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CHEMISTRY

9701/41

Paper 4 A Level Structured Questions

May/June 2018

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 **18** printed pages and **2** blank pages.

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

1 Sodium oxide, Na_2O , is a white crystalline solid with a high melting point.

(a) Write an equation for the reaction of sodium with oxygen, forming sodium oxide. Include state symbols.

..... [2]

(b) Explain why sodium oxide has a high melting point.

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

(c) When sodium oxide reacts with water an alkaline solution is obtained.

(i) Explain why the solution obtained is alkaline. You should use the Brønsted-Lowry theory of acids and bases in your answer.

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

(ii) Calculate the pH of the solution obtained when 3.10 g of sodium oxide are added to 400 cm^3 of water.

pH = ... [3]

- (d) Use the data below, and other suitable data from the *Data Booklet*, to calculate the lattice energy of sodium oxide, $\Delta H_{\text{latt}}^{\ominus} \text{Na}_2\text{O}(\text{s})$.

energy change	value / kJ mol^{-1}
standard enthalpy change of formation of sodium oxide, $\Delta H_{\text{f}}^{\ominus} \text{Na}_2\text{O}(\text{s})$	–416
standard enthalpy change of atomisation of sodium, $\Delta H_{\text{at}}^{\ominus} \text{Na}(\text{s})$	+109
electron affinity of $\text{O}(\text{g})$	–142
electron affinity of $\text{O}^-(\text{g})$	+844

$$\Delta H_{\text{latt}}^{\ominus} \text{Na}_2\text{O}(\text{s}) = \dots\dots\dots \text{kJ mol}^{-1} \quad [4]$$

- (e) State how $\Delta H_{\text{latt}}^{\ominus} \text{Na}_2\text{S}(\text{s})$ differs from $\Delta H_{\text{latt}}^{\ominus} \text{Na}_2\text{O}(\text{s})$.
Indicate this by placing a tick (✓) in the appropriate box in the table.

$\Delta H_{\text{latt}}^{\ominus} \text{Na}_2\text{S}(\text{s})$ is more exothermic than $\Delta H_{\text{latt}}^{\ominus} \text{Na}_2\text{O}(\text{s})$	$\Delta H_{\text{latt}}^{\ominus} \text{Na}_2\text{S}(\text{s})$ is the same as $\Delta H_{\text{latt}}^{\ominus} \text{Na}_2\text{O}(\text{s})$	$\Delta H_{\text{latt}}^{\ominus} \text{Na}_2\text{S}(\text{s})$ is less exothermic than $\Delta H_{\text{latt}}^{\ominus} \text{Na}_2\text{O}(\text{s})$

Explain your answer.

.....

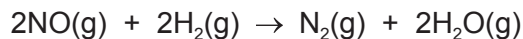
.....

.....

[2]

[Total: 15]

- 2 Nitrogen monoxide, NO(g), reacts with hydrogen, H₂(g), under certain conditions.



- (a) Define the term *rate of reaction*.

.....
 [1]

- (b) Identify a change in the reaction mixture that would enable the rate of this reaction to be studied.

..... [1]

The rate equation for this reaction is given.

$$\text{rate} = k[\text{NO}]^2[\text{H}_2]$$

The result of an experiment in which NO reacted with H₂ is shown in the table.

initial [NO]/mol dm ⁻³	initial [H ₂]/mol dm ⁻³	initial rate of reaction / mol dm ⁻³ s ⁻¹
2.50 × 10 ⁻³	2.50 × 10 ⁻³	1.27 × 10 ⁻³

- (c) Use the data and the rate equation to calculate a value for the rate constant *k*.
 Give the units of *k*.

$$k = \dots\dots\dots$$

$$\text{units} = \dots\dots\dots [2]$$

- (d) A second experiment is performed at the same temperature. The initial concentration of H₂(g) is 4.60 × 10⁻³ mol dm⁻³. The initial rate of the reaction is 2.31 × 10⁻³ mol dm⁻³ s⁻¹.

Calculate the initial concentration of NO(g).

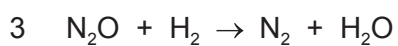
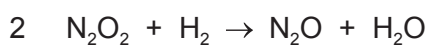
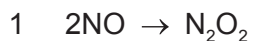
$$\text{initial concentration of NO(g)} = \dots\dots\dots \text{mol dm}^{-3} [1]$$

- (e) State the order of the reaction with respect to NO(g) and with respect to H₂(g), and the overall order of the reaction.

[NO]	
[H ₂]	
overall order	

[1]

- (f) The reaction is believed to proceed in three steps.



- (i) Deduce which of the three steps is the rate-determining step.

..... [1]

- (ii) Explain your answer to (i).

.....

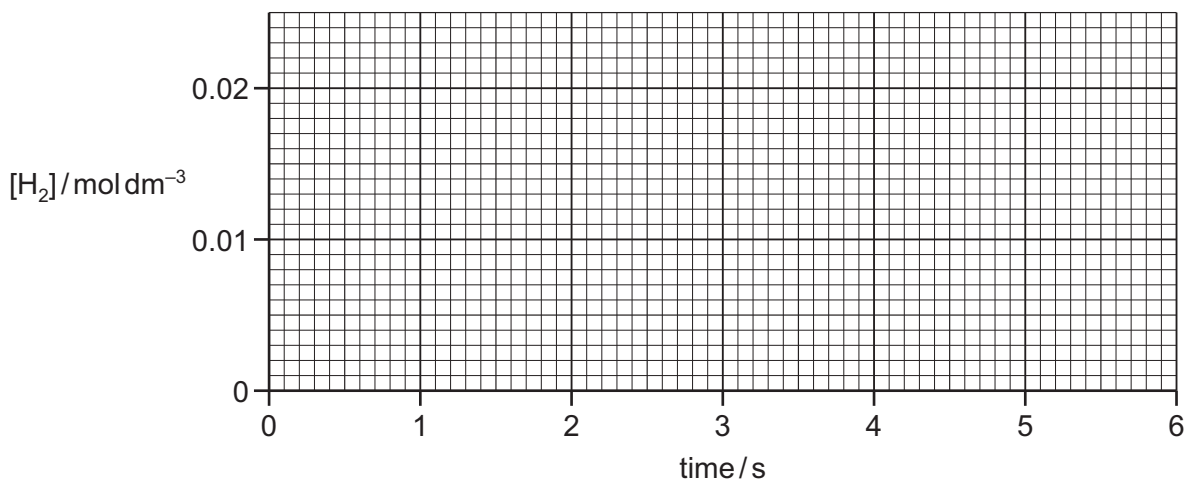
 [1]

- (g) A third experiment is performed under different conditions. A small amount of $\text{H}_2(\text{g})$ of concentration $0.0200 \text{ mol dm}^{-3}$ is mixed with a large excess of $\text{NO}(\text{g})$. The concentration of $\text{H}_2(\text{g})$ is found to have a constant half-life of 2.00 seconds under the conditions used.

(i) Define the term *half-life*.

.....
 [1]

(ii) Use the axes below to construct a graph of the variation in the concentration of $\text{H}_2(\text{g})$ during the first 6 seconds under the conditions used.



[2]

(h) $\text{NO}(\text{g})$ acts as a catalyst in the oxidation of atmospheric sulfur dioxide.

(i) Give two equations to describe how $\text{NO}(\text{g})$ acts as a catalyst in this process.

equation 1

equation 2

[1]

(ii) Explain why $\text{NO}(\text{g})$ can be described as a catalyst in this reaction.

.....
 [1]

(iii) Describe, with the aid of an equation, an environmental consequence of the oxidation of atmospheric sulfur dioxide.

.....
 [1]

[Total: 14]

- 3 (a) Complete the table, identifying the substance liberated at each electrode during electrolysis with inert electrodes.

electrolyte	substance liberated at the anode	substance liberated at the cathode
$\text{AgNO}_3(\text{aq})$		
concentrated $\text{NaCl}(\text{aq})$		
$\text{CuSO}_4(\text{aq})$		

[3]

- (b) Molten calcium iodide, CaI_2 , is electrolysed in an inert atmosphere with inert electrodes.

