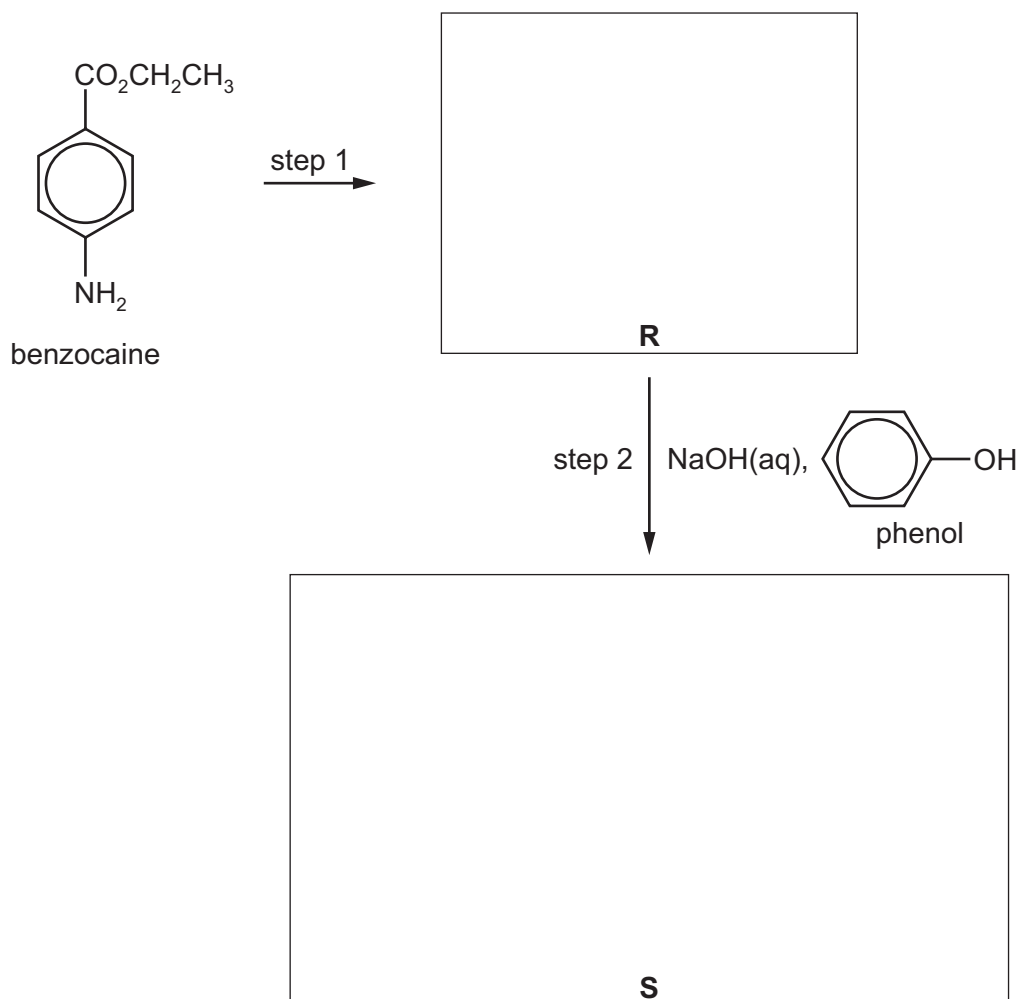
..... [1]

- (v) The proton NMR spectrum of benzocaine dissolved in D_2O was recorded.

Suggest how this spectrum would differ from the spectrum in (d)(ii).
Explain your answer.

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

- (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]

7 (a) Complete the following electronic structures.

- the iron atom, Fe $1s^2 2s^2 2p^6$
- the iron(III) ion, Fe^{3+} $1s^2 2s^2 2p^6$

[1]

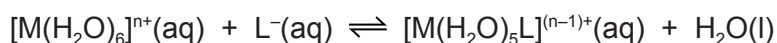
(b) Solutions of iron(III) salts are acidic due to the equilibrium shown.



Calculate the pH of a 0.25 mol dm^{-3} $FeCl_3$ solution.

pH = ... [2]

(c) The table shows numerical values of the stability constants for the following equilibrium where M can be one of the metal ions listed and L one of the ligands which replaces **one** H_2O molecule.



metal ion, M	ligand, L	stability constant, K_{stab}
Fe^{3+}	F^-	1.0×10^6
Fe^{3+}	Cl^-	2.5×10^1
Fe^{3+}	SCN^-	9.0×10^2
Hg^{2+}	Cl^-	5.0×10^6

(i) What is meant by the term *stability constant*, K_{stab} ?

.....
 [1]

(ii) Use the data in the table to predict the formula of the complex formed in the greatest amount when

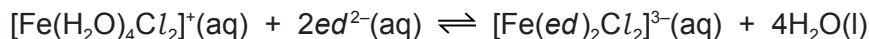
- a solution containing equal concentrations of both F^- and SCN^- ions is added to $Fe^{3+}(aq)$,

- a solution containing equal concentrations of both Fe^{3+} and Hg^{2+} ions is added to $Cl^-(aq)$.

[1]

Ethanedioate ions, O_2CCO_2^- , are bidentate ligands. The abbreviation ed^{2-} can be used to represent ethanedioate ions.

(d) The complex $[\text{Fe}(\text{ed})_2\text{Cl}_2]^{3-}$ can be formed according to the equation shown.



Write the expression for the equilibrium constant, K_{stab} , and state its units.

$K_{\text{stab}} =$

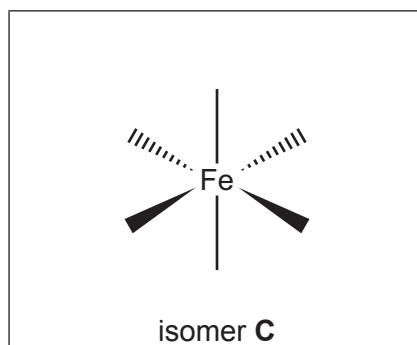
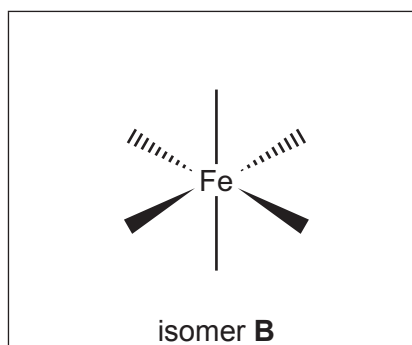
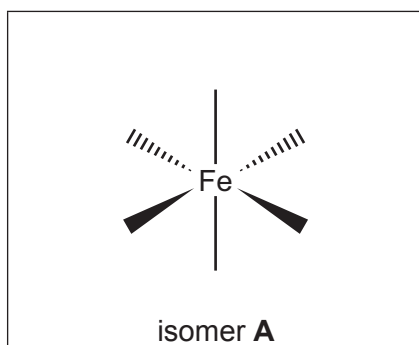
units

[2]

(e) $[\text{Fe}(\text{ed})_2\text{Cl}_2]^{3-}$ shows geometrical and optical isomerism.

(i) Complete the three-dimensional diagrams to show the three stereoisomers of $[\text{Fe}(\text{ed})_2\text{Cl}_2]^{3-}$.

You may use $\text{—O—CH}_2\text{—CH}_2\text{—O—}$ to represent ed^{2-} .



