YEAR 6 PRELIMINARY EXAMINATION II

CANDIDATE NAME					
CLASS	6				
CENTRE NUMBER	S				

INDEX NUMBER				

H2 CHEMISTRY

9647/01

Paper 1 Multiple Choice

23 September 2016

1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

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

Write your name, class, centre number and index number on the Answer Sheet in the spaces provided.

There are **forty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.

Choose the one you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.

Any rough working should be done in this booklet.

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

Section A

For each question there are four possible answers, **A, B, C** and **D**. Choose the **one** you consider to be correct.

1 For complete combustion of 20.0 g of heptane, what is the minimum volume of oxygen gas required at s.t.p.?

A 0.2 dm^3

B 2.2 dm^3

C 49.3 dm^3

D 52.8 dm^3

2 Element **X** exists as 3 different isotopes and has a relative atomic mass of 66.6.

Which of the following compositions of isotopes is correct?

A 25% ^{65}**X**, 50% ^{66}**X** and 25% ^{67}**X**

B 30% ^{65}**X**, 60% ^{66}**X** and 10% ^{67}**X**

C 50% ^{65}**X**, 20% ^{66}**X** and 30% ^{67}**X**

D 10% ^{65}**X**, 20% ^{66}**X** and 70% ^{67}**X**

3 Which of the following does **not** contain a singly occupied orbital?

A N^{2+} **B** S^- **C** Br^+ **D** Sc^{3+}

4 Dinitrogen tetroxide, N_2O_4, has a simple covalent structure.

Which of the following correctly describes the bonding within the dinitrogen tetroxide molecule?

	σ bond	**π bond**	**dative bond**
A	3	2	2
B	5	0	4
C	5	2	2
D	5	4	0

5 The Valence Shell Electron Pair Repulsion (VSEPR) theory is used to predict the shapes of molecules.

Which shape is correctly predicted by VSEPR?

	number of bonded electron pairs around central atom	**number of lone pairs around central atom**	**shape**
A	2	4	non-linear
B	3	2	T-shaped
C	4	1	square planar
D	3	2	see-saw

6 Equal masses of gaseous N_2, NH_3 and N_2O are injected into an evacuated container to produce a total pressure of 3 atm.

How do the partial pressures of N_2, NH_3 and N_2O compare?

A $p_{N_2} = p_{NH_3} = p_{N_2O}$

B $p_{N_2} < p_{NH_3} < p_{N_2O}$

C $p_{NH_3} < p_{N_2} < p_{N_2O}$

D $p_{N_2O} < p_{N_2} < p_{NH_3}$

7 *Use of the Data Booklet is relevant to this question.*

The enthalpy changes for three reactions are given below:

$Na(s) \rightarrow Na(g)$ $\Delta H = +107\ kJ\ mol^{-1}$

$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$ $\Delta H = -58\ kJ\ mol^{-1}$

$2Na^+(g) + 2H^+(aq) + 2e^- \rightarrow 2Na^+(aq) + H_2(g)$ $\Delta H = -1700\ kJ\ mol^{-1}$

What is the enthalpy change for the following reaction?

$$Na(s) + H_2O(l) \rightarrow Na^+(aq) + OH^-(aq) + \tfrac{1}{2}H_2(g)$$

A $-191\ kJ\ mol^{-1}$

B $-307\ kJ\ mol^{-1}$

C $-685\ kJ\ mol^{-1}$

D $-1041\ kJ\ mol^{-1}$

8 The dissolution of ammonium nitrate is a chemical reaction commonly used in cold packs that serve to relief pain in sports injury. A thin plastic membrane separates powdered ammonium nitrate and water. When the cold pack is squeezed, the membrane breaks and the ammonium nitrate dissolves in water.

$$NH_4NO_3(s) \rightarrow NH_4NO_3(aq)$$

What are the signs of ΔH, ΔS, ΔG for the overall process?

	ΔH	ΔS	ΔG
A	–	–	+
B	–	+	–
C	+	+	–
D	+	+	+

9 Hydrogen reacts with iodine according to the equation:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

P atm of hydrogen is allowed to react with Q atm of iodine at constant temperature.

At equilibrium, it is found that

A the partial pressure of hydrogen is greater than P.

B the total pressure of the system is $(P + Q)$ atm.

C the total pressure of the system is greater than $(P + Q)$ atm.

D the total pressure of the system is less than $(P + Q)$ atm.

10 When 10 cm^3 of 0.02 mol dm^{-3} aqueous $Ba(OH)_2$ is added to separate solutions of 10 cm^3 of 0.1 mol dm^{-3} $MgCl_2$ and 10 cm^3 of 0.1 mol dm^{-3} $CaCl_2$, what would be observed?

(K_{sp} of $Mg(OH)_2 = 3.2 \times 10^{-11}$ $mol^3\ dm^{-9}$; K_{sp} of $Ca(OH)_2 = 1.35 \times 10^{-5}$ $mol^3\ dm^{-9}$)

A Only $Ca(OH)_2$ would be precipitated.

B Only $Mg(OH)_2$ would be precipitated.

C Both $Mg(OH)_2$ and $Ca(OH)_2$ would be precipitated.

D Neither $Mg(OH)_2$ nor $Ca(OH)_2$ would be precipitated.

11 The auto-ionisation of water is represented by the following equation:

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \qquad \Delta H = +57\ \text{kJ mol}^{-1}$$

Given that the value of the equilibrium constant, K_w, is 1.0×10^{-14} $\text{mol}^2\ \text{dm}^{-6}$ at 298 K, which of the following statements is true?

A Water is not a neutral liquid at a temperature lower than 298 K.

B When water is heated, the concentration of OH^- increases.

C The pH of water at temperatures higher than 298 K is greater than 7.

D The association of water molecules by hydrogen bonding increases as temperature rises.

12 Consider the following reaction:

$$3X + Y \rightarrow X_3Y$$

The mechanism involves the following steps:

$2X \rightleftharpoons X_2$ (fast)

$X_2 + Y \rightleftharpoons X_2Y$ (slow)

$X_2Y + X \rightarrow X_3Y$ (fast)

Based on the information, what is the rate equation for this reaction?

A	Rate = $k[X]^2$	**B**	Rate = $k[X_2][Y]$
C	Rate = $k[X]^2[Y]$	**D**	Rate = $[X]^3[Y]$

13 The decomposition of compound **A** is a first order reaction which proceeds according to the equation:

$$\mathbf{A}(s) \rightarrow 2\mathbf{B}(s) + \mathbf{C}(g)$$

A sample of **A** gave 80 cm^3 of **C** on complete decomposition and it took 40 min for 40 cm^3 of **C** to be evolved.

For another identical sample of **A**, how long would it take for 70 cm^3 of **C** to be evolved?

A	40 min	**B**	70 min
C	80 min	**D**	120 min

14 The Daniell Cell comprises two half-cells – a copper electrode dipped in copper(II) sulfate solution and a zinc electrode dipped in zinc sulfate solution – linked by a salt bridge.

Which of the following will increase the cell e.m.f. of the Daniell Cell?

A Adding solid copper(II) sulfate to the copper half-cell.

B Increasing the mass of copper electrode.

C Increasing the concentration of the zinc sulfate solution.

D Allow the system to reach equilibrium before measuring cell e.m.f.

15 Two separate electrolyses were performed as follows, under the same conditions of temperature and pressure.

1. When aqueous hydrochloric acid was electrolysed for five minutes, 100 cm^3 of hydrogen were collected from the cathode.
2. When aqueous sulfuric acid was electrolysed for five minutes, 200 cm^3 of oxygen were collected from the anode.

If the current used in electrolysis 1 was I, what was the current used in electrolysis 2?

A $4I$ **B** $2I$ **C** I **D** $0.5I$

16 Which of the following is a trend across Period 3 of the Periodic Table?

A The radii of ions decrease.

B The first ionisation energy decreases.

C The melting points of elements decrease.

D The compounds of elements become increasingly covalent.

17 Which of the following equations represents the reaction when calcium nitrate is heated strongly?

A $Ca(NO_3)_2 \rightarrow CaO + N_2O_5$

B $Ca(NO_3)_2 \rightarrow Ca(NO_2)_2 + O_2$

C $2Ca(NO_3)_2 \rightarrow 2CaO + 4NO_2 + O_2$

D $3Ca(NO_3)_2 \rightarrow Ca_3N_2 + 4NO_2 + 5O_2$

18 *Use of the Data Booklet is relevant to this question.*

Which of the following solutions of halide will **not** change the colour of acidified potassium dichromate(VI) ?

A chloride **B** bromide **C** iodide **D** astatide

19 Which statement correctly **defines** a transition element?

A Transition elements exhibit more than one oxidation state in their compounds.

B Transition elements or their compounds are widely used as catalysts.

C Transition elements form many coloured compounds.

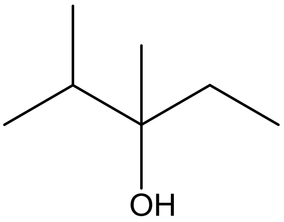
D Transition elements have partially filled d orbitals.

20 Which of the following compounds **cannot** be obtained from propene in a single reaction?

A CO_2 **B** $CH_3CH_2CH_3$

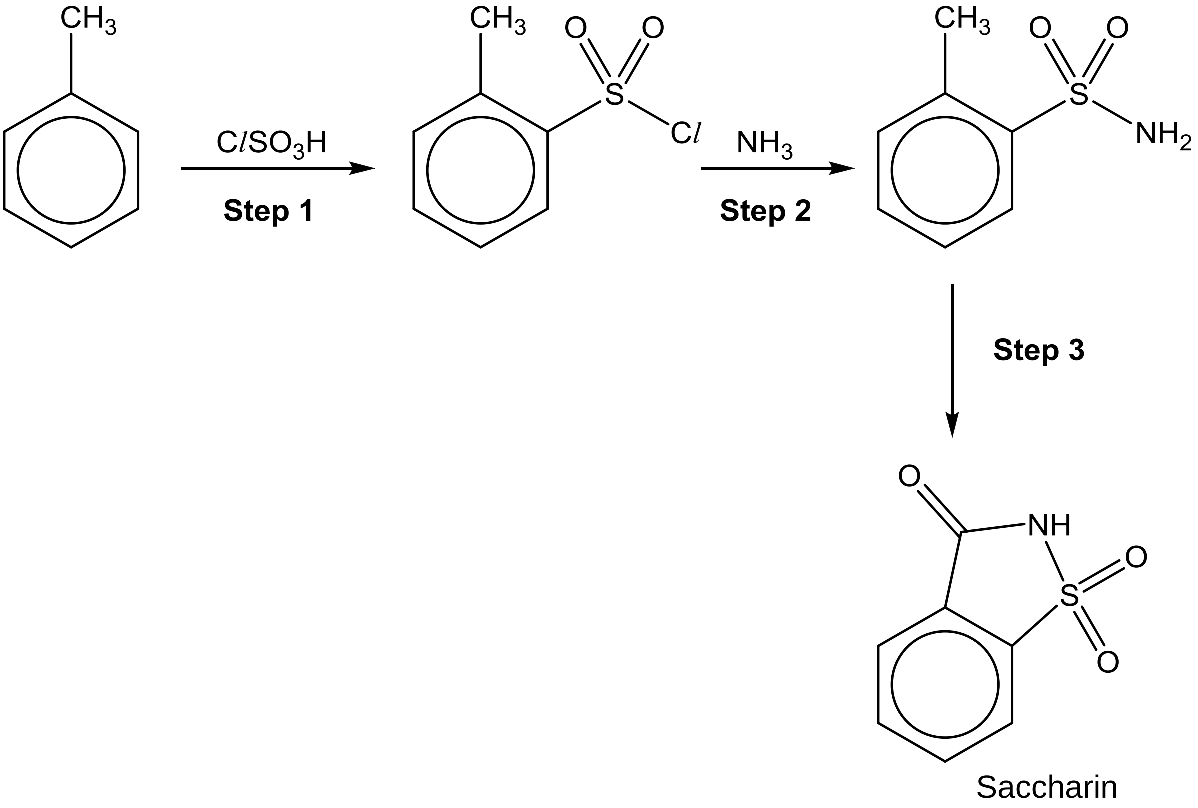
C $CH_3CH_2CH_2CN$ **D** $CH_2(OH)CH(OH)CH_3$

21 How many alkenes (including stereoisomers) can be formed when the following alcohol is heated with concentrated sulfuric acid?