- (i) Write ionic equations for the reactions occurring at the electrodes.

-
-

[2]

- (ii) The electrolysis of molten CaI_2 is a redox process.

Identify the ion that is oxidised and the ion that is reduced, explaining your answer by reference to oxidation numbers.

.....

 [2]

- (iii) Describe **two** visual observations that would be made during this electrolysis.

- 1
- 2 [1]

- (c) An oxide of iron dissolved in an inert solvent is electrolysed for 2.00 hours using a current of 0.800 A. The electrolysis products are iron and oxygen. The mass of iron produced is 1.11 g.

Calculate the oxidation number of Fe in the oxide of iron. Show **all** your working.

oxidation number of Fe = ... [3]

[Total: 11]

- 4 (a) Describe what you would see when calcium and barium are heated separately with oxygen.

calcium

barium

[2]

- (b) The decomposition temperatures of the Group 2 carbonates vary down the group.

State and explain the variation in the decomposition temperatures.

.....

.....

.....

.....

.....

..... [3]

- (c) Magnesium carbonate was heated in an open test-tube. It was difficult to see whether a thermal decomposition reaction took place.

Explain why.

.....

.....

..... [2]

[Total: 7]

5 Copper is a transition element with atomic number 29.

(a) Complete the electronic configurations of a Cu atom and a Cu⁺ ion.

Cu atom $1s^2 2s^2 2p^6$

Cu⁺ ion $1s^2 2s^2 2p^6$

[2]

(b) Cu⁺ ions form a linear complex with Cl⁻ ions, which are monodentate ligands.

Draw the structure of this complex and include its overall charge.

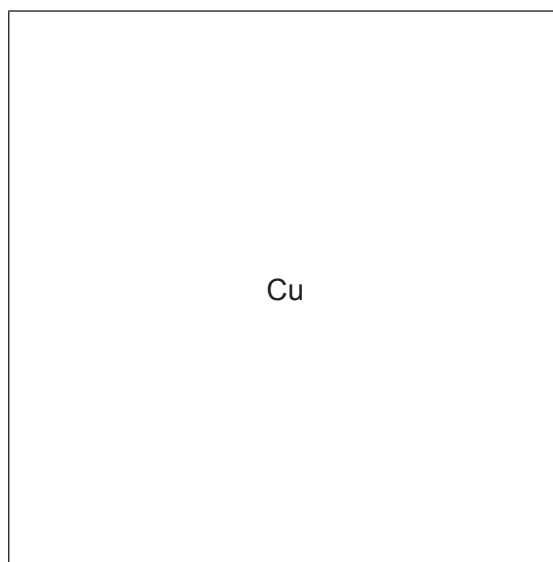
[2]

(c) Cu²⁺ ions exist as [Cu(H₂O)₆]²⁺ complex ions in aqueous solution.

Complete a three-dimensional diagram to show the shape of this complex.

Name its shape.

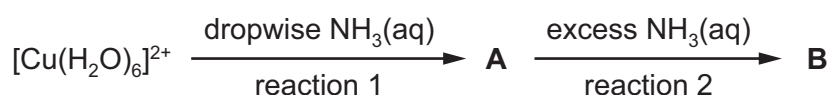
Label and state the value of one bond angle.



name of shape

[2]

- (d) When $\text{NH}_3(\text{aq})$ is added to $\text{Cu}^{2+}(\text{aq})$, dropwise at first and then in excess, two chemical reactions occur as shown.



For each reaction, describe what you would see and write an equation.

reaction 1

observation

.....

equation

reaction 2

observation

.....

equation

[4]

- (e) EDTA^{4-} is a polydentate ligand. When a solution of EDTA^{4-} is added to a solution containing $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ a new complex is formed. The formula of this complex is $[\text{CuEDTA}]^{2-}$.

- (i) Name the type of reaction occurring here.

..... [1]

- (ii) Write an expression for the stability constant, K_{stab} , of $[\text{CuEDTA}]^{2-}$ in this reaction.

[1]

- (iii) The numerical value of the K_{stab} of $[\text{CuEDTA}]^{2-}$ is 6.3×10^{19} at 298 K.

State what this tells us about the $[\text{CuEDTA}]^{2-}$ complex ion.

..... [1]

(f) Ethanedioate ions, $\text{C}_2\text{O}_4^{2-}$, can act as a bidentate ligand.

(i) Explain what is meant by the term *bidentate ligand*.

.....

.....

.....

..... [2]

(ii) When ethanedioate ions are added to a solution of zirconium ions, Zr^{4+} , a complex ion containing four $\text{C}_2\text{O}_4^{2-}$ ions and one Zr^{4+} ion is formed. All four ethanedioate ions act as bidentate ligands in this complex.

Give the formula of this complex ion and explain why this complex is not octahedral.

.....

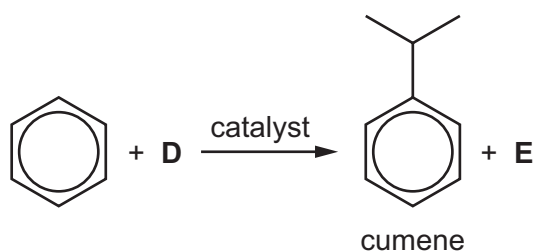
.....

.....

..... [2]

[Total: 17]

- 6 (a) Benzene reacts with **D** in the presence of a suitable catalyst to give cumene and non-organic product **E**. This is an electrophilic substitution reaction.



- (i) Name the reactant **D** and the non-organic product **E**.

D

E

[2]

- (ii) Give the name of the type of aromatic electrophilic substitution reaction taking place.

..... [1]

- (b) Cumene undergoes substitution reactions with chlorine to give several different isomeric products with the formula $C_9H_{11}Cl$. The substitution can occur in the aromatic ring or in the side-chain of cumene.

- (i) Describe the conditions that are used to ensure substitution takes place only in the **aromatic ring**.

..... [1]

- (ii) Draw the structures of the **two** major isomeric products of the reaction, formula $C_9H_{11}Cl$, when substitution takes place in the aromatic ring.

[1]

- (iii) Describe the conditions that are used to ensure substitution takes place only in the **side-chain**.

..... [1]

- (iv) Draw the structures of **two** isomeric products of the reaction, formula $C_9H_{11}Cl$, when substitution takes place in the side-chain.

[1]

- (c) Complete the following table to show the structures of the organic products formed when cumene reacts with each reagent.

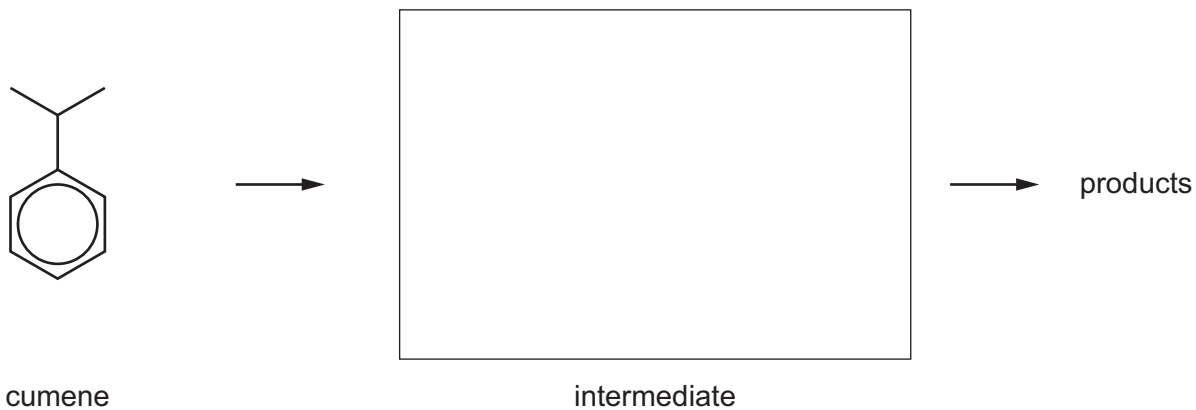
reagent	structure of organic product
hot $KMnO_4(aq)$	
$H_2 + Ni$, high pressure	

[2]

- (d) Cumene can be nitrated using a mixture of concentrated nitric and sulfuric acids. The mechanism for this reaction is similar to the mechanism for the nitration of benzene.