[3]

(ii) Give the letters of two isomers of $[\text{Fe}(\text{ed})_2\text{Cl}_2]^{3-}$ which are geometrical isomers of each other.

..... [1]

(iii) Give the letters of the two isomers of $[\text{Fe}(\text{ed})_2\text{Cl}_2]^{3-}$ which show optical isomerism.

..... [1]

(iv) Give the letter of the isomer which has **no** dipole moment.

..... [1]

[Total: 13]

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9701/42

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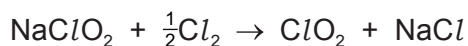
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This document consists of **19** printed pages and **1** blank page.

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

- 1 The compound chlorine dioxide, ClO_2 , can be prepared by the reaction shown.



- (a) Using oxidation numbers, explain why this reaction is a redox reaction.

.....

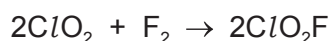
 [2]

- (b) The central atom in the molecule of ClO_2 is chlorine.

Draw the 'dot-and-cross' diagram for ClO_2 . Show outer electrons only.

[2]

- (c) The reaction between ClO_2 and F_2 is shown.



The rate of the reaction was measured at various concentrations of the two reactants and the following results were obtained.

experiment	$[\text{ClO}_2]/\text{mol dm}^{-3}$	$[\text{F}_2]/\text{mol dm}^{-3}$	initial rate $/\text{mol dm}^{-3}\text{s}^{-1}$
1	0.010	0.060	2.20×10^{-3}
2	0.025	0.060	to be calculated
3	to be calculated	0.040	7.04×10^{-3}

The rate equation is $\text{rate} = k[\text{ClO}_2][\text{F}_2]$.

- (i) What is meant by the term *order of reaction* with respect to a particular reagent?

.....
 [1]

- (ii) Use the results of experiment 1 to calculate the rate constant, k , for this reaction. Include the units of k .

rate constant, k = ... units [2]

- (iii) Use the data in the table to calculate

- the initial rate in experiment 2,

initial rate = ... $\text{mol dm}^{-3} \text{s}^{-1}$

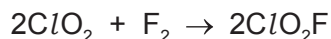
- $[\text{ClO}_2]$ in experiment 3.

$[\text{ClO}_2]$ = ... mol dm^{-3}
[2]

- (d) (i) What is meant by the term *rate-determining step*?

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

- (ii) The equation for the reaction between ClO_2 and F_2 is shown.



$$\text{rate} = k[\text{ClO}_2][\text{F}_2]$$

The mechanism for this reaction has two steps.

Suggest equations for the **two** steps of this mechanism, stating which of the two steps is the rate-determining step.

step 1

step 2

rate-determining step = ...

[2]

- (e) By considering the rate equation, explain why the rate increases with increasing temperature.

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

[Total: 13]

- 2 (a) When water is added to magnesium nitride, Mg_3N_2 , the products are a white suspension of $\text{Mg}(\text{OH})_2$ and an alkaline gas.

(i) Write an equation for this reaction.

..... [1]

(ii) A 2.52 g sample of Mg_3N_2 is added to an excess of water.

Calculate the mass of $\text{Mg}(\text{OH})_2$ formed.

mass of $\text{Mg}(\text{OH})_2$ = ... g [2]

(b) State and explain how the solubility of the Group 2 hydroxides varies down the group.

.....

 [4]

(c) Magnesium hydroxide is sparingly soluble in water. The concentration of its saturated solution at 298 K is $1.7 \times 10^{-4} \text{ mol dm}^{-3}$.

(i) Write an expression for the solubility product, K_{sp} , of $\text{Mg}(\text{OH})_2$.

$$K_{\text{sp}} =$$

[1]

(ii) Calculate the value of K_{sp} for $\text{Mg}(\text{OH})_2$ at 298 K and state its units.

$K_{\text{sp}} =$ units [2]

- (d) The temperature at which the Group 2 hydroxides and carbonates start to decompose increases down the group.

Suggest an explanation for this trend in the decomposition temperature of the Group 2 hydroxides.

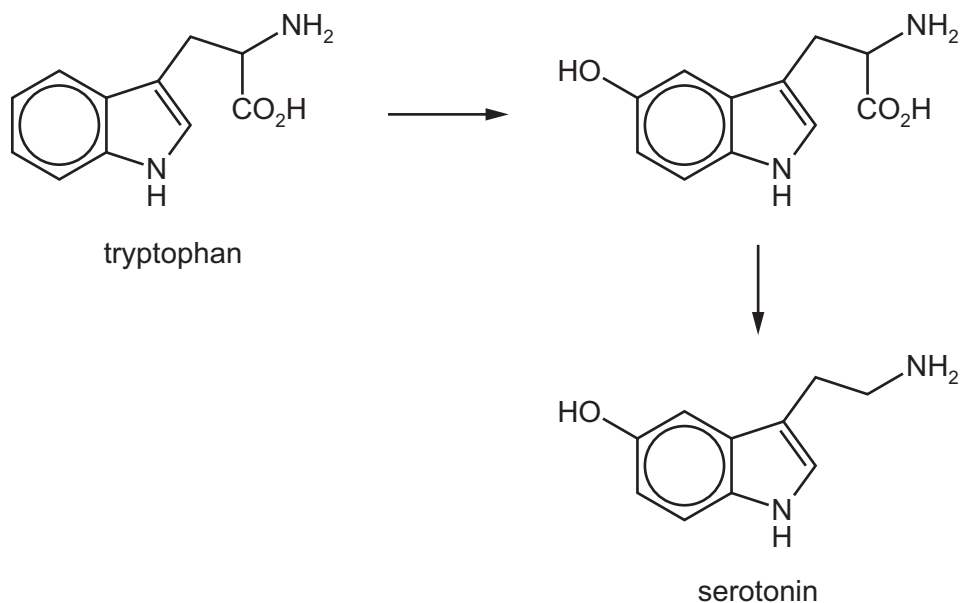
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..... [2]

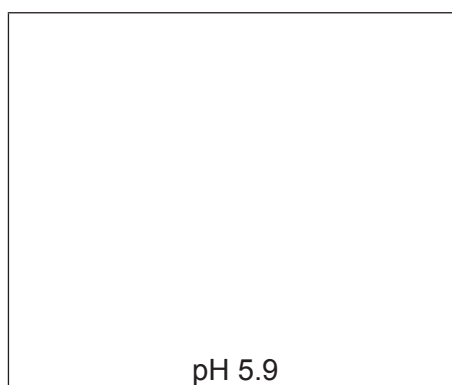
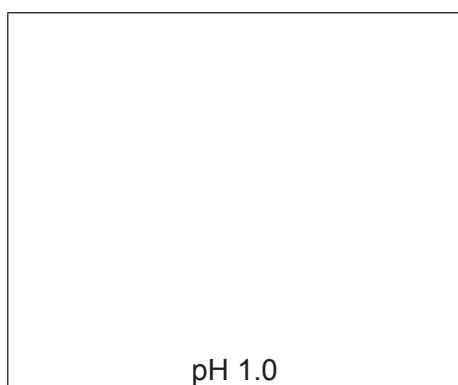
[Total: 12]

- 3 Serotonin can be synthesised from the amino acid tryptophan in two steps.



- (a) (i) In a buffer solution at pH 5.9, a sample of tryptophan does **not** move during electrophoresis.