A 0 **B** 2 **C** 3 **D** 4

22 Saccharin, an artificial sweetening agent, can be synthesised from methylbenzene using the following reaction scheme:



What type of reactions do steps **1** and **2** illustrate?

	Step 1	**Step 2**
A	Electrophilic substitution	Condensation
B	Electrophilic substitution	Nucleophilic Addition
C	Nucleophilic substitution	Condensation
D	Nucleophilic substitution	Nucleophilic Addition

23 Fluothane, $CF_3CHBrCl$, is a volatile liquid widely used as an anaesthetic.

Which of the following statements about fluothane is **not** correct?

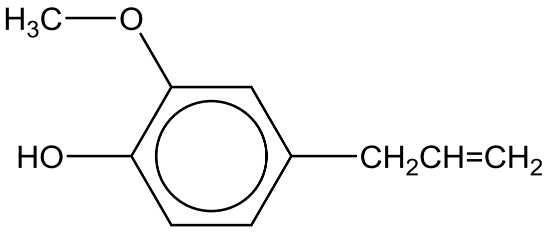
A Fluothane may cause the depletion of the ozone layer.

B Weak van der Waals' forces hold molecules of fluothane together.

C Fluothane undergoes elimination when treated with hot ethanolic NaOH.

D When a sample of fluothane is heated with aqueous silver nitrate, a mixture of white and cream precipitate is formed.

24 Eugenol is a common component of perfumes and essential oils. It is also used as an antiseptic.



eugenol

(You may treat the –OCH_3 group attached to the benzene ring as inert.)

Which of the following statements about eugenol is correct?

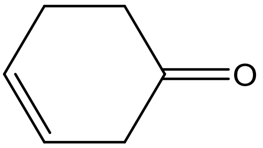
A It reacts with 2,4-DNPH to give an orange precipitate.

B It gives white fumes when reacted with thionyl chloride.

C It decolourises hot acidified potassium manganate(VII).

D It reacts with 2 moles of Br_2 in a suitable solvent to form a product with 4 bromine atoms incorporated.

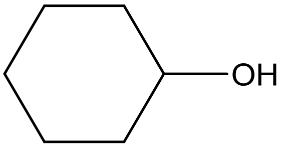
25 Cyclohex-3-en-1-one has the following structure:



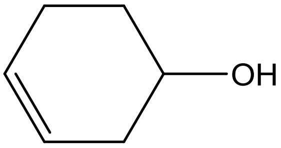
cyclohex-3-en-1-one

Which of the following compounds is formed when cyclohex-3-en-1-one is reacted with $NaBH_4$ dissolved in an organic solvent?

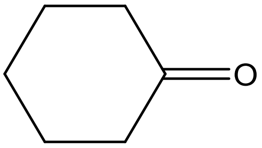
A



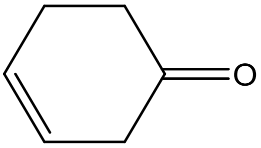
B



C



D



26 Compound **J** gives the following observations with Tollens' Reagent and Na_2CO_3(aq).

Reagent	Observation
Tollens' Reagent	Silver mirror observed
Na_2CO_3(aq)	No effervescence observed

From the above observations, what could be a possible structure for **J**?

A $(COOH)_2$

B CH_3COCHO

C $CH_3COCOOH$

D $CH_3COCOCH_3$

27 In the study of organic reaction mechanisms, radioactive oxygen-18, ^{18}O, is often used to tag organic molecules. The radioactivity of the products can then be detected to deduce which products contain ^{18}O.

When ^{18}O-tagged propan-1-ol is heated with ethanoic acid in the presence of a small amount of concentrated sulfuric acid, which of the following set of products will be obtained?

A $CH_3CH_2CH_2{}^{18}OCOCH_3$ and H_2O

B $CH_3CH_2CH_2OCOCH_3$ and $H_2{}^{18}O$

C $CH_3CH_2CH_2{}^{18}OCOCH_3$ and $H_2{}^{18}O$

D $CH_3CH_2CH_2OCOCH_3$ and H_2O

28 Which of the following correctly shows the compounds arranged in decreasing pK_a values?

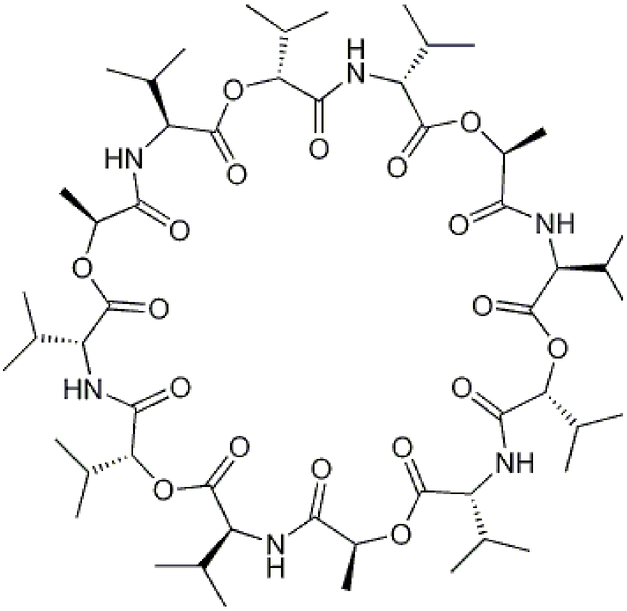
A $CH_2FCOOH > CH_2ClCOOH > CH_2BrCOOH$

B $CH_3COOH > C_6H_5COOH > C_6H_5OH$

C $CCl_3COOH > CHCl_2COOH > CH_2ClCOOH$

D $C_2H_5OH > C_6H_5OH > C_6H_5COOH$

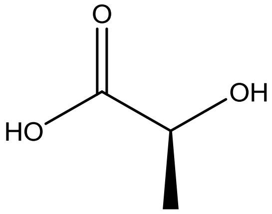
29 Valinomycin is a peptide-like molecule that disrupts plasma membrane formation in bacteria.



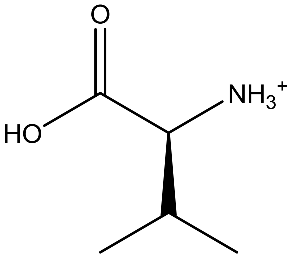
valinomycin

Which of the following will **not** be produced when valinomycin is heated with dilute H_2SO_4(aq) for a period of time?

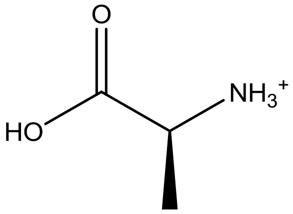
A



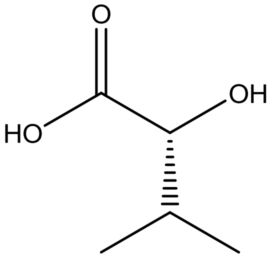
B



C



D



30 Denaturation of proteins occurs due to the destruction of the tertiary structure where various R group interactions are disrupted by external factors.

Which of the following correctly shows the R group interactions that will be affected by the corresponding external factor?

	R group interactions	**External factor**
A	disulfide bridges	extreme pH changes
B	ionic interactions	addition of alcohol
C	van der Waals’ forces	addition of heavy metal ions
D	hydrogen bonding	extreme pH changes

Section B

For each of the questions in this section, one or more of the three numbered statements **1** to **3** may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

The responses **A** to **D** should be selected on the basis of

A	**B**	**C**	**D**
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

No other combination of statements is used as a correct response.

31 Which statements about aluminium are correct?

1 It forms amphoteric oxides.

2 It forms an ionic compound with oxygen.

3 It forms an ionic compound with chlorine.

32 Between ethanol molecules, there exists

1 hydrogen bonds.

2 instantaneous dipole-induced dipole interactions.

3 covalent bonds.

33 For a first order reaction, which of the following graphs will be a straight line passing through the origin?

1 Initial rate vs concentration of reactant

2 Initial rate vs time taken for complete reaction

3 Concentration of reactant vs time taken for complete reaction

A	B	C	D
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

34 Which statements correctly describe an electrolytic cell?

1 It is driven by an external battery.

2 The polarities of the cathode and anode are negative and positive respectively.

3 It is used to extract unreactive metals from the ores.

35 Which of the following statements are true for astatine, the element below iodine in Group VII of the Periodic Table?

1 Silver astatide is insoluble in concentrated aqueous ammonia.

2 Astatine oxidises potassium chloride to chlorine.

3 Hydrogen astatide is more stable to heat than hydrogen iodide.

36 When placed in a strong magnetic field, paramagnetic objects are attracted to the field. Paramagnetism arises when an element has unpaired electrons.

Which of the following chemical species would you expect to exhibit paramagnetism?

1 Cr

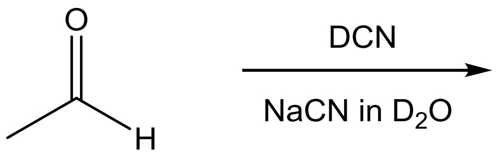
2 Mn

3 Cu^+

A	B	C	D
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

37 Deuterium, D, is the ^{2}H isotope of hydrogen.

Which of the following reactions could give an organic compound having a deuterium atom incorporated?

1


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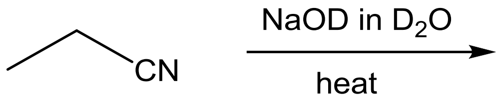

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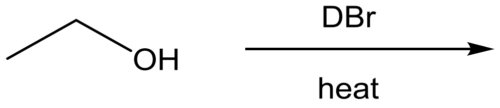
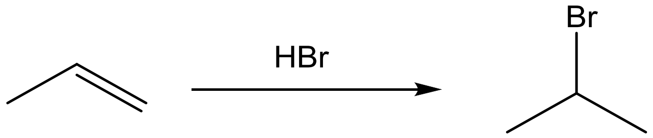


38 In which of the following reactions will the inorganic reagent act as the nucleophile?

1


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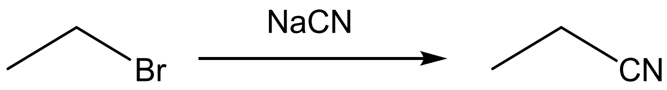
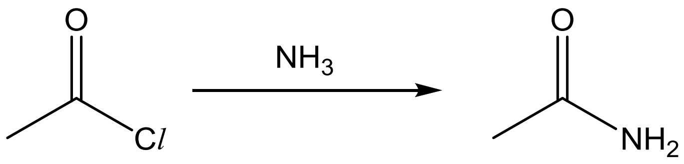
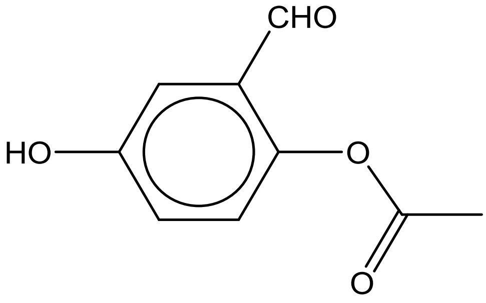


3


A	B	C	D
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

39 Compound **X** is a flavouring agent in food.



X

Which of the following reagents will cause a colour change when the reagent is added to a sample of compound **X**?