Complete the mechanism for this reaction.

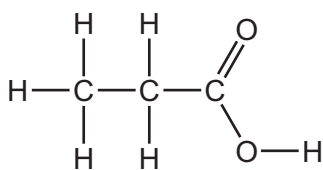
- Include all relevant charges and curly arrows showing the movement of electron pairs.
- Draw the structure of the intermediate.
- You do not need to draw the products.



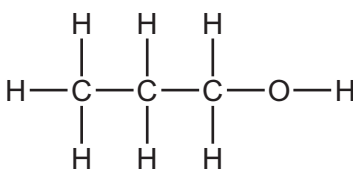
[4]

[Total: 13]

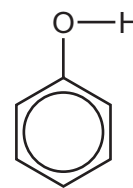
7 The three substances shown all have some acidic properties.



propanoic acid



propan-1-ol



phenol

(a) Write an equation for the reaction between propan-1-ol and sodium metal.

..... [1]

(b) (i) Give the order of the relative acidities of propanoic acid, propan-1-ol and phenol, stating the most acidic first.

..... [1]

(ii) Explain your answer to (i).

.....

 [2]

(c) Methanoic acid, HCO_2H , has a similar acid strength to propanoic acid.

Describe a chemical test to distinguish between these two acids. Name the acid which gives a positive result in this test and describe the observations that would be made.

.....

 [2]

- (d) The ester phenyl propanoate, $\text{C}_2\text{H}_5\text{CO}_2\text{C}_6\text{H}_5$, can be made from phenol and propanoic acid in a **two-step** synthesis. The first step produces an acyl chloride.

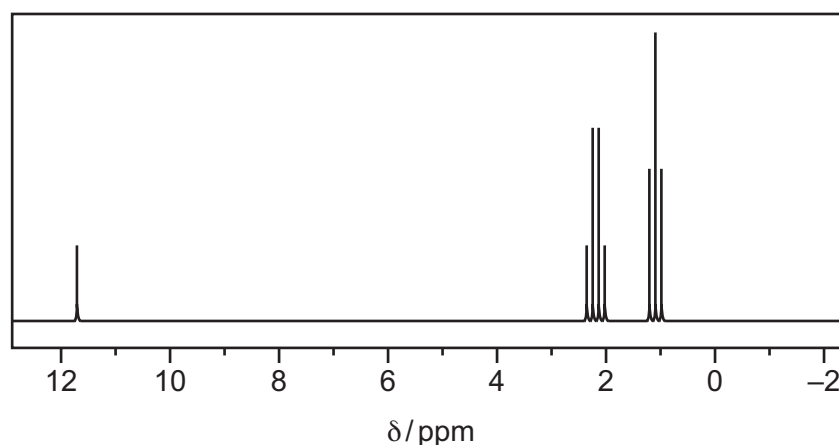
For this **two-step** synthesis,

- draw the structure of the product of the first step,
- state the reagents and conditions needed for each step of the synthesis.

.....

 [3]

- (e) An unknown compound, **Z**, is propan-1-ol, propanal or propanoic acid. The proton NMR spectrum of **Z** dissolved in CDCl_3 is shown.



- (i) From the proton NMR spectrum, identify **Z**.

..... [1]

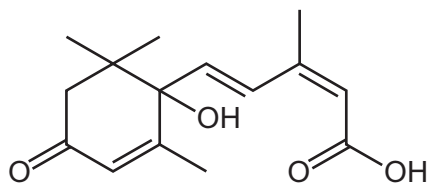
- (ii) State one feature that would be seen, and why, in the proton NMR spectra of each of the two compounds that are not **Z**.

.....

 [2]

[Total: 12]

- 8 Absciscic acid, $C_{15}H_{20}O_4$, is a plant hormone.



absciscic acid, $C_{15}H_{20}O_4$

- (a) On the diagram of absciscic acid, use an asterisk (*) to label each chiral carbon atom. [1]

- (b) Absciscic acid is reacted with an excess of $NaBH_4$.

Give the molecular formula of the organic product formed.

..... [1]

- (c) If absciscic acid is treated with an excess of hot, concentrated, acidified $KMnO_4$, three different carbon-containing products are formed.

- (i) Draw the skeletal formula of the carbon-containing product with the **largest** molecular mass.

[1]

- (ii) Identify the carbon-containing product with the **smallest** molecular mass. Explain how this product arises.

.....

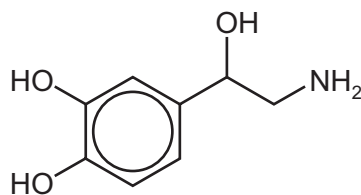
 [2]

- (iii) Identify the third carbon-containing product of this reaction by giving its displayed or structural formula.

[1]

[Total: 6]

- 9 Noradrenaline is a hormone found in humans.



noradrenaline

- (a) Give the molecular formula of noradrenaline.

..... [1]

- (b) State whether or not noradrenaline shows stereoisomerism. Explain your answer.

.....
 [1]

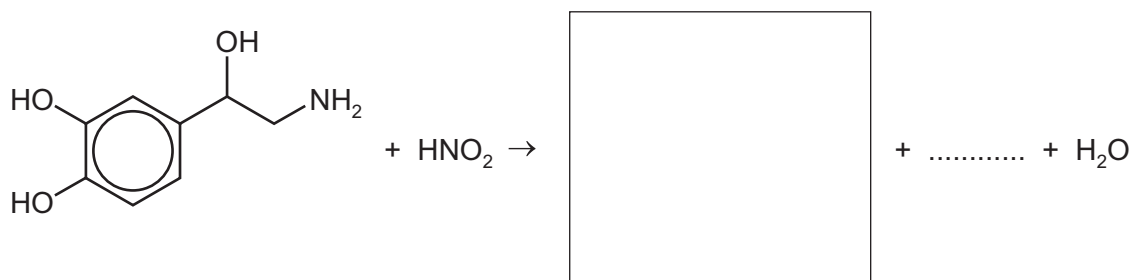
- (c) $\text{HNO}_2(\text{aq})$ is reacted at 5°C with separate samples of noradrenaline and phenylamine. The reaction with phenylamine produces a stable diazonium ion. The reaction with noradrenaline produces an unstable diazonium ion.

- (i) Suggest why the diazonium ion produced with phenylamine is stable.

.....
 [1]

- (ii) When one noradrenaline molecule reacts with one HNO_2 molecule, the products are one water molecule, one molecule of an unreactive gas, and one molecule of an organic compound made up of carbon, hydrogen and oxygen only.

Complete the chemical equation for this reaction.



[2]

[Total: 5]

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CHEMISTRY

9701/42

Paper 4 A Level Structured Questions

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

- 1 Silicon tetrachloride, SiCl_4 , is formed when silicon reacts with chlorine under suitable conditions. It is a colourless liquid with a low boiling point.

(a) Explain why SiCl_4 has a low boiling point.

.....

 [2]

(b) SiCl_4 reacts with water to produce an acidic solution.

(i) Write an equation for this reaction.

..... [1]

(ii) Describe **two** visual observations when silicon tetrachloride is added drop by drop to a small amount of water.

1

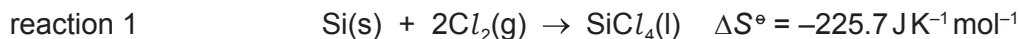
2 [2]

(iii) A sample of 0.8505 g of SiCl_4 is added to 800 cm^3 of water. All of the soluble acidic product is dissolved in the water.

Calculate the pH of the solution obtained.

pH = ... [3]

- (c) (i) Silicon tetrachloride can be prepared according to reaction 1.



standard entropy of silicon, $S^\circ \text{ Si(s)}$	$18.7 \text{ JK}^{-1} \text{ mol}^{-1}$
standard entropy of silicon tetrachloride, $S^\circ \text{ SiCl}_4(\text{l})$	$239.0 \text{ JK}^{-1} \text{ mol}^{-1}$

Calculate the standard entropy of chlorine, $S^\circ \text{ Cl}_2(\text{g})$. Show all your working.

$$S^\circ \text{ Cl}_2(\text{g}) = \dots\dots\dots \text{ JK}^{-1} \text{ mol}^{-1} \quad [2]$$

- (ii) Explain why the entropy change for reaction 1 is negative.