Draw the structures of the ions formed by tryptophan at pH 1.0 and pH 5.9.



[2]

- (ii) Tryptophan can combine with valine to form a dipeptide.

Use the *Data Booklet* to draw the structure of this dipeptide.

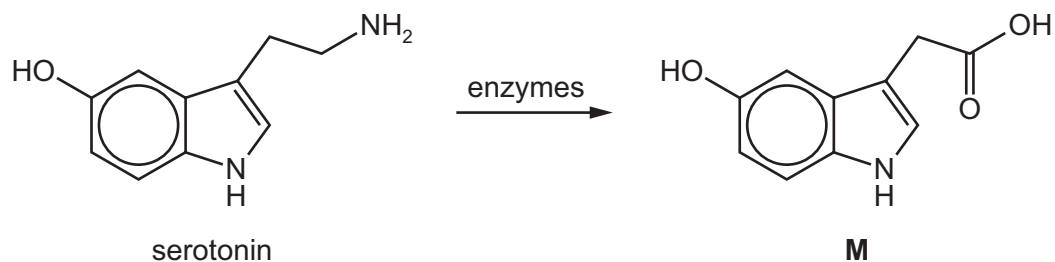
[2]

(b) Complete the following table to show the structures of the products formed and the *type of reaction* occurring when **serotonin** reacts with the four reagents in separate reactions.

reagent	structure of product	<i>type of reaction</i>
Na		
excess Br ₂ (aq)		
excess CH ₃ COCl		
excess H ₂ /Pt catalyst		

[8]

(c) Serotonin is converted by enzymes in the liver to compound **M**.



- (i) By reference to the *Data Booklet*, suggest how the infra-red spectrum of **M** would differ from that of serotonin.

.....
 [1]

- (ii) The proton NMR spectrum of **M** dissolved in CDCl_3 shows eight peaks due to the eight different types of proton present in the molecule.

The proton NMR spectrum of **M** dissolved in D_2O was recorded.

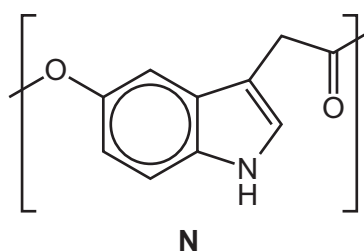
Predict the number of peaks that would be seen in the proton NMR spectrum of **M** in D_2O . Explain your answer.

number of peaks

explanation

[2]

(d) Compound **M** can be polymerised under certain conditions to form polymer **N**, shown.



Polymer **N** is biodegradable, unlike polyethene which is not.

Explain why **N** is biodegradable.

.....
 [1]

[Total: 16]

- 4 An electrochemical cell consists of a half-cell containing $V^{3+}(aq)$ and $V^{2+}(aq)$ ions and another half-cell containing $VO_2^+(aq)$ and $VO^{2+}(aq)$ ions.

(a) (i) Use data from the *Data Booklet* to calculate a value for the $E_{\text{cell}}^\ominus$.

$$E_{\text{cell}}^\ominus = \dots\dots\dots \text{ V [1]}$$

(ii) Write the ionic equation for the cell reaction.

..... [1]

(iii) Draw a fully labelled diagram of the apparatus you could use to measure the potential of this cell. Include the necessary chemicals.

[4]

- (b) Use data from the *Data Booklet* to predict whether a reaction might take place when the following pairs of aqueous solutions are mixed. If a reaction occurs, write an equation for it and calculate the E°_{cell} .

- $\text{V}^{2+}(\text{aq})$ and $\text{Sn}^{4+}(\text{aq})$

Does a reaction occur?

equation

E°_{cell}

- $\text{VO}^{2+}(\text{aq})$ and $\text{Fe}^{3+}(\text{aq})$

Does a reaction occur?

equation

E°_{cell}

[3]

[Total: 9]

- 5 (a) The arrangement of the anions around a cation is called the geometry of the cation; e.g. in $[\text{CuCl}_4]^{2-}$ the geometry of copper is tetrahedral and the co-ordination number of copper is 4.

The geometry of a cation in an ionic compound can be predicted from the ratio of the ionic radii of the cation and anion involved.

$\frac{\text{cation radius}}{\text{anion radius}}$	geometry of cation
0.155–0.225	trigonal planar
0.225–0.414	tetrahedral
0.414–0.732	octahedral

Use data from the *Data Booklet* to predict the geometry of, and hence the co-ordination number of, the cation for

- sodium chloride, NaCl ,

geometry of Na^+ = ... co-ordination number of Na^+ = ...

- magnesium chloride, MgCl_2 .

geometry of Mg^{2+} = ... co-ordination number of Mg^{2+} = ... [2]

- (b) Magnesium(I) chloride, MgCl , is an unstable compound and readily decomposes as shown.



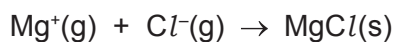
Use the following data to calculate the enthalpy change of this reaction.

$$\Delta H_f^\ominus \text{MgCl}(\text{s}) = -106 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\ominus \text{MgCl}_2(\text{s}) = -642 \text{ kJ mol}^{-1}$$

enthalpy change = ... kJ mol^{-1} [1]

- (c) (i) The equation for which ΔH is the lattice energy for MgCl is shown.



Use the equation, the following data, and relevant data from the *Data Booklet* to calculate a value for the lattice energy of MgCl . You might find it helpful to construct an energy cycle.

electron affinity of $\text{Cl}(\text{g})$ $= -349 \text{ kJ mol}^{-1}$
 enthalpy change of atomisation of $\text{Mg}(\text{s})$ $= +147 \text{ kJ mol}^{-1}$
 enthalpy change of formation of $\text{MgCl}(\text{s})$ $= -106 \text{ kJ mol}^{-1}$

lattice energy $\text{MgCl} = \dots\dots\dots \text{ kJ mol}^{-1}$ [3]

- (ii) Suggest how the lattice energies of MgCl_2 and NaCl will compare to that of MgCl .
 Explain your answers.

MgCl_2 and MgCl

.....

NaCl and MgCl

..... [3]

- (d) Define the term *electron affinity*.

.....

..... [2]

[Total: 11]

- 6 (a) Define the term *transition metal complex*.

.....
 [1]

- (b) Platinum can form the compound $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2][\text{PtCl}_4]$.

State the co-ordination numbers and the oxidation numbers of the platinum in the two ions of this compound.

	co-ordination number	oxidation number
$[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]^{2+}$		
$[\text{PtCl}_4]^{2-}$		

[2]

- (c) Draw three-dimensional diagrams to show the structures of the two isomers of $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]^{2+}$.

[2]

- (d) Solutions of the compounds $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Br}_2$ and $[\text{Pt}(\text{NH}_3)_4\text{Br}_2]\text{Cl}_2$ can be distinguished from each other by a simple chemical test. Assume that any species bonded to the platinum ion does not react in this test.

Complete the table with a test that could be used to positively identify each compound. Give details of expected observations with each compound.

test	observation with $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Br}_2$	observation with $[\text{Pt}(\text{NH}_3)_4\text{Br}_2]\text{Cl}_2$

[2]

- (e) In this question you should consider geometrical and optical isomerism.

What type of isomerism is shown by the following complexes?