1 aqueous bromine

2 neutral iron(III) chloride solution

3 hot acidified potassium dichromate(VI)

40 Which of the following descriptions about haemoglobin are correct?

1 Both O_2 and CO can bind to haemoglobin.

2 The quaternary structure of haemoglobin consists of two α-helices and two β-pleated sheets.

3 A maximum of six oxygen molecules may be bound to each haemoglobin molecule.

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YEAR 6 PRELIMINARY EXAMINATION II

CANDIDATE NAME	ANSWER KEY									
CLASS	6									
CENTRE NUMBER	S	3	0	4	4	INDEX NUMBER	0	0		

H2 CHEMISTRY 9647/01

Paper 1 Multiple Choice

23 September 2016

1 hour

1.	**C**	**11.**	**B**	**21.**	**D**	**31.**	**B**
2.	**D**	**12.**	**C**	**22.**	**A**	**32.**	**B**
3.	**D**	**13.**	**D**	**23.**	**C**	**33.**	**D**
4.	**C**	**14.**	**A**	**24.**	**C**	**34.**	**B**
5.	**B**	**15.**	**A**	**25.**	**B**	**35.**	**D**
6.	**D**	**16.**	**D**	**26.**	**B**	**36.**	**B**
7.	**A**	**17.**	**C**	**27.**	**A**	**37.**	**D**
8.	**C**	**18.**	**A**	**28.**	**D**	**38.**	**C**
9.	**B**	**19.**	**D**	**29.**	**C**	**39.**	**A**
10.	**C**	**20.**	**C**	**30.**	**D**	**40.**	**D**

YEAR 6 PRELIMINARY EXAMINATION II

CANDIDATE NAME	
CLASS	6
CENTRE NUMBER	S
INDEX NUMBER	

H2 CHEMISTRY 9647/02

Paper 2 Structured Questions

13 September 2016

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class, centre number and index number on all the work you hand in.
Write in dark blue or black pen on both sides of paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions in the space provided.
A Data Booklet is provided. Do NOT write anything on it.

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

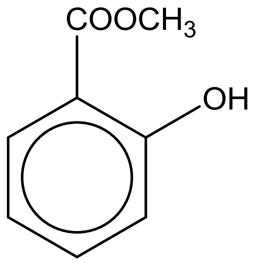
<table>
<tr><th colspan="9">For Examiner's Use</th></tr>
<tr><th colspan="9">Paper 2</th></tr>
<tr><th>Question Number</th><th>1</th><th>2</th><th>3</th><th>4</th><th>5</th><th>6</th><th></th><th>Total (Paper 2)</th></tr>
<tr><td>Marks</td><td>12</td><td>13</td><td>8</td><td>9</td><td>16</td><td>14</td><td></td><td>72</td></tr>
<tr><td colspan="2">Paper 1</td><td>40</td><td></td><td colspan="2">Paper 3</td><td>80</td><td>Total</td><td>192</td></tr>
</table>

This document consists of **18** printed pages and **2** blank pages.

1 Planning (P)

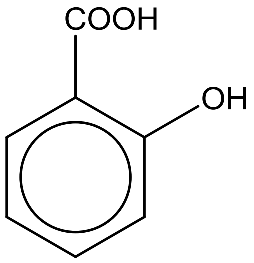
Salicylic acid is known for its ability to ease aches and pains as well as reduce fevers. Its analgesic and anti-inflammatory properties makes it one of the most important medications needed in a basic health system, placing it on the World Health Organisation Model List of Essential Medicines.

It can be synthesised via the alkaline hydrolysis of methyl salicylate, followed by acidification.



methyl salicylate

(M_r = 152)



salicylic acid

(M_r = 138)

Methyl salicylate is a liquid with a density of 1.174 g cm^{-3}.

Aqueous sodium hydroxide used for the hydrolysis has a concentration of 6.0 mol dm^{-3}.

Like most organic reactions, the yield of this reaction is less than 100%. Using the procedure described below, a typical yield of pure salicylic acid is 60%.

Methyl salicylate is mixed with aqueous sodium hydroxide in a molar ratio of 1:2. The reaction is heated under reflux conditions for around 30 minutes to form a di-sodium salicylate salt.

When the reaction mixture has cooled down, concentrated hydrochloric acid is added until in excess to cause the crude salicylic acid to precipitate. This process is highly exothermic.

The crude salicylic acid is then purified by recrystallisation from water.

(a) Using the information given above:

(i) write a balanced equation for the formation of the di-sodium salicylate salt;

[1]

(ii) calculate the volumes of methyl salicylate and aqueous sodium hydroxide you would use to prepare 10 g of pure salicylic acid, showing your working.

[2]

(b) Write a plan for the preparation of 10 g of pure salicylic acid.

In your plan, you should:

- draw a diagram of the assembled apparatus you would use when heating the reaction mixture;
- give a full description of the procedures, including the capacities of the apparatus involved, you would use to prepare and purify the salicylic acid;
- explain how you would minimise a potential safety hazard.

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…………………………………………………………………………………………………… **[9]**

[Total: 12]

2 Sodium azide is a chemical found in car safety airbags. When the car undergoes a head-on collision, a series of chemical reactions occur in the gas generator chamber. The first reaction produces nitrogen gas to fill the airbag. The equation for the reaction is shown below:

$$NaN_3(s) \rightarrow Na(s) + \frac{3}{2}N_2(g) \qquad \Delta H < 0$$

(a) The volume of a fully inflated airbag is 60 dm^3.

Calculate the mass of NaN_3 needed to fill such an airbag to an internal pressure of 150 kPa at 300 °C.

[2]

(b) **(i)** Given that ΔS_r = S(products) – S(reactants) and the following information, calculate ΔS for the above reaction.

Molar entropy of NaN_3(s)	70.5 J mol^{-1} K^{-1}
Molar entropy of Na(s)	51.3 J mol^{-1} K^{-1}
Molar entropy of N_2(g)	191.6 J mol^{-1} K^{-1}

[1]

(ii) Explain why the reaction is feasible at all temperatures.

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(iii) Suggest why the reaction in fact occurs only at temperatures above 300 °C.

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(c) Sodium metal formed in the above reaction is very reactive and is made to react with potassium nitrate present in the airbag, forming sodium oxide as one of the products.

(i) Explain what is meant by the lattice energy of sodium oxide.

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………………………………………………………………………………… **[1]**

(ii) Using the information given below and relevant information from the Data Booklet, construct an energy level diagram to calculate the lattice energy of sodium oxide.

Enthalpy change of formation of sodium oxide = –416 kJ mol^{-1}

Enthalpy change of atomisation of sodium = +107 kJ mol^{-1}

Sum of 1st and 2nd electron affinity of oxygen = +702 kJ mol^{-1}

[3]

(iii) Given that the 1st electron affinity of oxygen is –142 kJ mol^{-1}, calculate the 2nd electron affinity of oxygen and explain the significance of its sign.

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(d) A working airbag should become fully inflated within 0.04 s of the initial collision. At this point, it is actually unsafe for the driver's body to hit the inflated airbag due to the high internal pressure (150 kPa). The airbag is hence designed to deflate immediately such that by the time the driver's body hit the airbag, usually 2 s after the initial collision, the internal pressure of the airbag would have dropped to 101 kPa, providing a softer cushioning for the driver.

An airbag at a safety test has a depressurisation rate of 23 kPa s^{-1}.

Explain if this airbag is safe for use, showing relevant calculations.

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[Total: 13]

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3 **(a)** What do you understand by the term standard electrode potential?

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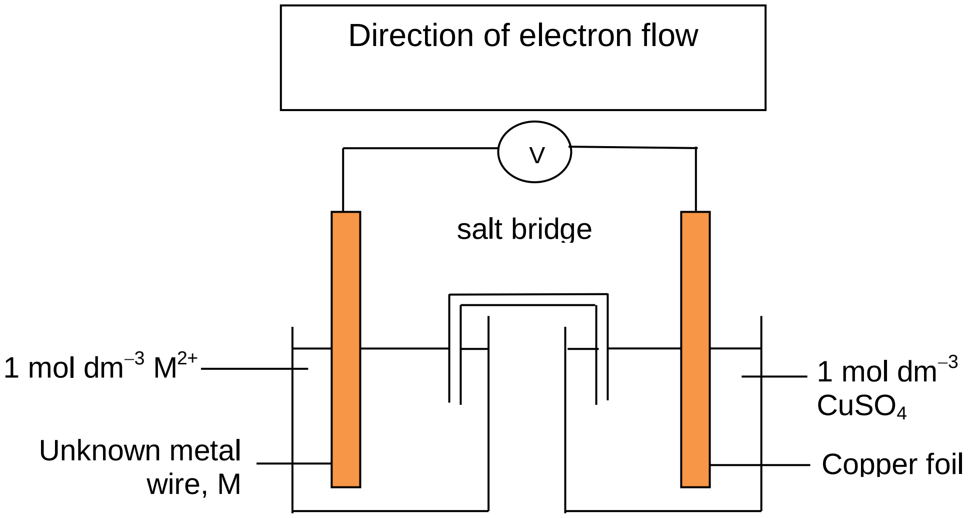
.... **[2]**

(b) The following cell was set up between a copper electrode and an unknown metal electrode $M^{2+}(aq)/M(s)$. The standard cell potential was found to be 0.76 V, and the copper foil was connected to the positive end of the voltmeter.



(i) Use the Data Booklet to calculate the standard electrode potential of the $M^{2+}(aq)/M(s)$ system.

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.... **[1]**

(ii) Draw an arrow in the box above to show the direction of electron flow through the voltmeter. **[1]**

(iii) Predict the outcomes of the following situations. Describe what you will see and write ionic equations, with state symbols, for any reactions that occur.

I A rod of metal M is dipped into a solution of 1 mol dm^{-3} $CuSO_4$.

....

....

.... **[2]**

II Dilute sulfuric acid is added into a beaker containing a powdered sample of metal M.

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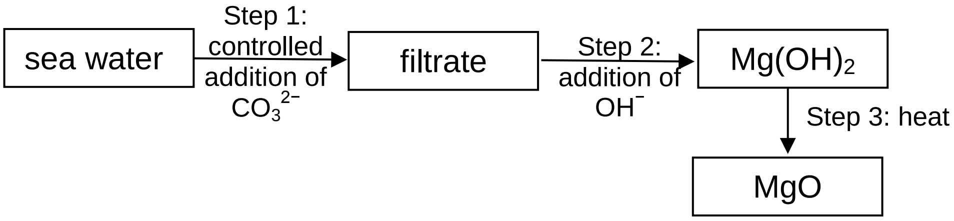
.... **[2]**

[Total: 8]

4 The four most abundant salts in sea-water are as follows.

Salt	kg per m^3
Sodium chloride	27.5
Magnesium chloride	6.75
Magnesium sulfate	5.625
Calcium sulfate	1.80

Magnesium oxide is obtained from sea-water by the following steps.



The relevant numerical values of the solubility products are given below.

Salt	K_{sp}
Sodium carbonate	-
Calcium carbonate	5.0×10^{-9}
Magnesium carbonate	1.0×10^{-5}
Magnesium hydroxide	1.5×10^{-11}
Calcium hydroxide	7.9×10^{-6}

(a) Explain why the addition of carbonate ions in Step 1 is necessary and has to be controlled.