.....
 [1]

- (d) The standard enthalpy change of formation of silicon tetrachloride, $\Delta H_f^\circ \text{ SiCl}_4(\text{l})$, is -640 kJ mol^{-1} .

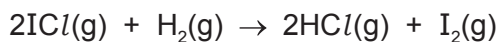
Reaction 1 is spontaneous at lower temperatures, but it is not spontaneous at very high temperatures.

Calculate the temperature above which reaction 1 is **not** spontaneous.

$$\text{temperature} = \dots\dots\dots \text{ K} \quad [2]$$

[Total: 13]

- 2 Iodine monochloride, ICl , is a yellow-brown gas. It reacts with hydrogen gas under certain conditions as shown.



Experiments are performed using different starting concentrations of ICl and H_2 . The initial rate of each reaction is measured. The following results are obtained.

experiment	$[\text{ICl}]/\text{mol dm}^{-3}$	$[\text{H}_2]/\text{mol dm}^{-3}$	relative rate of reaction
1	4.00×10^{-3}	4.00×10^{-3}	1.00
2	4.00×10^{-3}	7.00×10^{-3}	1.75
3	4.00×10^{-3}	1.00×10^{-2}	2.50
4	5.00×10^{-3}	8.00×10^{-3}	2.50
5	7.00×10^{-3}	8.00×10^{-3}	3.50

- (a) Identify a change, taking place in the reaction mixture, that would enable measurements of the rate of this reaction to be made.

..... [1]

- (b) Use the data in the table to show that the reaction is first order with respect to $\text{H}_2(\text{g})$.

.....

 [1]

- (c) Use the data in the table to show that the reaction is first order with respect to $\text{ICl}(\text{g})$.

.....

 [1]

- (d) Complete the rate equation for the reaction between $\text{ICl}(\text{g})$ and $\text{H}_2(\text{g})$.

rate = ... [1]

- (e) Use experiment 3 to calculate a numerical value for the rate constant, k .

$k = \dots\dots\dots$ [1]

- (f) The reaction $2\text{ICl(g)} + \text{H}_2\text{(g)} \rightarrow 2\text{HCl(g)} + \text{I}_2\text{(g)}$ is first order with respect to ICl(g) and first order with respect to $\text{H}_2\text{(g)}$.

Suggest a mechanism for this reaction. You should assume

- the mechanism has two steps,
- the first step is much slower than the second step.

first step $\dots\dots\dots \rightarrow \dots\dots\dots$

second step $\dots\dots\dots \rightarrow \dots\dots\dots$

[2]

- (g) An alternative method is used to show that the reaction is first order with respect to $\text{H}_2\text{(g)}$. This method uses a large excess of ICl(g) and measures how the concentration of $\text{H}_2\text{(g)}$ varies with time.

- (i) Describe two ways of using these results to show the reaction is first order with respect to $\text{H}_2\text{(g)}$ concentration.

$\dots\dots\dots$
 $\dots\dots\dots$
 $\dots\dots\dots$
 $\dots\dots\dots$
 $\dots\dots\dots$
 $\dots\dots\dots$
 $\dots\dots\dots$ [3]

- (ii) Explain the reason for using a large excess of ICl(g) .

$\dots\dots\dots$
 $\dots\dots\dots$ [1]

- (h) A chemical reaction may be speeded up by the presence of a catalyst.

Explain why a catalyst increases the rate of a chemical reaction.

$\dots\dots\dots$
 $\dots\dots\dots$ [1]

[Total: 12]

- 3 (a) Complete the table by predicting the identity of the substance liberated at each electrode during electrolysis with inert electrodes.

electrolyte	substance liberated at the anode	substance liberated at the cathode
NaOH(aq)		
dilute $\text{CuCl}_2(\text{aq})$		
concentrated $\text{MgCl}_2(\text{aq})$		

[3]

- (b) (i) The electrolysis of molten ZnBr_2 is a redox process.

Identify the ion that is oxidised and the ion that is reduced.

Use ionic half-equations to explain your answer.

.....

 [3]

- (ii) Describe **one** visual observation that would be made during this electrolysis.

..... [1]

- (c) Dilute sulfuric acid is electrolysed for 50.0 minutes using inert electrodes and a current of 1.20A. A different gas is collected above each electrode. The volumes of the two gases are measured under room conditions.

Calculate the maximum volume of gas that could be collected at the **cathode**.

volume = ... cm^3 [3]

[Total: 10]

- 4 (a) (i) Write an equation, including state symbols, for the reaction that takes place when a sample of anhydrous calcium nitrate, $\text{Ca}(\text{NO}_3)_2$, is heated strongly in a test-tube.

..... [2]

- (ii) Describe what will be seen during this reaction.

.....

.....

..... [2]

- (b) Describe and explain how the solubility of the Group 2 sulfates varies down the group.

.....

.....

.....

.....

.....

.....

.....

..... [4]

[Total: 8]

- 5 Cobalt is a transition element with atomic number 27. Cobalt forms ions with charges of +2 and +3. Both these ions form complexes.

(a) Complete the electronic configurations of a Co atom and a Co^{2+} ion.

Co atom $1s^2 2s^2 2p^6$

Co^{2+} ion $1s^2 2s^2 2p^6$

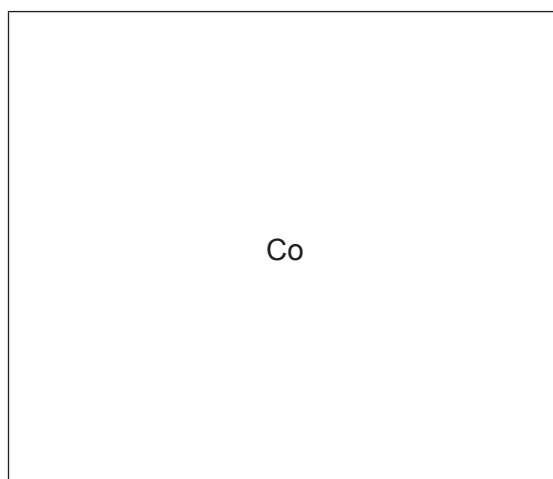
[2]

(b) One Co^{2+} ion can form a tetrahedral complex ion with four Cl^- ions. This complex is blue.

(i) What is meant by the term *complex ion*?

.....
 [1]

(ii) Draw the tetrahedral complex ion formed by one Co^{2+} ion with four Cl^- ions. Your drawing should clearly show three-dimensional shape, and should include the overall charge on the ion.



[2]

(iii) Explain why many transition metal complexes are coloured.

.....

 [3]

(iv) Using ideas from your answer to (iii) suggest why the colour of the complex formed by one Co^{2+} ion with four Cl^- ions is **blue**.

.....
 [1]

- (c) Describe the colour change that occurs when water is added to blue crystals of the cobalt(II)-chloride complex. Name the type of reaction responsible for this colour change.

colour change

type of reaction

[2]

- (d) $\text{Co}^{2+}(\text{aq})$ can be oxidised to $\text{Co}^{3+}(\text{aq})$.

- (i) Use the *Data Booklet* to suggest a suitable oxidising agent for this reaction.

..... [1]

- (ii) Calculate the $E_{\text{cell}}^{\ominus}$ of this reaction.