You should answer **geometrical**, **optical**, **both** or **neither**.

octahedral $[\text{Co}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2\text{Cl}_2]^+$

square planar $[\text{Ni}(\text{CN})_2\text{Cl}_2]^{2-}$

tetrahedral $[\text{CuBr}_2\text{Cl}_2]^{2-}$

[3]

- (f) Many enzymes contain transition metal complexes.

Describe, with the aid of a suitably labelled diagram, how an enzyme catalyses the breakdown of a substrate molecule.

.....

.....

.....

..... [3]

[Total: 13]

- 7 (a) Calcium carbide, CaC_2 , reacts readily with water, forming ethyne, C_2H_2 , and a sparingly soluble white ionic compound.

(i) Write an equation for the reaction of CaC_2 with water.

..... [1]

(ii) Draw a 'dot-and-cross' diagram for the carbide ion, C_2^{2-} . Show outer electrons only.

[1]

(b) Ethyne is the simplest member of the alkyne homologous series.



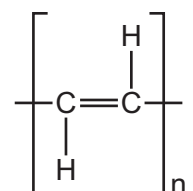
ethyne

Propyne, C_3H_4 , and butyne, C_4H_6 , are the next two members of the series.

Deduce the general formula for the alkynes.

..... [1]

(c) Ethyne can be polymerised into poly(acetylene), which is a conducting polymer.



poly(acetylene)

(i) Suggest why this polymer conducts electricity.

.....
 [1]

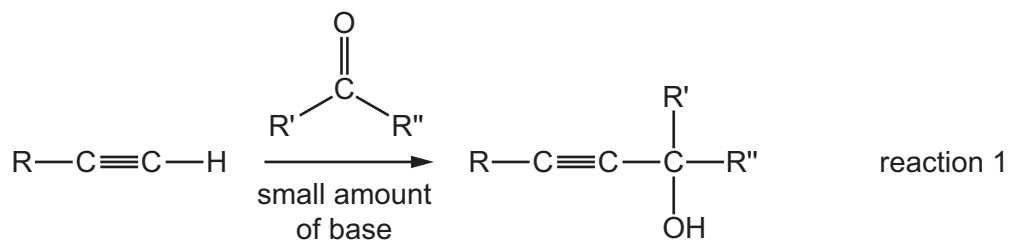
(ii) State the empirical formula of poly(acetylene).

..... [1]

(iii) By reference to a physical or chemical property, suggest **one** advantage of a conducting polymer when compared with metals.

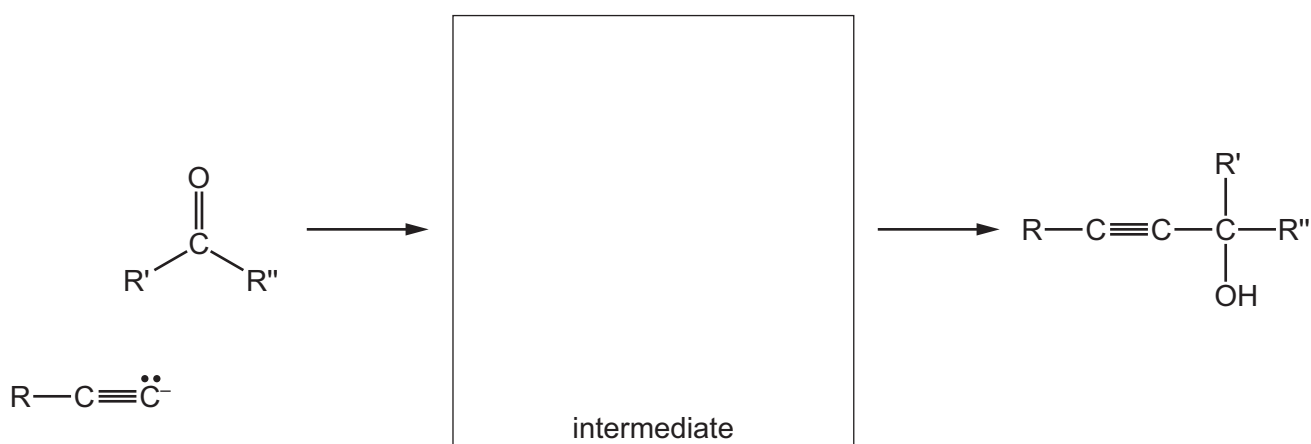
..... [1]

(d) Alkynes can react with carbonyl compounds under basic conditions as shown in reaction 1.



- (i) The first step of the mechanism of reaction 1 involves the alkyne anion reacting with the carbonyl compound.

Complete the first step of the mechanism and draw the intermediate for this reaction. Include all relevant dipoles, charges and curly arrows.

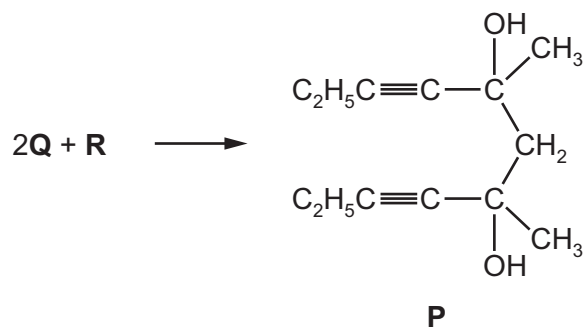


[3]

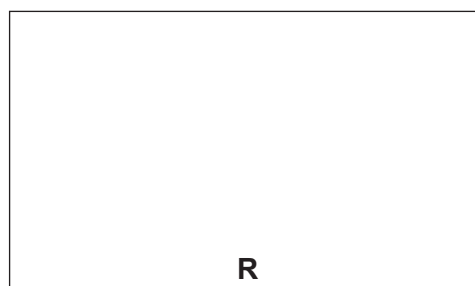
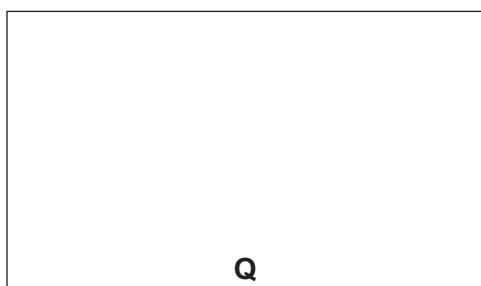
- (ii) Suggest the name of the mechanism in reaction 1.

..... [1]

(iii) An alkyne, **Q**, and a carbonyl compound, **R**, react together to form compound **P** as shown.



Use reaction 1 to suggest the structures of **Q** and **R**.



[2]

(e) A series of twelve separate experiments is carried out as shown in the table.

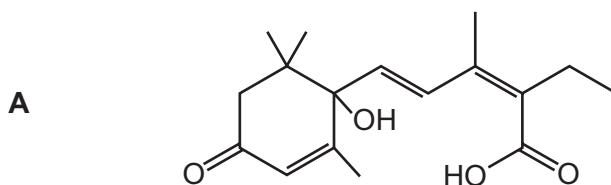
Complete the table by writing in **each** box a tick (✓) if a reaction occurs, or a cross (✗) if no reaction occurs.

	CH ₃ CHO	HCO ₂ H	CH ₃ COCH ₃	HO ₂ CCO ₂ H
hot, acidified MnO ₄ ⁻ (aq)				
alkaline I ₂ (aq)				
warm Tollens' reagent				

[4]

[Total: 16]

- 8 (a) Compound **A** can be produced from a plant hormone.



- (i) Compound **A** shows optical and geometrical isomerism.