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(b) Suggest why the Ksp value of sodium carbonate is not provided.

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………………………………………………………………………………………… **[1]**

(c) Using the reaction scheme above, Barny used 1 dm^3 of sea water to extract magnesium oxide.

(i) Calculate the concentration of Mg^{2+} in sea water.

[2]

(ii) Barny chose a pH of 9.5 to carry out the extraction of $Mg(OH)_2$.

Calculate the maximum mass of **magnesium oxide** that can be obtained at pH 9.5.

You may assume that negligible volumes of CO_3^{2-} and OH^- were used.

[3]

(iii) Suggest how Barny can modify his experiment to improve on the yield of MgO?

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[1]

[Total: 9]

5 **(a)** In the periodic table, elements can exhibit either single or variable oxidation states. One example of an element which can exhibit variable oxidation state is manganese, Mn, while aluminium, A*l* is an example of an element which cannot exhibit variable oxidation state.

(i) Draw a dot and cross diagram for aluminium chloride, A*l*C*l*$_3$.

[1]

(ii) In the vapour state, the M_r of aluminium chloride was found to be 267. However, when aluminium chloride is in the solid state, its M_r was found to be 133.5.

With the aid of suitable diagram, explain this behaviour exhibited by aluminium chloride and the type of bonding involved.

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(b) Manganese is often found in minerals in combination with iron and is a metal with important industrial metal alloy uses, particularly in stainless steels. Manganese is found in various black minerals known as pyrolusite. Pyrolusite consists mainly of manganese(IV) oxide. Manganese(IV) oxide is the most common starting material for the production of compounds of manganese in other oxidation states.

Manganese(IV) oxide undergoes a 2-step reaction to produce **Y** and **Z**.

$$MnO_2 \xrightarrow[\textbf{I}]{\text{Oxidation in alkaline medium}} MnO_4^{2-} \underset{\textbf{II}}{\overset{\text{Hot water / alkaline medium}}{\rightleftharpoons}} \text{Brown black solid } \textbf{Y} \text{ in a purple solution containing } \textbf{Z}$$

(i) Define the term *transition element*.

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(ii) Write the electronic configuration of Mn.

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(iii) Explain why manganese can exhibit variable oxidation state.

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…………………………………………………………………………… **[1]**

(iv) The brown black solid **Y** contains 63.8% by mass of manganese and 36.2% by mass oxygen.

Determine the empirical formula of **Y**.

[1]

(v) Suggest the identity of **Z** and state the type of reaction that occurs at step **II**.

Hence, construct a balanced equation for the reaction.

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(vi) With reference to your answer in **(v)**, suggest how bubbling carbon dioxide gas into the hot solution of MnO_4^{2-} increases the yield of **Y** and **Z**.

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(c) Manganese(II) carbonate, $MnCO_3$, undergoes thermal decomposition in a similar way to a Group II carbonate.

$MnCO_3$ decomposes at 200 °C while $CaCO_3$ decomposes at 840 °C.

(i) Write an equation, with state symbols, for the thermal decomposition of $MnCO_3$.

………………………………………………………………………… **[1]**

(ii) Explain why $MnCO_3$ decompose at a lower temperature than $CaCO_3$.

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[Total: 16]

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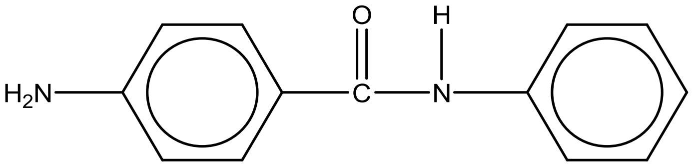
6 **(a)** 4-Amino-N-phenylbenzamide, the structure of which is drawn below, is used in the treatment of epilepsy.



4-amino-N-phenylbenzamide

(i) 4-Amino-N-phenylbenzamide is hydrolysed by warm aqueous sodium hydroxide. Draw the displayed formulae of the two hydrolysis products below.

A **B** **[2]**

(ii) Which of the two hydrolysis product **A** & **B** is a liquid?

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(iii) When the other product is carefully neutralised with an aqueous mineral acid to pH 7, **C** is obtained.

Draw the structure of **C**.

[1]

(iv) Upon evaporation of all the solvent from the solution of **C**, a white solid is obtained.

Suggest a physical property of the solid.

……………………………………………………………………………… **[1]**

(b) State the reagents and conditions required for the conversion of benzene into phenylamine in two steps. In your answer, identify the structure of the intermediate.

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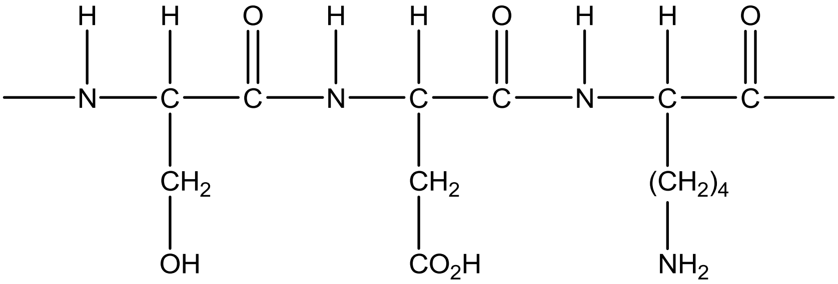
[3]

(c) The following structure shows part of a protein molecule.



(i) Using suitable diagrams, describe **two** interactions that the protein fragment above can exhibit in its tertiary structure

[3]

(ii) In solution, amino acids exist as zwitterions. Choose one of the amino acids that can be hydrolysed from the protein molecule above to illustrate what is meant by this term.

[1]

(iii) Amino acids act as buffers in solution. By means of equations, show how your chosen amino acid can act as a buffer when:

(I) dilute hydrochloric acid is added to its solution;

[1]

(II) dilute sodium hydroxide is added to its solution.

[1]

[Total: 14]

– End of Paper –

YEAR 6 PRELIMINARY EXAMINATION II

CANDIDATE NAME

CLASS 6

CENTRE NUMBER S

INDEX NUMBER

H2 CHEMISTRY 9647/02

Paper 2 Structured Questions

13 September 2016

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

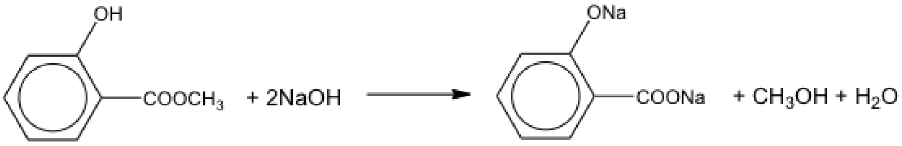
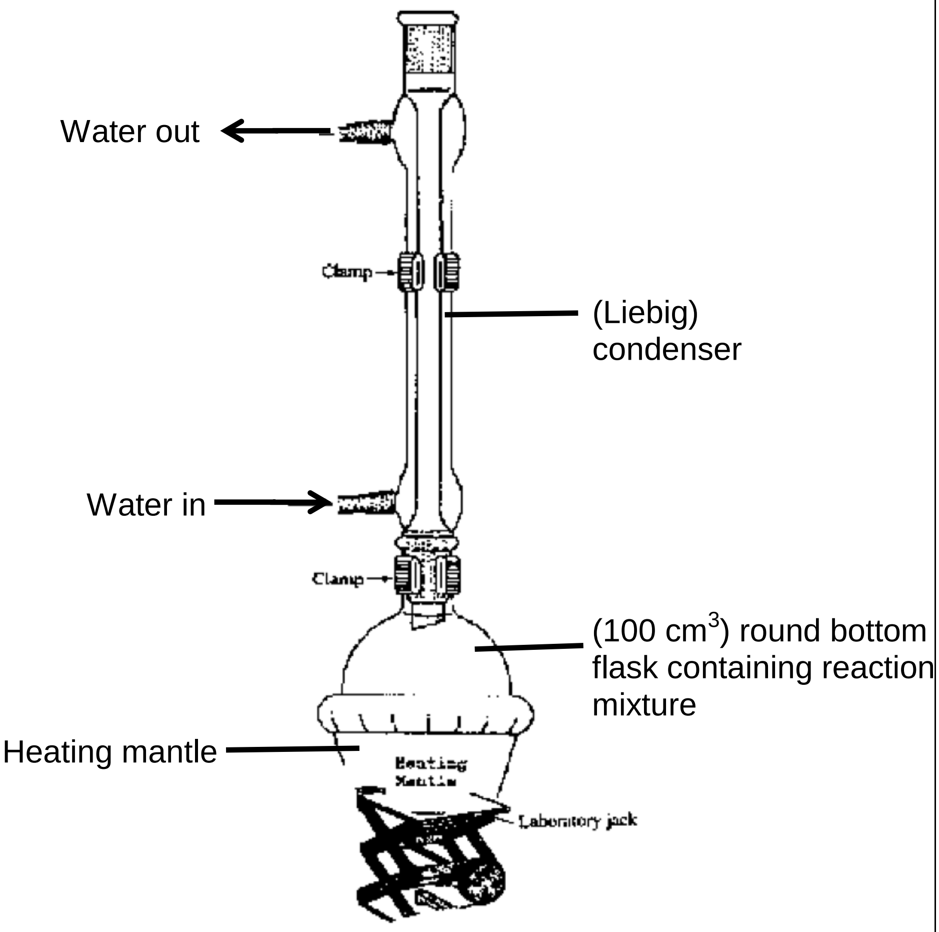
Write your name, class, centre number and index number on all the work you hand in.
Write in dark blue or black pen on both sides of paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions in the space provided.
A Data Booklet is provided. Do NOT write anything on it.

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

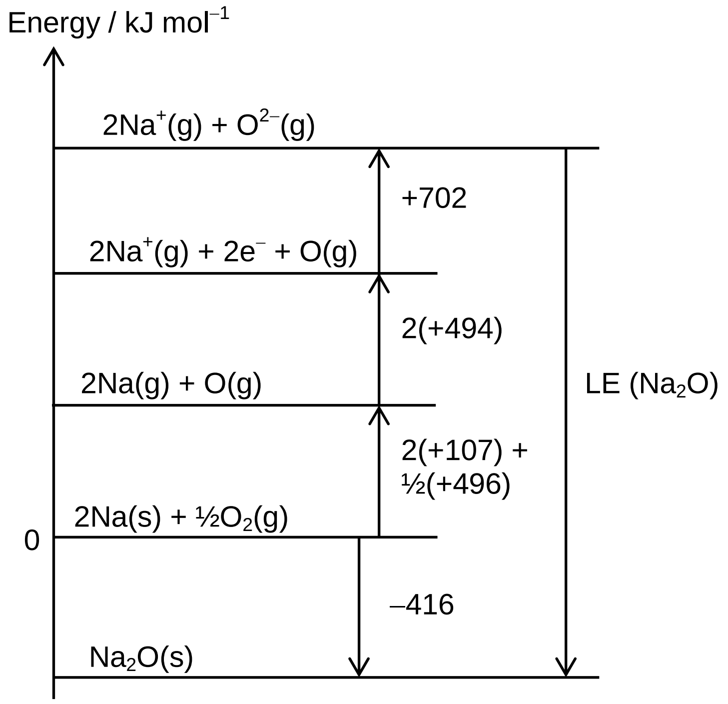
<table>
<tr><th colspan="9">For Examiner's Use</th></tr>
<tr><th colspan="9">Paper 2</th></tr>
<tr><th>Question Number</th><th>1</th><th>2</th><th>3</th><th>4</th><th>5</th><th>6</th><th></th><th>Total (Paper 2)</th></tr>
<tr><td>Marks</td><td>12</td><td>13</td><td>8</td><td>9</td><td>16</td><td>14</td><td></td><td>72</td></tr>
<tr><td colspan="2">Paper 1</td><td>40</td><td></td><td colspan="2">Paper 3</td><td>80</td><td>Total</td><td>192</td></tr>
</table>