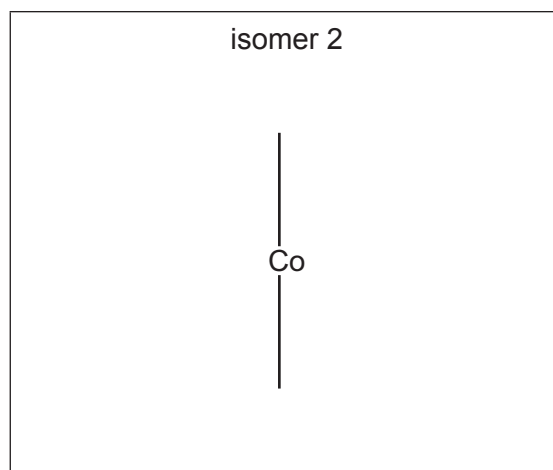
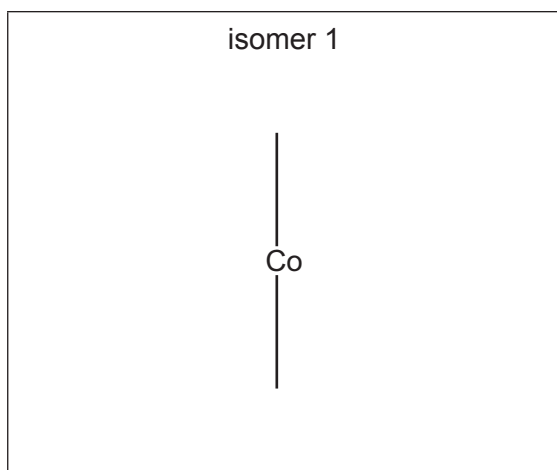
$$E_{\text{cell}}^{\ominus} = \dots\dots\dots \text{V} \quad [1]$$

- (iii) Write an equation for the reaction between Co^{2+} and the oxidising agent you chose in (d)(i).

..... [1]

- (e) Cobalt(III) forms two isomeric octahedral complexes with the formula $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$. The NO_2^- ion is monodentate.

Complete the diagrams to show the three-dimensional structures of the two isomers and suggest the type of isomerism shown here.



type of isomerism

[3]

[Total: 17]

6 Phenol is an important industrial chemical used in the manufacture of dyestuff and other substances.

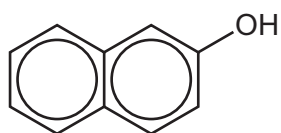
- (a) Suggest **two** different substances that react with phenol to produce potassium phenoxide, $\text{C}_6\text{H}_5\text{O}^-\text{K}^+$. Identify the second product formed in each case.

substance second product

substance second product

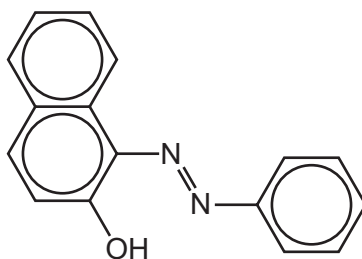
[3]

(b)



2-naphthol

2-naphthol can show similar properties to phenol. It can be used to produce Sudan I, an orange coloured dyestuff.



Sudan I

- (i) On the diagram of Sudan I above **circle** the bond or bonds that make this substance a dyestuff. [1]
- (ii) Describe how Sudan I can be made using phenylamine and 2-naphthol as the organic starting materials.

.....

.....

.....

.....

.....

.....

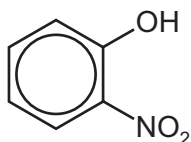
.....

.....

.....

..... [3]

(c) Phenol can be used to make 2-nitrophenol.



2-nitrophenol

The nitration reaction of phenol to form 2-nitrophenol shows that phenol is more reactive than benzene.

(i) Describe the conditions used for the nitration of phenol.

Explain how these conditions show phenol to be more reactive than benzene.

conditions

explanation

.....

..... [2]

(ii) Suggest why phenol is more reactive than benzene.

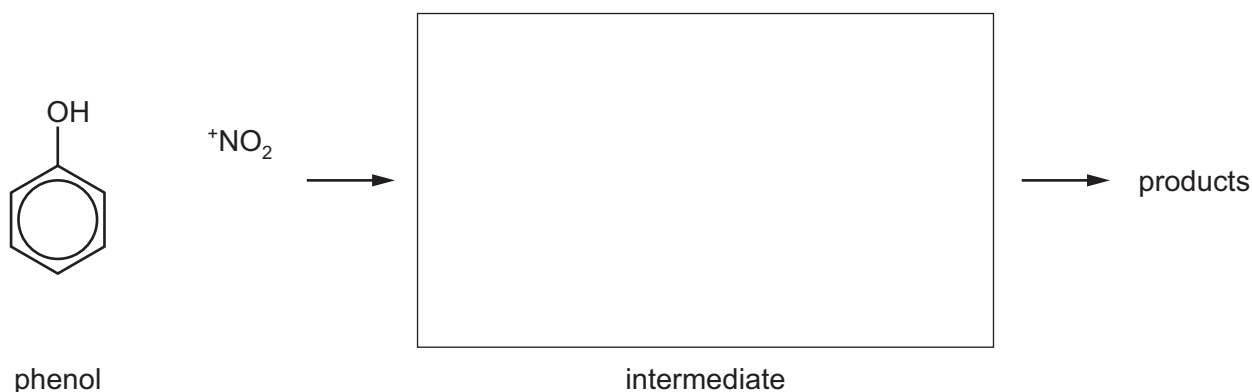
.....

.....

..... [1]

(iii) Complete the mechanism for the nitration of phenol to form 2-nitrophenol. You should assume that the mechanism is the same as that for the nitration of benzene.

- Include all relevant charges and curly arrows to show the movement of electron pairs.
- Draw the structure of the intermediate.
- You do not need to draw the products.



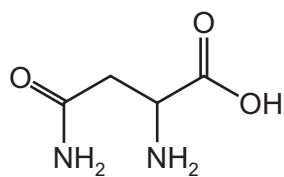
[3]

(iv) Name the isomer of 2-nitrophenol which is also a major product of this reaction.

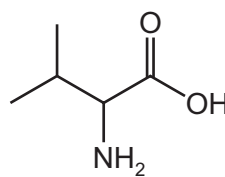
..... [1]

[Total: 14]

- 7 Asparagine and valine are two naturally occurring amino acids.



asparagine



valine

- (a) Give the molecular formula of asparagine.

..... [1]

- (b) Name **all** of the functional groups in an asparagine molecule.

..... [2]

- (c) Draw the structure of the dipeptide formed by valine and asparagine.

The peptide bond should be shown displayed and should be clearly labelled.

[2]

- (d) A solution of valine in water acts as a buffer solution.

- (i) Explain what is meant by a *buffer solution*.

.....

 [2]

- (ii) Write **two** equations to explain how valine can act as a buffer. Use the formula $\text{H}_2\text{NCH(R)CO}_2\text{H}$ for valine in your equations.

.....

 [2]

- (e) Each valine molecule has one chiral carbon atom.

Draw three-dimensional diagrams to show the two optical isomers of valine.
The $(\text{CH}_3)_2\text{CH}$ group can be represented as R.

[2]

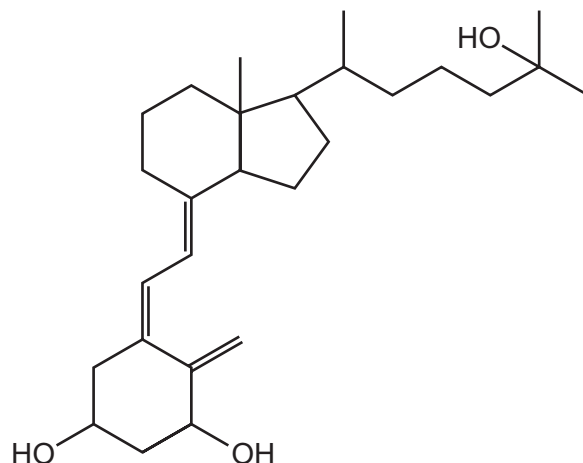
- (f) Asparagine is hydrolysed when heated with aqueous sulfuric acid.

Write an equation for this reaction.

..... [2]

[Total: 13]

- 8 Calcitriol is a steroid hormone found in human blood.



calcitriol

- (a) Give the number of primary, secondary and tertiary alcohol groups in one molecule of calcitriol.

primary secondary tertiary [1]

- (b) Give the number of chiral carbon atoms in one molecule of calcitriol.