On the structure of **A** above,

- draw a **line** through the bond(s) that give rise to geometrical isomerism,
- **circle** all chiral carbon atoms.

[2]

- (ii) Give the **names** of four functional groups present in **A**.

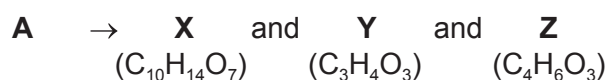
.....
 [2]

- (iii) A molecule of **A** has 17 carbon atoms.

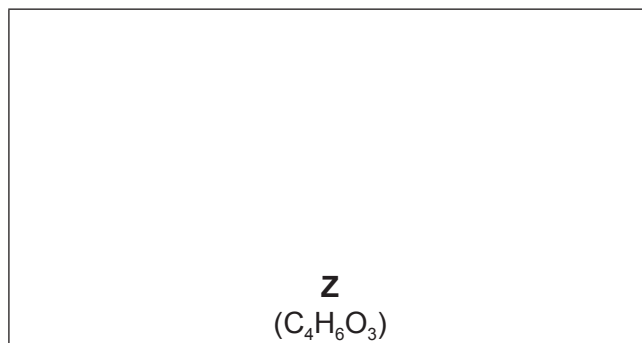
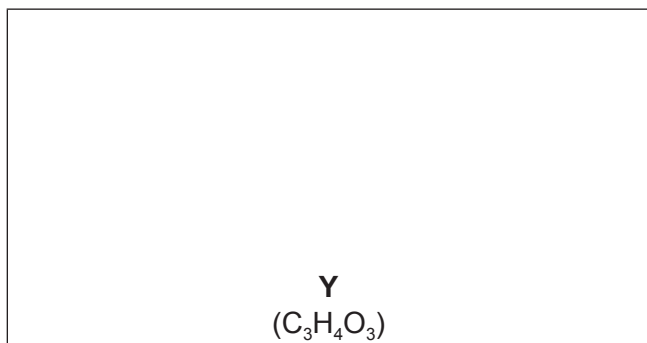
State the number of carbon atoms that are sp , sp^2 and sp^3 hybridised in **A**.

sp carbons = ... sp^2 carbons = ... sp^3 carbons = ... [1]

- (iv) When **A** is reacted with an excess of hot, concentrated manganate(VII) ions, a mixture of three organic compounds is formed.

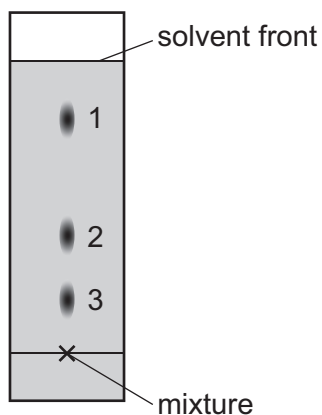


Suggest the structures of **Y** and **Z**.



[2]

- (b) A mixture of three different compounds, **J**, **K** and **L**, was analysed by thin layer chromatography using a polar stationary phase and a non-polar mobile phase. The three compounds all have similar molecular masses. The resulting chromatogram is shown.



- (i) Identify which spot corresponds to each compound.

compound	spot
J $\text{CH}_3\text{COCO}_2\text{H}$	
K $\text{HO}_2\text{CCO}_2\text{H}$	
L $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$	

[1]

- (ii) Explain your answers to (b)(i).

.....
 [1]

- (iii) What is meant by the term R_f value?

.....
 [1]

[Total: 10]

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CHEMISTRY

9701/43

Paper 4 A Level Structured Questions

October/November 2017

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, candidate number and name on all the work you hand in.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

DO **NOT** WRITE IN ANY BARCODES.

Answer **all** questions.

Electronic calculators may be used.

You may lose marks if you do not show your working or if you do not use appropriate units.

A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.

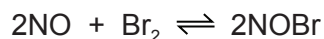
The number of marks is given in brackets [] at the end of each question or part question.

This document consists of **17** printed pages and **3** blank pages.



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

- 1 The compound nitrosyl bromide, NOBr, can be formed by the reaction shown.



- (a) Using oxidation numbers, explain why this reaction is a redox reaction.

.....

 [2]

- (b) Nitrosyl bromide contains a trivalent nitrogen atom.

Draw the 'dot-and-cross' diagram for NOBr. Show outer electrons only.

[2]

- (c) The rate of the reaction was measured at various concentrations of the two reactants, NO and Br₂, and the following results were obtained.

experiment	[NO]/mol dm ⁻³	[Br ₂]/mol dm ⁻³	initial rate /mol dm ⁻³ s ⁻¹
1	0.03	0.02	3.4×10^{-3}
2	0.03	0.04	6.8×10^{-3}
3	0.09	0.04	6.1×10^{-2}
4	0.12	0.06	to be calculated

The general form of the rate equation for this reaction is as follows.

$$\text{rate} = k[\text{NO}]^a[\text{Br}_2]^b$$

- (i) What is meant by the term *order of reaction* with respect to a particular reagent?

.....
 [1]

- (ii) Use the data in the table to deduce the values of a and b in the rate equation.
Show your reasoning.

.....

 [2]

- (iii) Use the data in the table to calculate the initial rate for experiment 4.

initial rate = ... $\text{mol dm}^{-3} \text{s}^{-1}$ [1]

- (iv) Use the results of experiment 1 to calculate the rate constant, k , for this reaction.
Include the units of k .

rate constant, k = ... units [2]

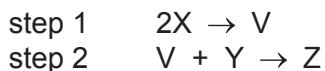
- (v) By considering the rate equation, explain why the rate decreases with decreasing temperature.

.....
 [1]

- (d) The reaction between X and Y was studied.



The following sequence of steps is a proposed mechanism for the reaction.



The general form of the rate equation for this reaction is as follows.

$$\text{rate} = k[\text{X}]^m[\text{Y}]^n$$

Step 1 is the slower step in the mechanism.

Deduce the values of m and n in the rate equation.

m = ... n = ... [1]

[Total: 12]

- 2 (a) The table lists values of solubility products, K_{sp} , of some Group 2 carbonates.

	solubility product in water at 298 K, $K_{sp} / \text{mol}^2 \text{dm}^{-6}$
MgCO_3	1.0×10^{-5}
CaCO_3	5.0×10^{-9}
SrCO_3	1.1×10^{-10}

Use the data in the table to describe the trend in the solubility of the Group 2 carbonates down the group.

.....
 [1]

- (b) (i) Write an equation to show the equilibrium for the solubility product for MgCO_3 .
 Include state symbols.

$\rightleftharpoons$

..... [1]

- (ii) With reference to your equation in (i), suggest what is observed when a few cm^3 of concentrated $\text{Na}_2\text{CO}_3(\text{aq})$ are added to a saturated solution of MgCO_3 . Explain your answer.

.....

 [2]

- (c) Use the data in the table to calculate the solubility of MgCO_3 in water at 298 K, in g dm^{-3} .

solubility of MgCO_3 = ... g dm^{-3} [2]

- (d) (i) Magnesium nitrate decomposes at a **lower** temperature than barium nitrate.

Explain why.

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

- (ii) A sample of barium nitrate was heated strongly until no further change occurred. A white solid was formed.

Write an equation for the action of heat on barium nitrate.

..... [1]

- (iii) When water was added to the white solid produced in (d)(ii), an alkaline solution was produced. Adding sulfuric acid to this solution produced a white precipitate.