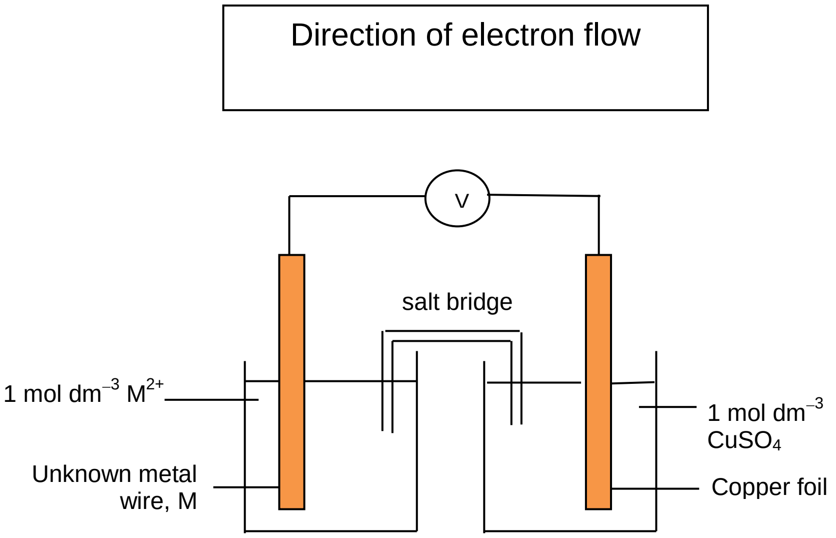
[Turn over

1	**(a)**	**(i)**		**[1]**
		(ii)	Amount of salicylic acid in 10 g = $\frac{10}{138}$ = 0.0725 mol Theoretical amount of salicylic acid = $\frac{0.0725}{60}$ × 100 = 0.121 mol Amount of methyl salicylate required = 0.121 mol Mass of methyl salicylate required = 0.121 × 152 = 18.4 g Volume of methyl salicylate required = $\frac{18.4}{1.174}$ = <u>15.7 cm^3</u> Amount of sodium hydroxide required = 0.121 × 2 = 0.242 mol Volume of sodium hydroxide required = $\frac{0.242}{6.0}$ ×1000 = <u>40.3 cm^3</u>	**[2]**
	(b)			

		1. Using a 25 cm^3 measuring cylinder, measure 16 cm^3 (accept up to 20 cm^3) of methyl salicylate and place it in a 100 cm^3 round bottom flask. 2. Using a 50 cm^3 measuring cylinder, measure 41 cm^3 (accept up to 50 cm^3) of aqueous sodium hydroxide and place it into the 100 cm^3 round bottom flask. Add some boiling chips to the mixture. 3. Set up the reflux set-up shown in the above diagram and heat the mixture for 30 minutes. 4. Allow the reaction mixture to cool down to room temperature and remove the boiling chips. 5. Place the round bottom flask in an ice bath. 6. Add concentrated hydrochloric acid to the reaction mixture slowly, with stirring. 7. Test the acidity of the mixture with a blue litmus paper. 8. Filter the mixture and wash the residue (crude salicylic acid) with a small amount of cold water. 9. Transfer the crude salicylic acid to a clean 100 cm^3 conical flask. Add a small volume of water and heat the mixture until all the crude product dissolves. 10. Filter the hot solution, using a fluted filter paper, into a pre-warmed clean and dry conical flask. Allow the solution to cool down slowly for crystals to form. 11. When the solution is cooled to room temperature, submerge the conical flask into an ice bath to allow more crystals to form. 12. Filter the mixture to obtain the pure salicylic acid crystals and pat dry the crystals using filter paper.	**[9]**
		[Total: 12]	

2	**(a)**		pV = nRT $(150 \times 10^3)(60 \times 10^{-3}) = n(8.31)(300 + 273)$ Amount of nitrogen gas = 1.89 mol Amount of sodium azide = $\frac{1.89}{3/2}$ = 1.26 mol Mass of sodium azide = 1.26 × 65.0 = 81.9 g	**[2]**
	(b)	**(i)**	$\Delta S = (51.3 + \frac{3}{2} \times 191.6) - 70.5 = +268.2\ \text{J mol}^{-1}\ \text{K}^{-1}$	**[1]**
		(ii)	ΔH is negative, ΔS is positive, $-T\Delta S$ is negative. Since $\Delta G = \Delta H - T\Delta S$, ΔG is always negative regardless of temperature.	**[1]**

		(iii)	The activation energy of the reaction is very high.	**[1]**
	(c)	**(i)**	Lattice energy of sodium oxide is the enthalpy change when one mole of solid sodium oxide is formed from its constituent gaseous ions Na^+ and O^{2-}.	**[1]**
		(ii)	 LE (Na_2O) = –416 – 2(+107) – ½(+496) – 2(+494) – (+702) = –2568 kJ mol^{-1}	
				[3]
		(iii)	2nd electron affinity = +702 – (–142) = +844 kJ mol^{-1} The positive sign of 2nd EA means that energy is required to overcome the repulsion between the anion and the electron to be added since both are negatively charged.	**[2]**
	(d)	Safe depressurisation rate = $\frac{(150-101)}{2-0.04}$ = 25 kPa s^{-1} Since the airbag being tested depressurises more slowly than the safe depressurisation rate, it is not safe for use.		**[2]**
		[Total: 13]		

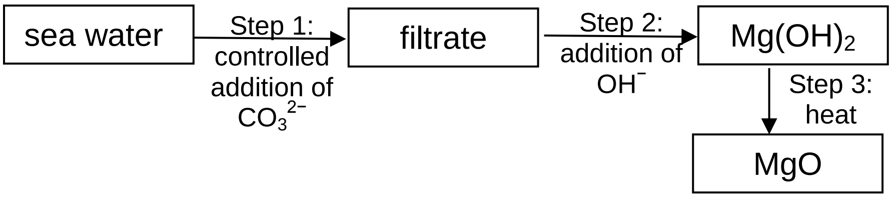
3	**(a)**	What do you understand by the term standard electrode potential?	
		Standard electrode potential, *E*$^{\ominus}$, of an electrode is the *relative* potential of this electrode under standard conditions compared with the standard hydrogen electrode whose electrode potential is assigned as 0 V. The standard hydrogen electrode consists of H_2(g) at 1 atm bubbling over platinum electrode coated with finely divided platinum which is dipped into 1 mol dm^{-3} H^+(aq) at 298 K.	**[2]**
	(b)	The following cell was set up between a copper electrode and an unknown metal electrode M^{2+}(aq)/M(s). The standard cell potential was found to be 0.76 V, and the copper foil was connected to the positive end of the voltmeter.  	
		(i) Use the Data Booklet to calculate the standard electrode potential of the M^{2+}(aq)/M(s) system.	
		Since copper is the positive electrode of the galvanic cell, it is the cathode. Standard electrode potential of the M^{2+}(aq)/M(s) $= 0.34 - 0.76 = -0.42$ V	**[1]**
		(ii) Draw an arrow in the box above to show the direction of electron flow through the voltmeter.	
		→	**[1]**
		(iii) Predict the outcomes of the following situations. Describe what you will see and write ionic equations, with state symbols, for any reactions that occur.	

		I	A rod of metal M is dipped into a solution of 1 mol dm^{-3} $CuSO_4$.	
			Metal M dissolves in (blue) solution and pink solid of Cu is formed. (Blue solution lightens in colour.) $M(s) + Cu^{2+}(aq) \longrightarrow Cu(s) + M^{2+}(aq)$	**[2]**
		II	Dilute sulfuric acid is added into a beaker containing a powdered sample of metal M.	
			Efferversence is observed; colourless odourless gas evolved that extinguishes a lighted splint with a pop sound. Metal M dissolves in (colourless) solution. $2H^{+}(aq) + M(s) \longrightarrow M^{2+}(aq) + H_2(g)$	**[2]**
			[Total: 8]	

4 The four most abundant salts in sea-water are as follows.

Salt	kg per m^3
Sodium chloride	27.5
Magnesium chloride	6.75
Magnesium sulfate	5.625
Calcium sulfate	1.80

Magnesium oxide is obtained from sea-water by the following steps.



The relevant numerical values of the solubility products are given below.

Salt	K_{sp}
Sodium carbonate	-
Calcium carbonate	5.0×10^{-9}
Magnesium carbonate	1.0×10^{-5}
Magnesium hydroxide	1.5×10^{-11}
Calcium hydroxide	7.9×10^{-6}

(a) Explain why the addition of carbonate ions in Step 1 is necessary and has to be controlled.

Both calcium carbonate and magnesium carbonate are sparingly soluble salts. Carbonate ions are added to precipitate out calcium carbonate first.

In Step 1, the addition of carbonate must be controlled such that little/no magnesium carbonate is precipitated/magnesium ions remain in the filtrate. **[2]**

(b) Suggest why the Ksp value of sodium carbonate is not provided.

Sodium carbonate is not a sparingly soluble salt/it is very soluble in water. **[1]**

(c) Using the reaction scheme above, Barny used 1 dm^3 of sea water to extract magnesium oxide.

(i) Calculate the concentration of Mg^{2+} in sea water.

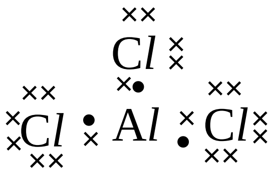
In 1 dm^3 of sea water,

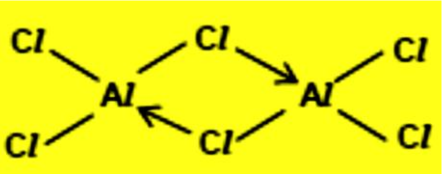
Amount of $MgCl_2 = \frac{6.75\times10^3}{10^3} \div (24.3 + 35.5 \times 2)$
$= 7.08 \times 10^{-2}$ mol

Amount of $MgSO_4 = \frac{5.625\times10^3}{10^3} \div (24.3 + 32.1 + 16.0 \times 4)$
$= 4.67 \times 10^{-2}$ mol

$[Mg^{2+}] = 0.118$ mol dm^{-3} **[2]**

		(ii)	Barny chose a pH of 9.5 to carry out the extraction of $Mg(OH)_2$. Calculate the maximum mass of **magnesium oxide** that can be obtained at pH 9.5. You may assume that negligible volumes of CO_3^{2-} and OH^- were used.	
			At pH 9.5, $[OH^-] = 10^{-4.5}$ mol dm^{-3} $K_{sp} = [Mg^{2+}][OH^-]^2$ Max $[Mg^{2+}]$ after addition of OH^-(aq) $= 1.5 \times 10^{-11} \div (10^{-4.5})^2$ $= 0.0150$ mol dm^{-3} Amount of Mg^{2+} precipitated = 0.118 – 0.0150 = 0.103 mol Maximum mass of MgO = 0.103 × (24.3 + 16.0) = **<u>4.13 g</u>** **(or 4.15 g)**	**[3]**
		(iii)	Suggest how Barny can modify his experiment to improve on the yield of MgO?	
			He can use a higher pH to lower the concentration of Mg^{2+}(aq) to increase his yield/He can lower the temperature to lower the K_{sp}/ He can add NaOH(aq) directly to sea water in a controlled manner.	**[1]**
			[Total: 9]	

5	**(a)**	In the periodic table, elements can exhibit either single or variable oxidation states. One example of an element which can exhibit variable oxidation state is manganese, Mn, while aluminium, A*l* is an example of an element which cannot exhibit variable oxidation state.		
		(i)	Draw a dot and cross diagram for aluminium chloride, $AlCl_3$.	
				**[1]**
		(ii)	In the vapour state, the M_r of aluminium chloride was found to be 267. However, when aluminium chloride is in the solid state, its M_r was found to be 133.5. With the aid of suitable diagram, explain this behaviour exhibited by aluminium chloride and the type of bonding involved.	