..... [1]

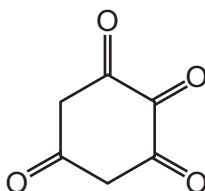
- (c) Calcitriol shows geometrical isomerism.

Give the number of geometrical isomers of calcitriol, including calcitriol.

..... [1]

- (d) A sample of calcitriol is treated with an excess of hot, concentrated, acidified potassium manganate(VII). There are three different carbon-containing products of this reaction.

One of these three products, **X**, is shown.



X

- (i) Predict the number of peaks in the carbon-13 NMR spectrum of **X**.

..... [1]

- (ii) For the carbon-13 NMR spectrum of **X**, state the expected chemical shift ranges (δ) of the peaks predicted in (i) and the number of peaks in each range.

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

- (iii) Predict the number of peaks this compound would show in its proton NMR spectrum.

..... [1]

- (iv) For each of the peaks in the proton NMR spectrum you have identified in (iii) give the expected splitting pattern. Explain your reasoning.

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

- (e) In addition to the product shown in (d), two other carbon-containing products are formed when a sample of calcitriol is treated with an excess of hot, concentrated, acidified potassium manganate(VII).

- (i) Of these two other carbon-containing products, identify the product with the **smaller** molecular mass. Explain how this product is formed.

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

- (ii) Of these two other carbon-containing products, identify the product with the **larger** molecular mass by drawing its skeletal formula in the space below.

[1]

[Total: 13]

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CHEMISTRY

9701/43

Paper 4 A Level Structured Questions

May/June 2018

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 **18** printed pages and **2** blank pages.

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

1 Sodium oxide, Na_2O , is a white crystalline solid with a high melting point.

(a) Write an equation for the reaction of sodium with oxygen, forming sodium oxide. Include state symbols.

..... [2]

(b) Explain why sodium oxide has a high melting point.

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

(c) When sodium oxide reacts with water an alkaline solution is obtained.

(i) Explain why the solution obtained is alkaline. You should use the Brønsted-Lowry theory of acids and bases in your answer.

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

(ii) Calculate the pH of the solution obtained when 3.10 g of sodium oxide are added to 400 cm³ of water.

pH = ... [3]

- (d) Use the data below, and other suitable data from the *Data Booklet*, to calculate the lattice energy of sodium oxide, $\Delta H_{\text{latt}}^{\ominus} \text{Na}_2\text{O}(\text{s})$.

energy change	value / kJ mol^{-1}
standard enthalpy change of formation of sodium oxide, $\Delta H_{\text{f}}^{\ominus} \text{Na}_2\text{O}(\text{s})$	–416
standard enthalpy change of atomisation of sodium, $\Delta H_{\text{at}}^{\ominus} \text{Na}(\text{s})$	+109
electron affinity of $\text{O}(\text{g})$	–142
electron affinity of $\text{O}^-(\text{g})$	+844

$$\Delta H_{\text{latt}}^{\ominus} \text{Na}_2\text{O}(\text{s}) = \dots\dots\dots \text{kJ mol}^{-1} \quad [4]$$

- (e) State how $\Delta H_{\text{latt}}^{\ominus} \text{Na}_2\text{S}(\text{s})$ differs from $\Delta H_{\text{latt}}^{\ominus} \text{Na}_2\text{O}(\text{s})$.
Indicate this by placing a tick (✓) in the appropriate box in the table.

$\Delta H_{\text{latt}}^{\ominus} \text{Na}_2\text{S}(\text{s})$ is more exothermic than $\Delta H_{\text{latt}}^{\ominus} \text{Na}_2\text{O}(\text{s})$	$\Delta H_{\text{latt}}^{\ominus} \text{Na}_2\text{S}(\text{s})$ is the same as $\Delta H_{\text{latt}}^{\ominus} \text{Na}_2\text{O}(\text{s})$	$\Delta H_{\text{latt}}^{\ominus} \text{Na}_2\text{S}(\text{s})$ is less exothermic than $\Delta H_{\text{latt}}^{\ominus} \text{Na}_2\text{O}(\text{s})$

Explain your answer.

.....

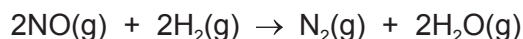
.....

.....

[2]

[Total: 15]

- 2 Nitrogen monoxide, NO(g), reacts with hydrogen, H₂(g), under certain conditions.



- (a) Define the term *rate of reaction*.

.....
 [1]

- (b) Identify a change in the reaction mixture that would enable the rate of this reaction to be studied.

..... [1]

The rate equation for this reaction is given.

$$\text{rate} = k[\text{NO}]^2[\text{H}_2]$$

The result of an experiment in which NO reacted with H₂ is shown in the table.

initial [NO]/mol dm ⁻³	initial [H ₂]/mol dm ⁻³	initial rate of reaction / mol dm ⁻³ s ⁻¹
2.50 × 10 ⁻³	2.50 × 10 ⁻³	1.27 × 10 ⁻³

- (c) Use the data and the rate equation to calculate a value for the rate constant *k*.
 Give the units of *k*.

$$k = \dots\dots\dots$$

$$\text{units} = \dots\dots\dots [2]$$

- (d) A second experiment is performed at the same temperature. The initial concentration of H₂(g) is 4.60 × 10⁻³ mol dm⁻³. The initial rate of the reaction is 2.31 × 10⁻³ mol dm⁻³ s⁻¹.

Calculate the initial concentration of NO(g).

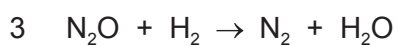
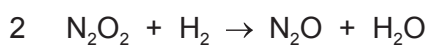
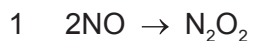
$$\text{initial concentration of NO(g)} = \dots\dots\dots \text{mol dm}^{-3} [1]$$

- (e) State the order of the reaction with respect to NO(g) and with respect to H₂(g), and the overall order of the reaction.

[NO]	
[H ₂]	
overall order	

[1]

- (f) The reaction is believed to proceed in three steps.



- (i) Deduce which of the three steps is the rate-determining step.

..... [1]

- (ii) Explain your answer to (i).

.....

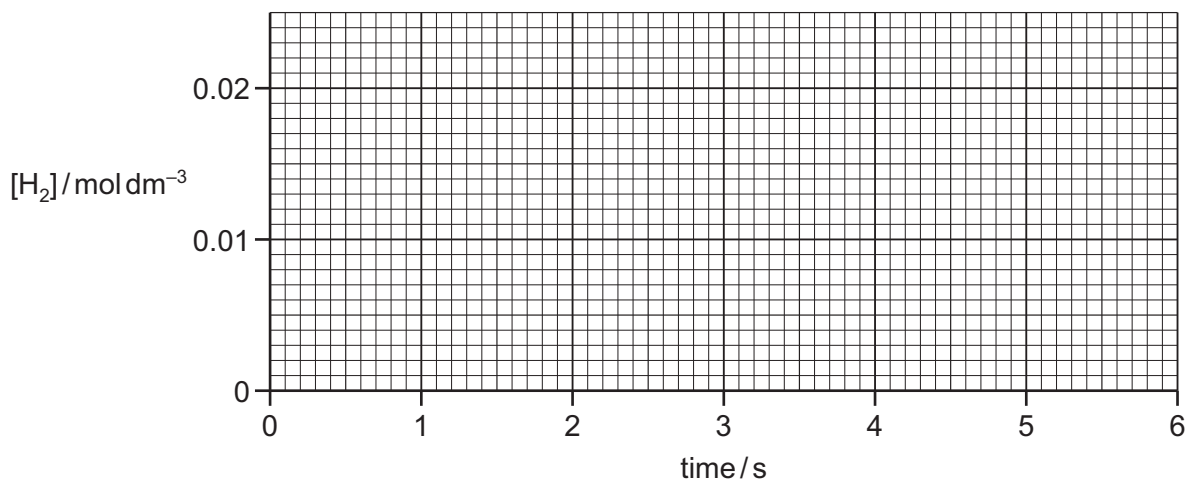
 [1]

- (g) A third experiment is performed under different conditions. A small amount of $\text{H}_2(\text{g})$ of concentration $0.0200 \text{ mol dm}^{-3}$ is mixed with a large excess of $\text{NO}(\text{g})$. The concentration of $\text{H}_2(\text{g})$ is found to have a constant half-life of 2.00 seconds under the conditions used.