Write equations to explain these observations.

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

[Total: 11]

3 (a) Define the term *standard cell potential*.

.....

.....

..... [2]

(b) (i) Draw a fully labelled diagram of the experimental set-up you could use to measure the standard electrode potential of the $\text{Pb}^{2+}(\text{aq})/\text{Pb}(\text{s})$ electrode. Include the necessary chemicals.

[4]

(ii) The $E^\ominus$ for a $\text{Pb}^{2+}(\text{aq})/\text{Pb}(\text{s})$ electrode is -0.13 V .

Suggest how the E for this electrode would differ from its $E^\ominus$ value if the concentration of $\text{Pb}^{2+}(\text{aq})$ ions is reduced. Indicate this by placing a tick (✓) in the appropriate box in the table.

more negative	no change	less negative

Explain your answer.

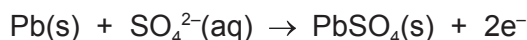
.....

.....

..... [2]

- (c) Car batteries are made up of rechargeable lead-acid cells. Each cell consists of a negative electrode made of Pb metal and a positive electrode made of PbO₂. The electrolyte is H₂SO₄(aq).

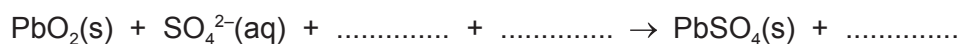
When a lead-acid cell is in use, Pb²⁺ ions are precipitated out as PbSO₄(s) at the negative electrode.



- (i) Calculate the mass of Pb that is converted to PbSO₄ when a current of 0.40A is delivered by the cell for 80 minutes.

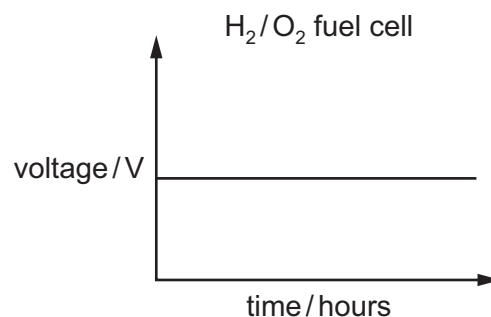
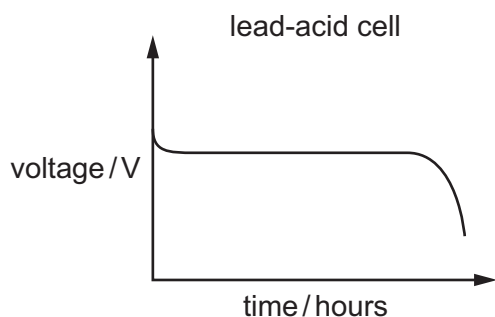
mass of Pb = ... g [2]

- (ii) Complete the half-equation for the reaction taking place at the positive electrode.



[1]

- (d) The diagrams show how the voltage across two different cells changes with time when each cell is used to provide an electric current.



Suggest a reason why

- the voltage of the lead-acid cell changes after several hours,

.....

- the voltage of the fuel cell remains constant.

.....

[2]

[Total: 13]

- 4 (a) Describe and explain how the density and melting point of cobalt compare to those of calcium.

density of cobalt

explanation

.....

melting point of cobalt

explanation

.....

[3]

- (b) Transition metals can form complexes.

What is meant by the term *transition metal complex*?

.....

..... [1]

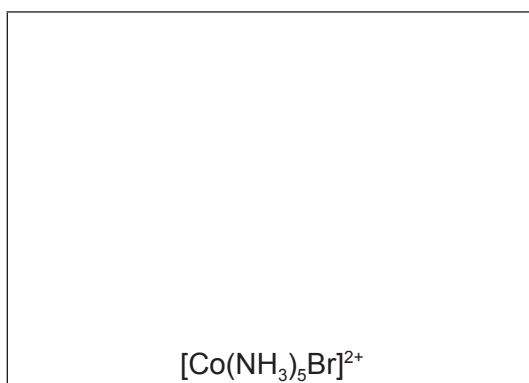
- (c) (i) Cobalt can form the compounds $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$.
These two compounds are structural isomers.

Define the term *structural isomer*.

.....

..... [1]

- (ii) Draw a three-dimensional diagram to show the structure of the ion $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+}$.
Name its shape.



shape [1]

- (iii) State the type of bonding between the cobalt ion and NH_3 groups in the $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+}$ ion.

..... [1]

(iv) State the oxidation number of cobalt in

- $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+}$ oxidation number of Co = ...
- $[\text{Co}(\text{NH}_3)_5\text{SO}_4]^+$ oxidation number of Co = ... [1]

(d) Solutions of the compounds $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ can be distinguished from each other by simple chemical tests.
Assume that any species bonded to the cobalt ion does not react in these tests.

Complete the table with two **different** tests that could be used to positively identify each compound. Give the expected observation with each compound.

test	observation with [Co(NH ₃) ₅ Br]SO ₄ (aq)	observation with [Co(NH ₃) ₅ SO ₄]Br(aq)

[2]

(e) The two compounds $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ are different colours.

Explain why the colours of the two compounds are different.

..... [2]

(f) Some transition metals and their compounds act as catalysts. The catalysis can be classified as heterogeneous or homogeneous.

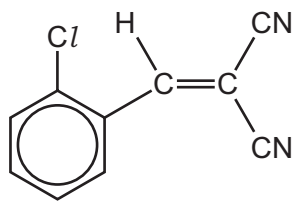
Complete the table by placing **one** tick (✓) in each row to indicate the type of catalysis in each reaction.

	heterogeneous	homogeneous
Fe in the Haber process		
Fe^{2+} in the $\text{I}^-/\text{S}_2\text{O}_8^{2-}$ reaction		
NO_2 in the oxidation of SO_2		
V_2O_5 in the Contact process		

[2]

[Total: 14]

- 5 Compound **P** contains several functional groups.



P

- (a) Name the functional groups present in **P**.

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

- (b) Compound **P** can be polymerised.

Draw a section of the polymer of **P** showing **two** repeat units.
Name the type of polymerisation.

type of polymerisation [2]

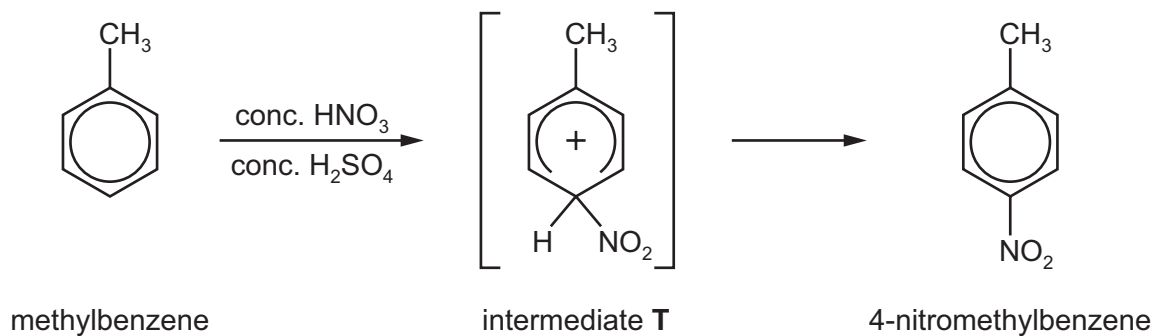
- (c) Complete the following table to show the structures of the products formed and the *type of organic reaction* when **P** reacts with the four reagents.

reagent	structure(s) of product(s)		<i>type of organic reaction</i>
excess Br ₂ (aq)			
excess hot, concentrated, acidified MnO ₄ ⁻ (aq)			
excess hot HCl(aq)			
excess H ₂ /Pt catalyst			

[8]

[Total: 12]

- 6 (a) 4-nitromethylbenzene can be prepared via an electrophilic substitution reaction as shown.