			Aluminium chloride molecules can form dimers (between themselves) where one aluminium chloride molecule forms dative covalent bonds with another Aluminium chloride molecule. Hence, the observed M_r of the dimer is 267 at vapour state.  Dative bond is formed. The <u>lone pair on the C*l* atom</u> of $\mathrm{A}l\mathrm{C}l_3$ is donated to the <u>empty orbital of the electron-deficient A*l*</u> in $\mathrm{A}l\mathrm{C}l_3$ to form a <u>dative (covalent) bond</u> so that A*l* can attain a stable octet configuration.	**[3]**
	(b)	Manganese is often found in minerals in combination with iron. Manganese is a metal with important industrial metal alloy uses, particularly in stainless steels. Manganese is found in various black minerals known as pyrolusite. Pyrolusite consists mainly of manganese(IV) oxide. Manganese(IV) oxide is the most common starting material for the production of compounds of manganese in other oxidation states. Manganese(IV) oxide undergoes a 2-step reaction to produce **Y** and **Z**. $\mathrm{MnO_2} \xrightarrow[\mathrm{I}]{\text{Oxidation in alkaline medium}} \mathrm{MnO_4^{2-}} \underset{\mathrm{II}}{\overset{\text{Hot water / alkaline medium}}{\rightleftharpoons}}$ Brown black solid **Y** in a purple solution containing **Z**		
		(i)	Define the term *transition element*.	
			A transition element is a d-block element which forms at least one stable simple ion in which there is a partially-filled d subshell.	**[1]**
		(ii)	Write the electronic configuration of Mn.	
			Mn : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$	**[1]**
		(iii)	Explain why manganese can exhibit variable oxidation state.	
			3d and 4s electrons are of similar energies, hence a variable number of 3d and 4s electrons can be involved in bonding (ionic or covalent).	**[1]**

(iv) The brown black solid **Y** contains 63.8% by mass of manganese and 36.2% by mass oxygen.

Determine the empirical formula of **Y**.

element	Mn	O
mass ratio	63.8	36.2
mole ratio	$\frac{63.8}{54.9} = 1.16$	$\frac{36.2}{16.0} = 2.26$
simplest ratio	$\frac{36.2}{16.0}$ $\frac{1.16}{1.16} = 1.00$	$\frac{2.26}{1.16} = 1.94$
	1	2

Empirical formula: MnO_2.

[1]

(v) Suggest the identity of **Z** and state the type of reaction that occurs at step **II**.

Hence, construct a balanced equation for the reaction.

Z is MnO_4^-

Step **II** is a **disproportionation/redox** reaction.

$3MnO_4^{2-} + 2H_2O \rightarrow 2MnO_4^- + MnO_2 + 4OH^-$

[3]

(vi) With reference to your answer in **(v)**, suggest how bubbling carbon dioxide gas into the hot solution of MnO_4^{2-} increases the yield of **Y** and **Z**.

CO_2 is acidic in nature. It can remove the OH^-.

Equilibrium position of $3MnO_4^{2-} + 2H_2O \rightleftharpoons 2MnO_4^- + MnO_2 + 4OH^-$ shifts to the right to replenish the OH^-, hence it helps in the disproportionation.

[2]

(c) Manganese(II) carbonate, $MnCO_3$, undergoes thermal decomposition in a similar way to a Group II carbonate.

$MnCO_3$ decomposes at 200 °C while $CaCO_3$ decomposes at 840 °C.

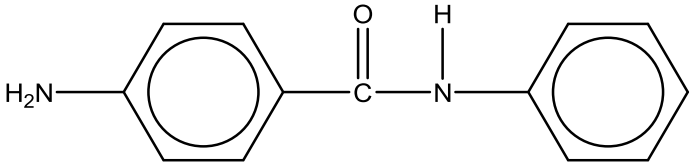
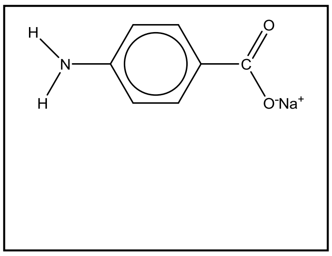
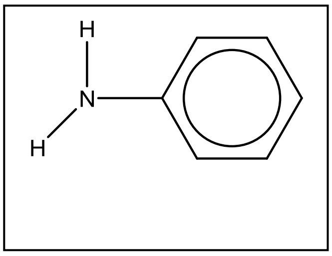
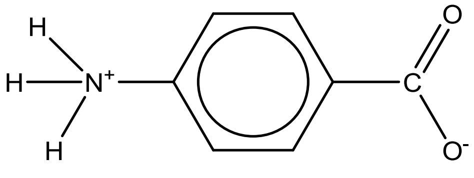
(i) Write an equation, with state symbols, for the thermal decomposition of $MnCO_3$.

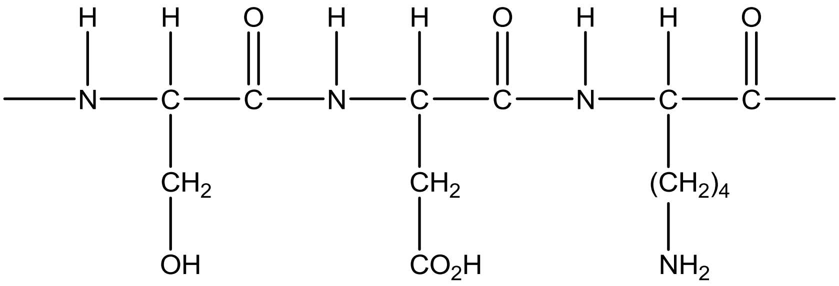
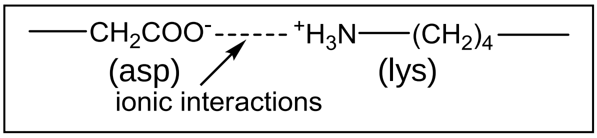
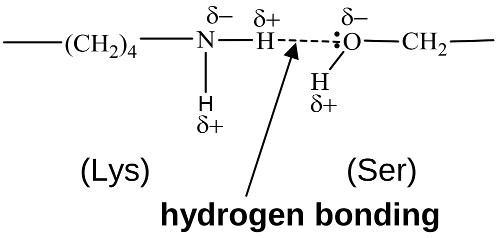
$MnCO_3(s) \rightarrow MnO(s) + CO_2(g)$

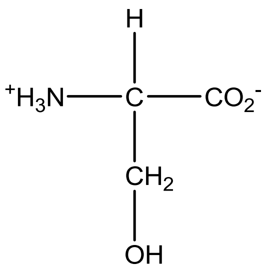
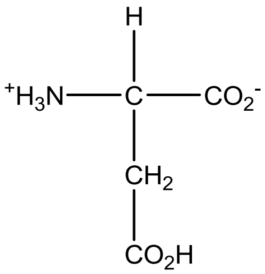
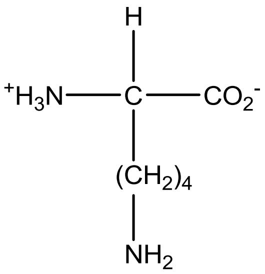
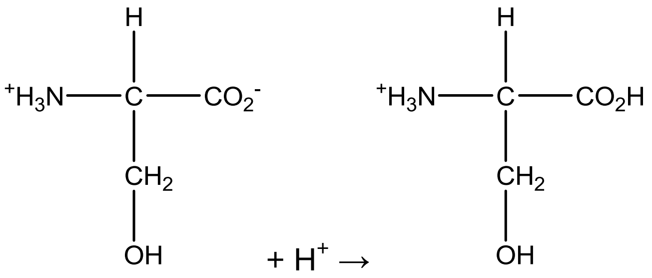
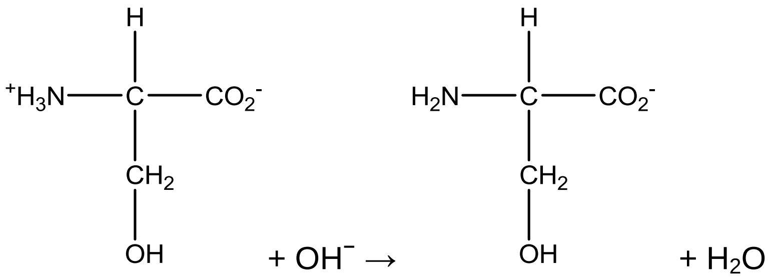
[1]

(ii) Explain why $MnCO_3$ decompose at a lower temperature than $CaCO_3$.

			The ionic radius of Mn^{2+} is smaller, hence Mn^{2+} has a higher charge density than Ca^{2+}. As a result, the ability of Mn^{2+} to polarise the large CO_3^{2-} anion is greater and the C–O bonds are weakened to a larger extent. Hence $MnCO_3$ decomposes at a lower temperature than $CaCO_3$.	**[2]**
			[Total: 16]	

6	**(a)**	4-Amino-N-phenylbenzamide, the structure of which is drawn below, is used in the treatment of epilepsy.  4-amino-N-phenylbenzamide		
		(i)	4-Amino-N-phenylbenzamide is hydrolysed by warm aqueous sodium hydroxide. Draw the displayed formulae of the two hydrolysis products below.	**[2]**
			  **A** **B**	
		(ii)	Which of the two hydrolysis product **A** & **B** is a liquid?	**[1]**
			B	
		(iii)	When the other product is carefully neutralised with an aqueous mineral acid to pH 7, **C** is obtained. Draw the structure of **C**.	**[1]**
				

		(iv)	Upon evaporation of all the solvent from the solution of **C**, a white solid is obtained. Suggest a physical property of the solid.	**[1]**
			High melting and boiling point / conduct electricity in molten or aqueous state	
	(b)	State the reagents and conditions required for the conversion of benzene into phenylamine in two steps. In your answer, identify the structure of the intermediate.		**[3]**
		Step 1: concentrated H_2SO_4, concentrated HNO_3, 55°C Step 2: Sn, Concentrated HC*l*, heat, followed by NaOH(aq) Intermediate: nitrobenzene		
	(c)	The following structure shows part of a protein molecule. 		
		(i)	Using suitable diagrams, describe **two** interactions that the protein fragment above can exhibit in its tertiary structure	**[3]**
			Hydrogen bonding between serine and aspartic acid/serine and lysine (reject aspartic acid and lysine) Ionic interactions between aspartic acid and lysine  **E.g. of hydrogen bonding** 	

		(ii)	In solution, amino acids exist as zwitterions. Choose one of the amino acids that can be hydrolysed from the protein molecule above to illustrate what is meant by this term.	**[1]**
			 $^{+}H_3NCH(CH_2OH)CO_2^{-}$ OR  $^{+}H_3NCH(CH_2CO_2H)CO_2^{-}$ OR  $^{+}H_3NCH((CH_2)_4NH_2)CO_2^{-}$ **[1]**	
		(iii)	Amino acids act as buffers in solution. By means of equations, show how your chosen amino acid can act as a buffer when (I) dilute hydrochloric acid (II) dilute sodium hydroxide is added to its solution.	**[2]**
			I  $^{+}H_3NCH(CH_2OH)CO_2^{-} + H^{+} \rightarrow {}^{+}H_3NCH(CH_2OH)CO_2H$ II  $^{+}H_3NCH(CH_2OH)CO_2^{-} + OH^{-} \rightarrow H_2NCH(CH_2OH)CO_2^{-} + H_2O$	
			[Total: 14]	

YEAR 6 PRELIMINARY EXAMINATION II

CANDIDATE NAME	
CLASS	6
CENTRE NUMBER	S
INDEX NUMBER	

H2 CHEMISTRY 9647/03

Paper 3 Free Response

21 September 2016
2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Cover Page
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class, centre number and index number on all the work you hand in.
Write in dark blue or black pen on both sides of paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** questions.
Begin each question on a fresh sheet of paper.
A Data Booklet is provided. Do not write anything on it.
You are reminded of the need for good English and clear presentation in your answers.