(i) Define the term *half-life*.

.....
 [1]

(ii) Use the axes below to construct a graph of the variation in the concentration of $\text{H}_2(\text{g})$ during the first 6 seconds under the conditions used.



[2]

(h) $\text{NO}(\text{g})$ acts as a catalyst in the oxidation of atmospheric sulfur dioxide.

(i) Give two equations to describe how $\text{NO}(\text{g})$ acts as a catalyst in this process.

equation 1

equation 2

[1]

(ii) Explain why $\text{NO}(\text{g})$ can be described as a catalyst in this reaction.

.....
 [1]

(iii) Describe, with the aid of an equation, an environmental consequence of the oxidation of atmospheric sulfur dioxide.

.....
 [1]

[Total: 14]

- 3 (a) Complete the table, identifying the substance liberated at each electrode during electrolysis with inert electrodes.

electrolyte	substance liberated at the anode	substance liberated at the cathode
$\text{AgNO}_3(\text{aq})$		
concentrated $\text{NaCl}(\text{aq})$		
$\text{CuSO}_4(\text{aq})$		

[3]

- (b) Molten calcium iodide, CaI_2 , is electrolysed in an inert atmosphere with inert electrodes.

- (i) Write ionic equations for the reactions occurring at the electrodes.

-
-

[2]

- (ii) The electrolysis of molten CaI_2 is a redox process.

Identify the ion that is oxidised and the ion that is reduced, explaining your answer by reference to oxidation numbers.

.....

 [2]

- (iii) Describe **two** visual observations that would be made during this electrolysis.

- 1
- 2 [1]

- (c) An oxide of iron dissolved in an inert solvent is electrolysed for 2.00 hours using a current of 0.800 A. The electrolysis products are iron and oxygen. The mass of iron produced is 1.11 g.

Calculate the oxidation number of Fe in the oxide of iron. Show **all** your working.

oxidation number of Fe = ... [3]

[Total: 11]

- 4 (a) Describe what you would see when calcium and barium are heated separately with oxygen.

calcium

barium

[2]

- (b) The decomposition temperatures of the Group 2 carbonates vary down the group.

State and explain the variation in the decomposition temperatures.

.....

.....

.....

.....

.....

..... [3]

- (c) Magnesium carbonate was heated in an open test-tube. It was difficult to see whether a thermal decomposition reaction took place.

Explain why.

.....

.....

..... [2]

[Total: 7]

5 Copper is a transition element with atomic number 29.

(a) Complete the electronic configurations of a Cu atom and a Cu⁺ ion.

Cu atom 1s²2s²2p⁶

Cu⁺ ion 1s²2s²2p⁶

[2]

(b) Cu⁺ ions form a linear complex with Cl⁻ ions, which are monodentate ligands.

Draw the structure of this complex and include its overall charge.

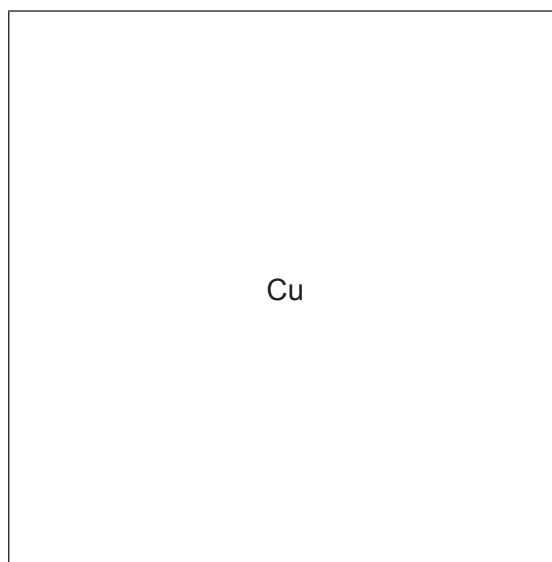
[2]

(c) Cu²⁺ ions exist as [Cu(H₂O)₆]²⁺ complex ions in aqueous solution.

Complete a three-dimensional diagram to show the shape of this complex.

Name its shape.

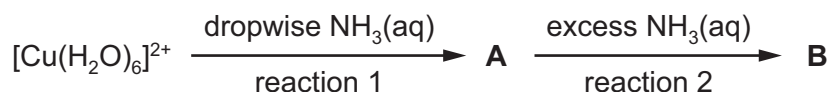
Label and state the value of one bond angle.



name of shape

[2]

- (d) When $\text{NH}_3(\text{aq})$ is added to $\text{Cu}^{2+}(\text{aq})$, dropwise at first and then in excess, two chemical reactions occur as shown.



For each reaction, describe what you would see and write an equation.

reaction 1

observation

.....

equation

reaction 2

observation

.....

equation

[4]

- (e) EDTA^{4-} is a polydentate ligand. When a solution of EDTA^{4-} is added to a solution containing $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ a new complex is formed. The formula of this complex is $[\text{CuEDTA}]^{2-}$.

- (i) Name the type of reaction occurring here.

..... [1]

- (ii) Write an expression for the stability constant, K_{stab} , of $[\text{CuEDTA}]^{2-}$ in this reaction.

[1]

- (iii) The numerical value of the K_{stab} of $[\text{CuEDTA}]^{2-}$ is 6.3×10^{19} at 298 K.

State what this tells us about the $[\text{CuEDTA}]^{2-}$ complex ion.

..... [1]

(f) Ethanedioate ions, $\text{C}_2\text{O}_4^{2-}$, can act as a bidentate ligand.

(i) Explain what is meant by the term *bidentate ligand*.

.....

.....

.....

..... [2]

(ii) When ethanedioate ions are added to a solution of zirconium ions, Zr^{4+} , a complex ion containing four $\text{C}_2\text{O}_4^{2-}$ ions and one Zr^{4+} ion is formed. All four ethanedioate ions act as bidentate ligands in this complex.

Give the formula of this complex ion and explain why this complex is not octahedral.

.....

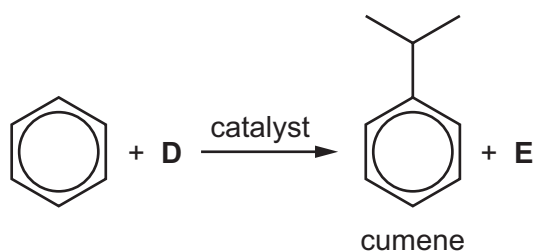
.....

.....

..... [2]

[Total: 17]

- 6 (a) Benzene reacts with **D** in the presence of a suitable catalyst to give cumene and non-organic product **E**. This is an electrophilic substitution reaction.



- (i) Name the reactant **D** and the non-organic product **E**.

D

E

[2]

- (ii) Give the name of the type of aromatic electrophilic substitution reaction taking place.

..... [1]

- (b) Cumene undergoes substitution reactions with chlorine to give several different isomeric products with the formula $C_9H_{11}Cl$. The substitution can occur in the aromatic ring or in the side-chain of cumene.

- (i) Describe the conditions that are used to ensure substitution takes place only in the **aromatic ring**.

..... [1]

- (ii) Draw the structures of the **two** major isomeric products of the reaction, formula $C_9H_{11}Cl$, when substitution takes place in the aromatic ring.

[1]

- (iii) Describe the conditions that are used to ensure substitution takes place only in the **side-chain**.

..... [1]

- (iv) Draw the structures of **two** isomeric products of the reaction, formula $C_9H_{11}Cl$, when substitution takes place in the side-chain.

[1]

- (c) Complete the following table to show the structures of the organic products formed when cumene reacts with each reagent.