- (i) This reaction also forms an isomer of 4-nitromethylbenzene as a by-product.

Draw the structure of this by-product.

[1]

- (ii) Write an equation for the reaction between HNO_3 and H_2SO_4 that forms the electrophile for this reaction.

..... [1]

- (iii) Describe how the **structure and bonding** of the six-membered ring in intermediate T differs from that in methylbenzene.

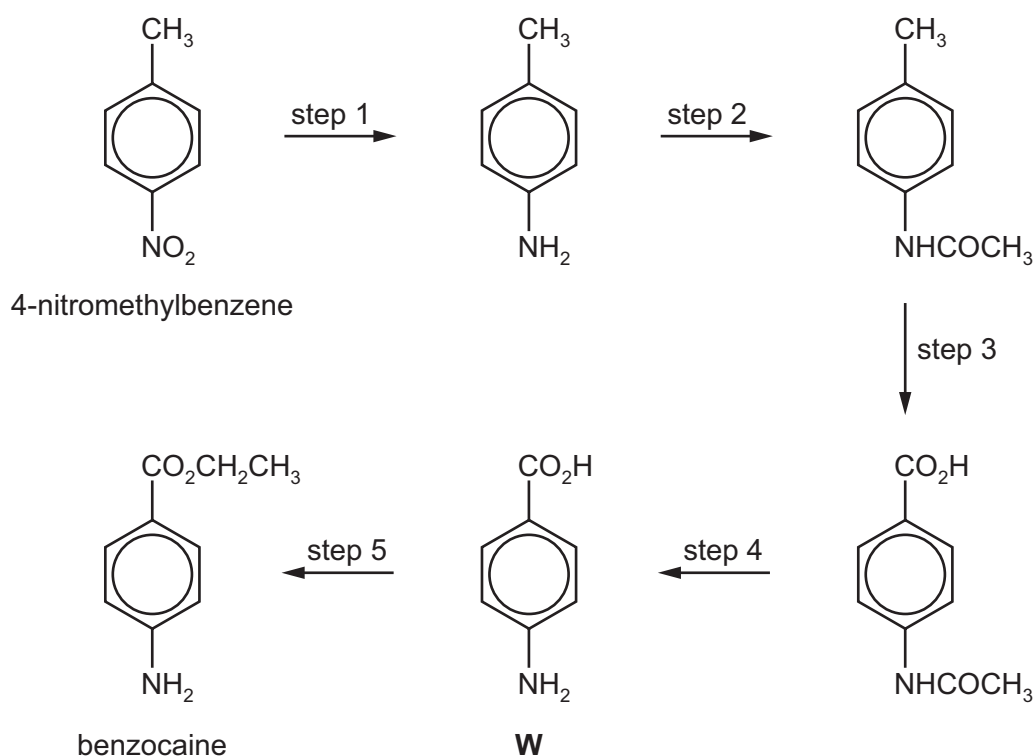
.....

.....

.....

..... [3]

- (b) Benzocaine is used as a local anaesthetic. It can be synthesised from 4-nitromethylbenzene by the route shown.



- (i) Give the systematic name of compound **W**.

..... [1]

- (ii) Suggest the reagents and conditions for steps 1–5.

step 1

step 2

step 3

step 4

step 5

[6]

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

.....

.....

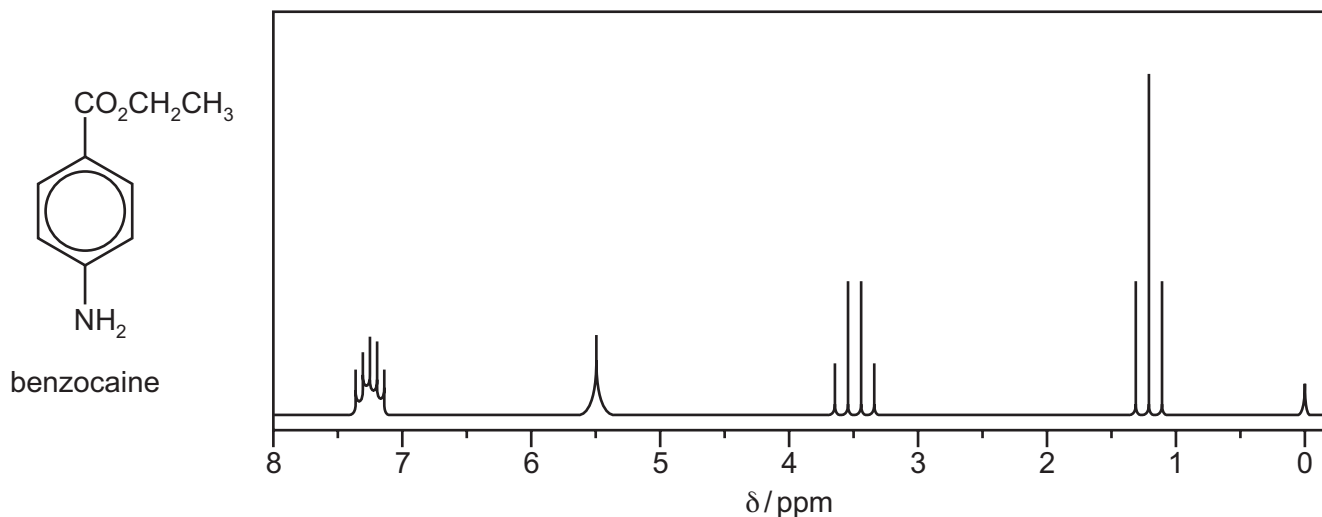
..... [2]

(d) A sample of benzocaine, shown below, was analysed by proton NMR and carbon-13 NMR spectroscopy.

(i) Predict the number of peaks that would be seen in the carbon-13 NMR spectrum.

..... [1]

(ii) Benzocaine was dissolved in CDCl_3 and the proton NMR spectrum of this solution was recorded.



Suggest why CDCl_3 and not CHCl_3 is used as the solvent when obtaining a proton NMR spectrum.

..... [1]

(iii) Use the *Data Booklet* and the spectrum in (d)(ii) to complete the table for the proton NMR spectrum of benzocaine. The actual chemical shifts, δ , for the four absorptions have been added.

δ/ppm	group responsible for the peak	number of ^1H atoms responsible for the peak	splitting pattern
1.2			
3.5			
5.5			
7.1–7.4			multiplet

[4]

(iv) Explain the splitting pattern for the absorption at $\delta 1.2$ ppm.