The number of marks is given in brackets [ ] at the end of each question or part question.
At the end of the examination, fasten all your work securely together, with the cover page on top.

This document consists of **10** printed pages and **2** blank pages.

[Turn over

Answer any **four** questions.

1 Many compounds of chlorine are manufactured from brine, NaC*l*(aq). The electrolysis of brine produces Cl_2(g) and NaOH(aq). In some industrial electrolytic cells, these two substances are allowed to react further. The products formed in this second reaction dependp on the operating conditions used.

(a) Write balanced equations for the reaction between Cl_2(g) and

(i) cold aqueous NaOH; **[1]**

(ii) hot aqueous NaOH. **[1]**

(b) Chlorine dioxide, ClO_2, is used in the treatment of water. It is formed from ClO_3^- ions in an acidic solution.

$$ClO_3^- + 2H^+ + e^- \rightleftharpoons ClO_2 + H_2O$$

(i) Draw the dot-and-cross diagrams of ClO_2 and H_2O_2.

You may assume that there is no dative bond in either compound. **[2]**

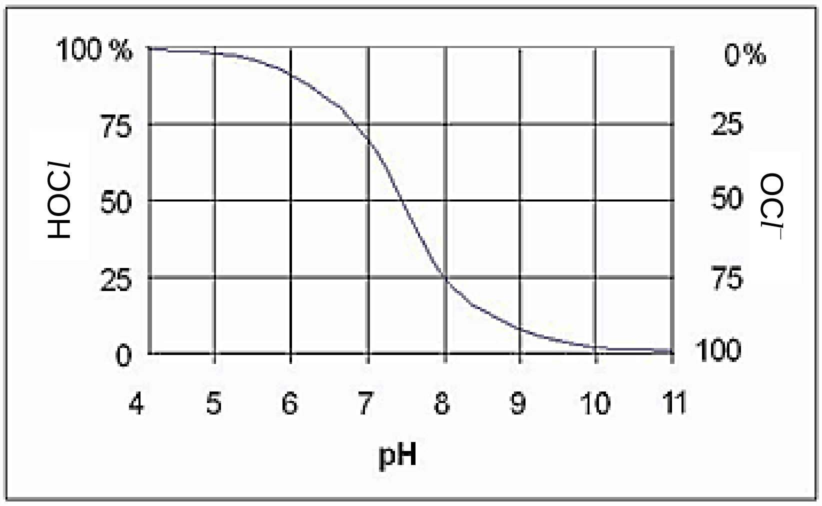
(ii) Construct the overall equation for the reaction of ClO_3^- ions with H_2O_2 in acidic solution. **[1]**

(iii) What is the role of H_2O_2 in the reaction? **[1]**

(c) Chlorine can also be used to disinfect water. When chlorine is added to water, it produces hypochlorous acid, HOC*l*. Hypochlorous acid is a weak acid that dissociates into hypochlorite ions, OCl^-, according to the following equation.

$$HOCl(aq) \rightleftharpoons H^+(aq) + OCl^-(aq)$$

Free chlorine refers to the total chlorine content in HOC*l* and OCl^-. The dissociation curve below illustrates the ratio of hypochlorous acid to hypochlorite at different pH values.



[Source: www.hach.com]

(i) Determine the pK_a of hypochlorous acid. **[1]**

(ii) Hence, calculate the pH of a 0.0025 mol dm^{-3} hypochlorous acid solution. **[2]**

To determine whether the free chlorine in a sample of tap water meets the regulatory limit (4 mg C*l* per litre), OCl^- is quantitatively reduced to Cl^- by I^- ions, which is in turn oxidised to I_2. The I_2 is titrated with standard sodium thiosulfate. The following reaction takes place during the titration.

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

(iii) Construct a balanced equation between OCl^-(aq) and acidified KI(aq). **[1]**

(iv) When 2 dm^3 of tap water was tested, 6.0 cm^3 of 0.00455 mol dm^{-3} sodium thiosulfate was required to discharge the colour of iodine. Calculate the concentration of OCl^- in the sample of water. **[2]**

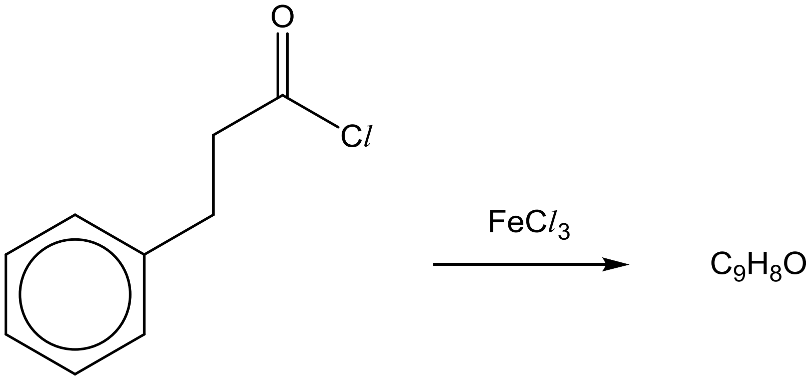
(v) Suggest why the calculated concentration of OCl^- has the same value as the concentration of *free* chlorine. **[2]**

(vi) Determine if the sample of tap water is safe for consumption. **[2]**

(d) Chlorine is also used in organic chemistry to produce the Lewis acid catalyst, $FeCl_3$, for the reaction between methylbenzene and chlorine.

(i) Describe the mechanism of the above reaction. **[3]**

(ii) $FeCl_3$ reacts in a similar way with acyl chlorides. Predict the structure of the product of the following reaction.



[1]

[Total: 20]

2 **(a)** Nitrous oxide or dinitrogen oxide, N_2O, is commonly known as "laughing gas" due to the euphoric effects of inhaling it. It is used in surgery and dentistry for its anesthetic and analgesic effects. To produce N_2O, ammonium nitrate is decomposed at 170 °C. Water is a by-product of this reaction.

(i) Write an equation for the production of dinitrogen oxide from ammonium nitrate. **[1]**

(ii) In the manufacturing of N_2O gas, 1 kg of N_2O gas is produced for every 2.1 kg of ammonium nitrate used. Determine the percentage yield of dinitrogen oxide. **[2]**

(b) At 1200 K, in the presence of gold wire, dinitrogen oxide decomposes as shown:

$$2N_2O(g) \longrightarrow 2N_2(g) + O_2(g).$$

To follow the rate of reaction, the change in concentration of a sample of N_2O is measure against time. The results are shown below:

Time, t / s	**Concentration of N_2O / × 10^{-3} mol dm^{-3}**
0	2.50
1000	2.01
2000	1.62
3000	1.31
4000	1.05
5000	0.85
6000	0.68
7000	0.55

(i) What do you understand by the term *half-life* of N_2O? **[1]**

(ii) Plot the above data on a graph paper.

Use the following scale:

- 2 cm to represent 1000 s on the x-axis; and
- 2 cm to represent to represent 0.25 × 10^{-3} mol dm^{-3} on the y-axis. **[2]**

(iii) From your graph, deduce the order of the reaction with respect to N_2O. **[2]**

(iv) Calculate the rate constant for the reaction and state its units. **[2]**

(v) The gold wire acts as a *heterogeneous catalyst* in this reaction.

Explain the terms *in italics* and outline the mode of action of the catalyst. **[3]**

(c) Alkenes react with carbenes R_2C**:** to yield cyclopropanes.

One way to generate a substituted carbene is by reacting chloroform, $CHCl_3$, with a strong base.

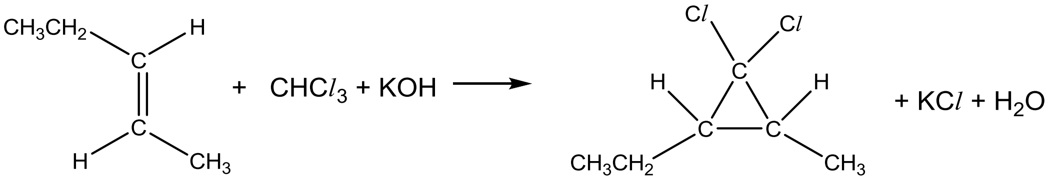
The mechanism to generate a carbene is described below.

1. Potassium hydroxide, KOH, removes the proton from $CHCl_3$, leaving behind the electron pair. An anionic intermediate is formed.
2. Cl^- is lost and a neutral dichlorocarbene is formed.

(i) Based on the description above, draw a mechanism to show the generation of dichlorocarbene.

Show relevant lone pairs and use curly arrows to indicate the movement of electron pairs. **[3]**

An example of a reaction between an alkene and a carbene is as shown:



(ii) Suggest the structure of the product formed when cyclohexene reacts with chloroform in the presence of KOH. **[1]**

(iii) Suggest the role of carbene in its reaction with an alkene. Explain your answer. **[2]**

(iv) Suggest the type of reaction when carbene reacts with an alkene. **[1]**

[Total: 20]

3 Copper is a rare element, constituting only 6.8×10^{-3} percent of the Earth's crust by mass. However, it has a wide range of uses such as in alloys, plumbing and in electrical cables. The common oxidation states of copper are +2 and +1.

(a) Copper can be obtained by roasting a copper ore, $CuFeS_2$, to give Cu_2S, which is further oxidised to form metallic copper. This impure copper can be purified by electrolysis.

(i) Draw a diagram to illustrate the electrolytic cell used in the purification of copper, using $CuSO_4$(aq) as the electrolyte. **[2]**

(ii) If a current of 0.8 A was passed through the cell, calculate the time required for 0.25 g of pure copper to be collected. **[2]**

(b) Anhydrous copper(II) sulfate, $CuSO_4$(s), is a white powder. It dissolves in water to form a pale blue solution.

(i) State the species responsible for the pale blue colour of the solution. **[1]**

(ii) Explain why the solution is pale blue in colour. **[3]**

(iii) Describe the colour changes observed when the following solutions are added to the pale blue solution, giving the formulae of all relevant species.

I. Dilute NH_3(aq), until in excess;

II. KI(aq). **[4]**

(c) When Na_2CO_3 is added to a solution of $CuSO_4$ and the resultant mixture is filtered, a green solid, cupric carbonate, is obtained. The formula of this solid is $Cu_2(OH)_{\boldsymbol{a}}(CO_3)_{\boldsymbol{b}}$.

0.10 mol of $Cu_2(OH)_{\boldsymbol{a}}(CO_3)_{\boldsymbol{b}}$ required 0.40 mol of hydrochloric acid for complete reaction. The products of this reaction include copper(II) chloride, carbon dioxide and water.