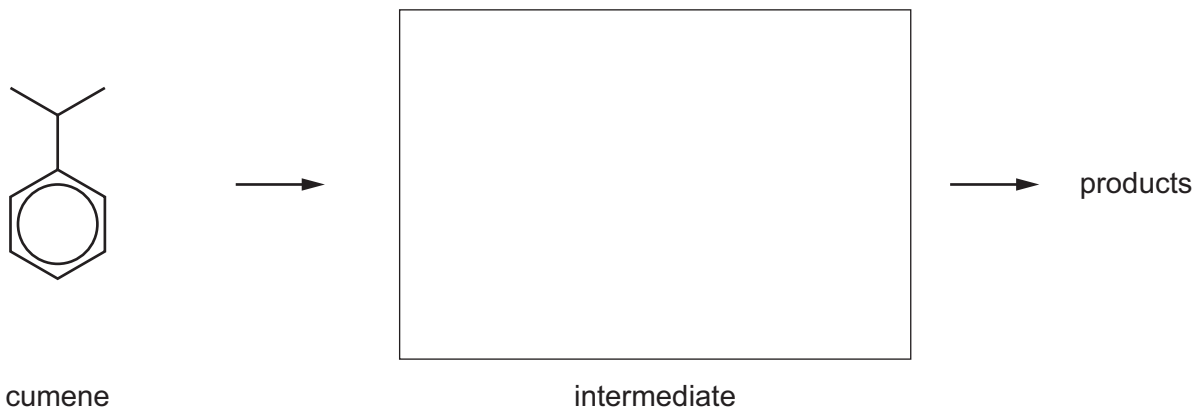
reagent	structure of organic product
hot $KMnO_4(aq)$	
$H_2 + Ni$, high pressure	

[2]

- (d) Cumene can be nitrated using a mixture of concentrated nitric and sulfuric acids. The mechanism for this reaction is similar to the mechanism for the nitration of benzene.

Complete the mechanism for this reaction.

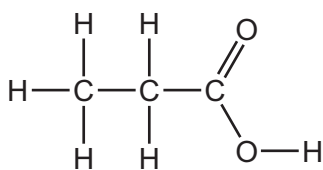
- Include all relevant charges and curly arrows showing the movement of electron pairs.
- Draw the structure of the intermediate.
- You do not need to draw the products.



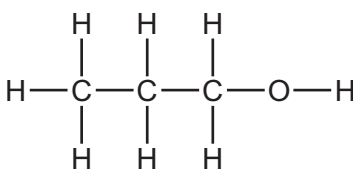
[4]

[Total: 13]

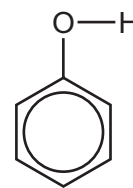
7 The three substances shown all have some acidic properties.



propanoic acid



propan-1-ol



phenol

(a) Write an equation for the reaction between propan-1-ol and sodium metal.

..... [1]

(b) (i) Give the order of the relative acidities of propanoic acid, propan-1-ol and phenol, stating the most acidic first.

..... [1]

(ii) Explain your answer to (i).

.....

 [2]

(c) Methanoic acid, HCO_2H , has a similar acid strength to propanoic acid.

Describe a chemical test to distinguish between these two acids. Name the acid which gives a positive result in this test and describe the observations that would be made.

.....

 [2]

- (d) The ester phenyl propanoate, $\text{C}_2\text{H}_5\text{CO}_2\text{C}_6\text{H}_5$, can be made from phenol and propanoic acid in a **two-step** synthesis. The first step produces an acyl chloride.

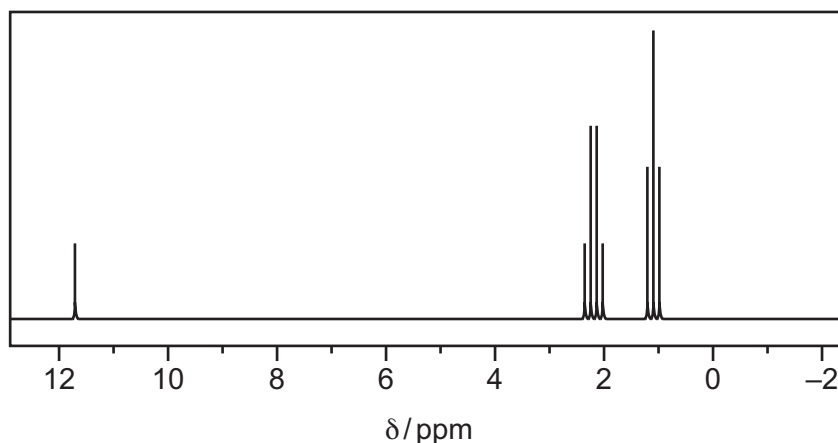
For this **two-step** synthesis,

- draw the structure of the product of the first step,
- state the reagents and conditions needed for each step of the synthesis.

.....

 [3]

- (e) An unknown compound, **Z**, is propan-1-ol, propanal or propanoic acid. The proton NMR spectrum of **Z** dissolved in CDCl_3 is shown.



- (i) From the proton NMR spectrum, identify **Z**.

..... [1]

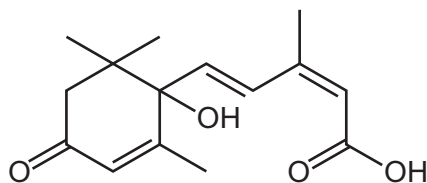
- (ii) State one feature that would be seen, and why, in the proton NMR spectra of each of the two compounds that are not **Z**.

.....

 [2]

[Total: 12]

- 8 Absciscic acid, $C_{15}H_{20}O_4$, is a plant hormone.



absciscic acid, $C_{15}H_{20}O_4$

- (a) On the diagram of absciscic acid, use an asterisk (*) to label each chiral carbon atom. [1]

- (b) Absciscic acid is reacted with an excess of $NaBH_4$.

Give the molecular formula of the organic product formed.

..... [1]

- (c) If absciscic acid is treated with an excess of hot, concentrated, acidified $KMnO_4$, three different carbon-containing products are formed.

- (i) Draw the skeletal formula of the carbon-containing product with the **largest** molecular mass.

[1]

- (ii) Identify the carbon-containing product with the **smallest** molecular mass. Explain how this product arises.

.....

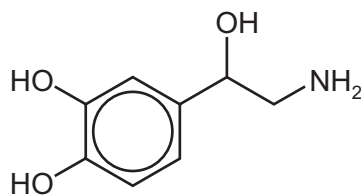
 [2]

- (iii) Identify the third carbon-containing product of this reaction by giving its displayed or structural formula.

[1]

[Total: 6]

- 9 Noradrenaline is a hormone found in humans.



noradrenaline

- (a) Give the molecular formula of noradrenaline.

..... [1]

- (b) State whether or not noradrenaline shows stereoisomerism. Explain your answer.

.....
 [1]

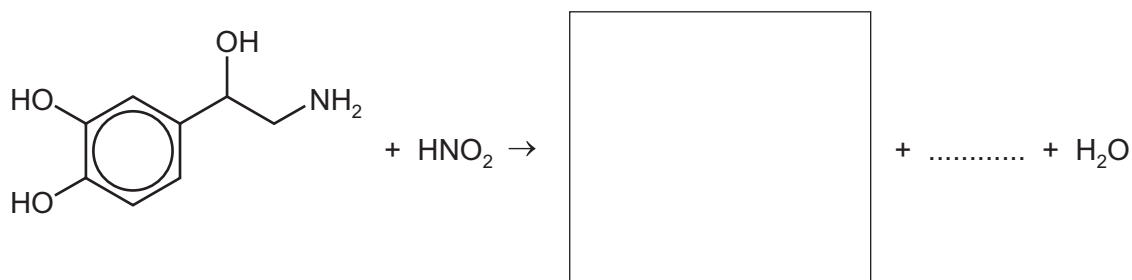
- (c) $\text{HNO}_2(\text{aq})$ is reacted at 5°C with separate samples of noradrenaline and phenylamine. The reaction with phenylamine produces a stable diazonium ion. The reaction with noradrenaline produces an unstable diazonium ion.

- (i) Suggest why the diazonium ion produced with phenylamine is stable.

.....
 [1]

- (ii) When one noradrenaline molecule reacts with one HNO_2 molecule, the products are one water molecule, one molecule of an unreactive gas, and one molecule of an organic compound made up of carbon, hydrogen and oxygen only.

Complete the chemical equation for this reaction.



[2]

[Total: 5]

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