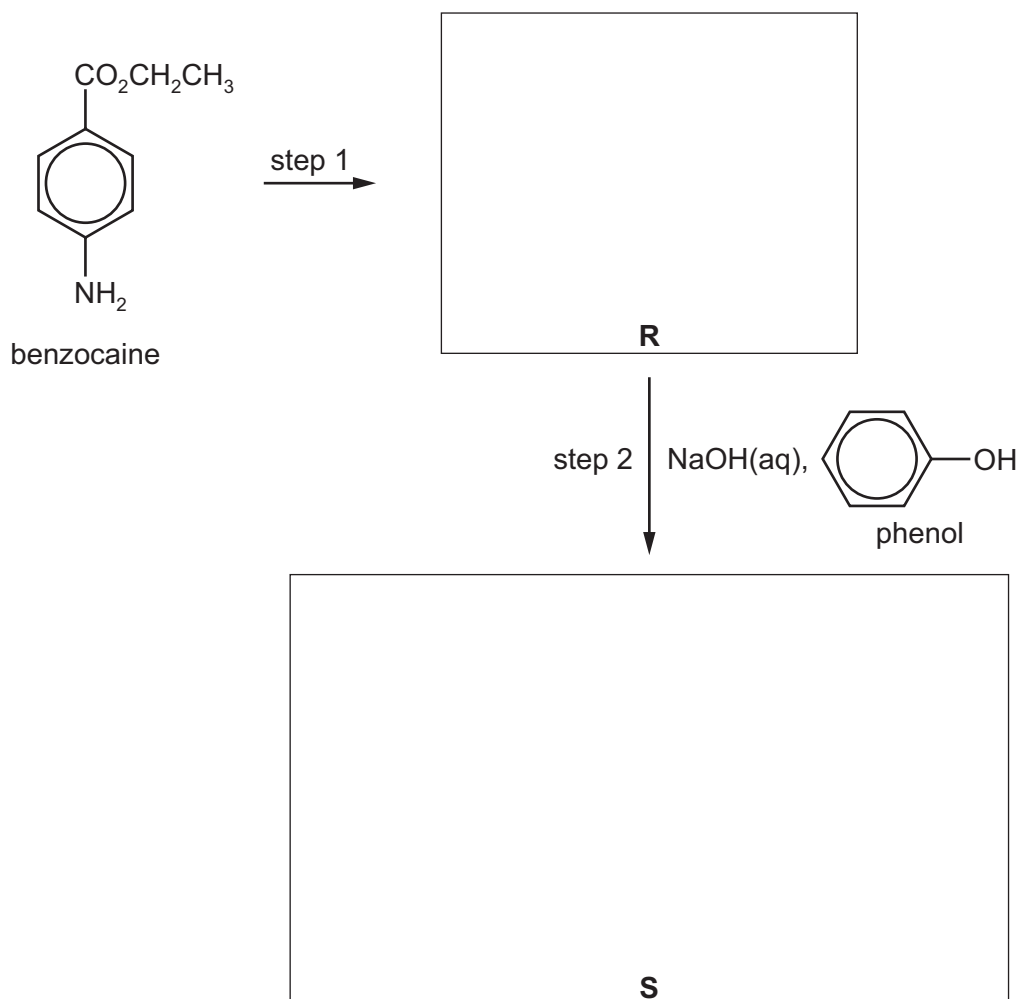
..... [1]

- (v) The proton NMR spectrum of benzocaine dissolved in D_2O was recorded.

Suggest how this spectrum would differ from the spectrum in (d)(ii).
Explain your answer.

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

- (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]

7 (a) Complete the following electronic structures.

- the iron atom, Fe $1s^2 2s^2 2p^6$
- the iron(III) ion, Fe^{3+} $1s^2 2s^2 2p^6$

[1]

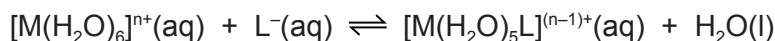
(b) Solutions of iron(III) salts are acidic due to the equilibrium shown.



Calculate the pH of a 0.25 mol dm^{-3} $FeCl_3$ solution.

pH = ... [2]

(c) The table shows numerical values of the stability constants for the following equilibrium where M can be one of the metal ions listed and L one of the ligands which replaces **one** H_2O molecule.



metal ion, M	ligand, L	stability constant, K_{stab}
Fe^{3+}	F^-	1.0×10^6
Fe^{3+}	Cl^-	2.5×10^1
Fe^{3+}	SCN^-	9.0×10^2
Hg^{2+}	Cl^-	5.0×10^6

(i) What is meant by the term *stability constant*, K_{stab} ?

.....
 [1]

(ii) Use the data in the table to predict the formula of the complex formed in the greatest amount when

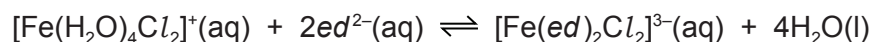
- a solution containing equal concentrations of both F^- and SCN^- ions is added to $Fe^{3+}(aq)$,

- a solution containing equal concentrations of both Fe^{3+} and Hg^{2+} ions is added to $Cl^-(aq)$.

[1]

Ethanedioate ions, O_2CCO_2^- , are bidentate ligands. The abbreviation ed^{2-} can be used to represent ethanedioate ions.

(d) The complex $[\text{Fe}(\text{ed})_2\text{Cl}_2]^{3-}$ can be formed according to the equation shown.



Write the expression for the equilibrium constant, K_{stab} , and state its units.

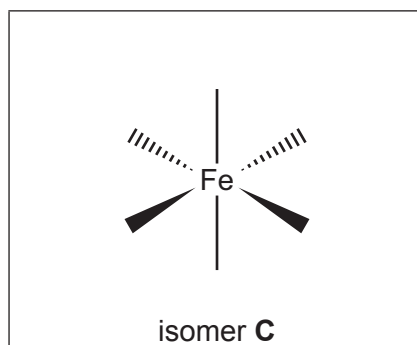
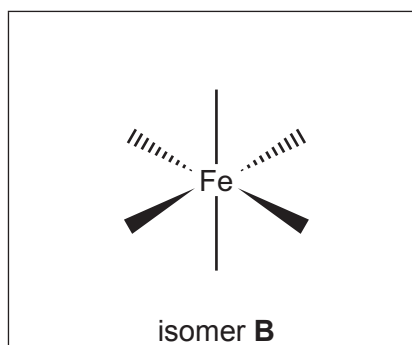
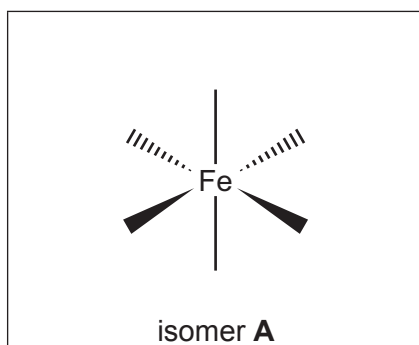
$K_{\text{stab}} =$

units
[2]

(e) $[\text{Fe}(\text{ed})_2\text{Cl}_2]^{3-}$ shows geometrical and optical isomerism.

(i) Complete the three-dimensional diagrams to show the three stereoisomers of $[\text{Fe}(\text{ed})_2\text{Cl}_2]^{3-}$.

You may use $\text{—O—CH}_2\text{—CH}_2\text{—O—}$ to represent ed^{2-} .



[3]

(ii) Give the letters of two isomers of $[\text{Fe}(\text{ed})_2\text{Cl}_2]^{3-}$ which are geometrical isomers of each other.

..... [1]

(iii) Give the letters of the two isomers of $[\text{Fe}(\text{ed})_2\text{Cl}_2]^{3-}$ which show optical isomerism.

..... [1]

(iv) Give the letter of the isomer which has **no** dipole moment.

..... [1]

[Total: 13]

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