(i) Given that 2.4 dm^3 of CO_2 was formed at room temperature and pressure, determine the values of ***a*** and ***b***. **[2]**

(ii) Hence, write an equation for the reaction of cupric carbonate with hydrochloric acid. **[1]**

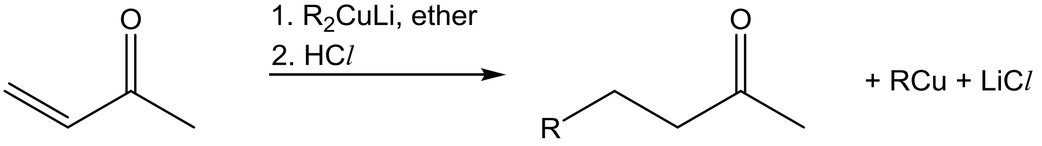
(d) Cu_2O, a brick red solid, is a compound where copper is in the oxidation state of +1. It can be formed by reacting an alkaline solution of complexed Cu^{2+} with a particular organic functional group.

(i) State the functional group that will produce Cu_2O with the alkaline solution of complexed Cu^{2+}. **[1]**

(ii) Name the type of reaction undergone by the functional group in **(i)**. **[1]**

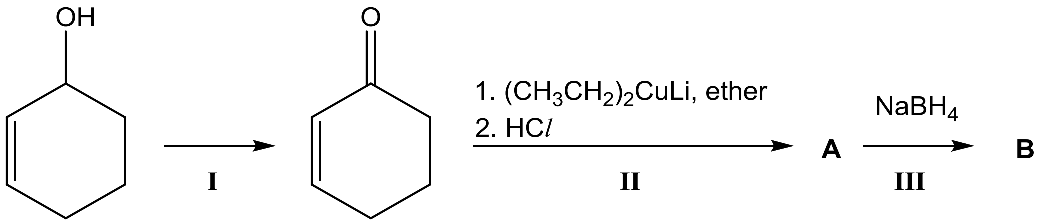
(e) Organocopper compounds are useful reagents in organic synthesis. One such class of compounds is the Gilman reagents, with the general formula R_2CuLi, where R represents an alkyl group.

Gilman reagents are effective nucleophiles used in conjugate addition reactions. Conjugate addition involves the addition of a nucleophile across a C=C bond instead of across a C=O bond. This is illustrated in the example below:



The Gilman reagent can be seen as providing the "R^-" nucleophile while a mineral acid (e.g. HC*l*) provides the proton that is added to one of the carbon atoms in the C=C bond.

The following synthesis involves a Gilman reagent for one of the steps:



Suggest the reagent and conditions for Step **I** and the structures of compounds **A** and **B**. **[3]**

[Total: 20]

4 **(a)** Copper(I) chloride is used as a precursor of a fungicide and a catalyst for a variety of organic reactions. It is sparingly soluble in water.

(i) Define the standard enthalpy change of hydration of an ion. **[1]**

(ii) Using the data given in the following table, draw an appropriate energy cycle and calculate the standard enthalpy change of solution for copper(I) chloride.

$\Delta H^\ominus_{hyd}(Cu^+)$	–593 kJ mol^{-1}
$\Delta H^\ominus_{hyd}(Cl^-)$	–378 kJ mol^{-1}
Lattice Energy of CuCl	–979 kJ mol^{-1}

[3]

(b) **(i)** Explain what is meant by the term *entropy* of a chemical system. **[1]**

Describe and explain how the entropy of the following systems will change during the stated process. Assume the pressure of each system remains at 1 atm throughout.

(ii) 1 mol of Cl_2(g) at 298 K is heated to 500 K. **[1]**

(iii) 1 mol of Cl_2(g) at 298 K is reacted with copper according to the following equation.

$$Cu(s) + Cl_2(g) \rightarrow CuCl_2(s)$$ **[1]**

(c) Copper(II) ions are pollutants found in water. One method of purification is via precipitation of $Cu(OH)_2$ and CuS.

	K_{sp} (298 K)
CuS	6.3 × 10$^{–36}$
$Cu(OH)_2$	2.0 × 10$^{–19}$

Using the above data, calculate:

(i) the minimum concentration of Cu^{2+} for a precipitate of CuS to form in 10 ppm $S^{2–}$ solution;

(1 ppm = 1 mg dm$^{–3}$) **[2]**

(ii) the maximum pH of a solution containing 0.100 mol dm$^{–3}$ Cu^{2+} ions. **[3]**

(d) Many organic compounds also contain chlorine. An example would be 1,2-dichlorocyclohexane, which exhibits both geometrical and optical isomerism.

(i) Explain why 1,2-dichlorocyclohexane can exhibit geometrical isomerism. **[1]**

(ii) The effect of plane polarised light on 1,2-dichlorocyclohexane was investigated. Three different types of 1,2-dichlorocyclohexane was identified:

- Molecule **X** rotated plane polarised light to the left
- Molecule **Y** rotated plane polarised light to the right
- Molecule **Z** had no effect on plane polarised light

Suggest an explanation for these observations. **[3]**

(e) Compounds **C** and **D** both have the molecular formula C_7H_7Cl. In an experiment, both compounds are separately heated under reflux for some time with aqueous sodium hydroxide. The resulting solutions are cooled and acidified with dilute nitric acid. When aqueous silver nitrate is added subsequently, a white precipitate is formed with **C** while no precipitate is formed with **D**.

Suggest the structures of **C** and **D**. Explain your reasoning for **each** compound. **[4]**

[Total: 20]

5 **(a)** The electrical conductivities of some Period 3 elements are shown below.

Element	Na	Mg	A*l*	P	S	C*l*

Electrical conductivity at 298 K / × 10^7 S m^{-1}	2.1	2.3	3.5	Non-conductors

(i) With reference to the data above, describe and explain the difference in electrical conductivities of the elements above. **[3]**

(ii) Silicon carbide (SiC), also known as carborundum and moissanite, is used in abrasive and cutting tools.

Suggest the structure and bonding of SiC. **[2]**

(b) Chlorides of Period 3 elements dissolve in water to give solutions of varying pH.

Explain the following pH values and write the chemical equations for any reactions that occur:

(i) $AlCl_3$ dissolves readily in water to form an acidic solution (pH = 3). **[3]**

(ii) $SiCl_4$(l) dissolves in water to form a strongly acidic solution (pH = 2). **[2]**

(c) Caffeic acid is an organic compound found in all plants as it is a key intermediate in the biosynthesis of lignin, one of the principal components of plant biomass.

Caffeic acid has the molecular formula $C_9H_8O_4$. Caffeic acid reacts with Br_2(l) to give $C_9H_8O_4Br_2$. When treated with hot $KMnO_4$ and H_2SO_4, caffeic acid reacts to give **F**, $C_7H_6O_4$, and a colourless gas that produces a white solid with $Ca(OH)_2$(aq). **F** reacts with PCl_5 to give **G**, $C_7H_5O_3Cl$, with the production of steamy white fumes. **G** reacts with water to form an acidic solution. When added to neutral $FeCl_3$(aq), **G** also forms a violet colouration. **G** reacts with Br_2(aq) to give **H**, $C_7H_3O_4Br_3$.

Use the information above to deduce the structures of caffeic acid and compounds **F** to **H**, explaining all the reactions involved. **[10]**

[Total: 20]

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YEAR 6 PRELIMINARY EXAMINATION II

CANDIDATE NAME	
CLASS	6
CENTRE NUMBER	S
INDEX NUMBER	

H2 CHEMISTRY 9647/03

Paper 3 Free Response

21 September 2016

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Cover Page
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class, centre number and index number on all the work you hand in.
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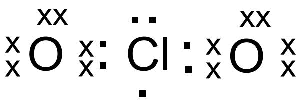
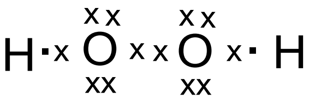
Begin each question on a fresh sheet of paper.
A Data Booklet is provided. Do not write anything on it.
You are reminded of the need for good English and clear presentation in your answers.

The number of marks is given in brackets [ ] at the end of each question or part question.
At the end of the examination, fasten all your work securely together, with the cover page on top.

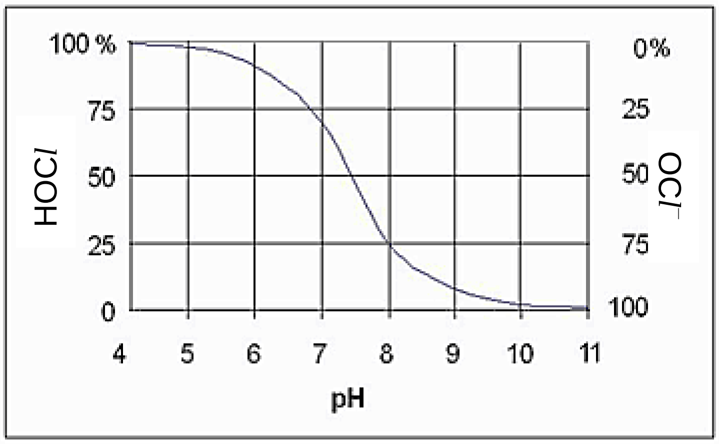
[Turn over

	Answer any **four** questions.			
1	Many compounds of chlorine are manufactured from brine, $NaCl(aq)$. The electrolysis of brine produces $Cl_2(g)$ and $NaOH(aq)$. In some industrial electrolytic cells, these two substances are allowed to react further. The products formed in this second reaction depends on the operating conditions used.			
	(a)	Write balanced equations for the reaction between $Cl_2(g)$ and		
		(i)	cold aqueous NaOH;	**[1]**
			$Cl_2 + 2NaOH \rightarrow NaCl + NaClO + H_2O$	
		(ii)	hot aqueous NaOH.	**[1]**
			$3Cl_2 + 6NaOH \rightarrow 5NaCl + NaClO_3 + 3H_2O$	
	(b)	Chlorine dioxide, ClO_2, is used in the treatment of water. It is formed from ClO_3^- ions in an acidic solution. $ClO_3^- + 2H^+ + e^- \rightleftharpoons ClO_2 + H_2O$		
		(i)	Draw the dot-and-cross diagrams of ClO_2 and H_2O_2. *You may assume that there is no dative bond in either compound.*	**[2]**
			 	
		(ii)	Construct the overall equation for the reaction of ClO_3^- ions with H_2O_2 in acidic solution.	**[1]**
			$2ClO_3^- + 2H^+ + H_2O_2 \rightarrow 2ClO_2 + 2H_2O + O_2$	
		(iii)	What is the role of H_2O_2 in the reaction?	**[1]**
			Reducing agent	

(c) Chlorine can also be used to disinfect water. When chlorine is added to water, it produces hypochlorous acid, $\mathrm{HOC}l$. Hypochlorous acid is a weak acid that dissociates into hypochlorite ions, $\mathrm{OC}l^-$, according to the following equation.

$$\mathrm{HOC}l(aq) \rightleftharpoons H^+(aq) + \mathrm{OC}l^-(aq)$$

Free chlorine refers to the total chlorine content in $\mathrm{HOC}l$ and $\mathrm{OC}l^-$. The dissociation curve below illustrates the ratio of hypochlorous acid to hypochlorite at different pH values.



[Source: www.hach.com]

(i) Determine the pK_a of hypochlorous acid **[1]**

pH = pK_a when [HA] = [A^-]. From the graph, pH = 7.5 when [$\mathrm{OC}l^-$] = [$\mathrm{HOC}l$]. Therefore, pK_a is 7.4 – 7.6.

(ii) Hence, calculate the pH of a 0.0025 mol dm^{-3} hypochlorous acid solution. **[2]**

pK_a = 7.5, $K_a = 10^{-7.5} = 3.16 \times 10^{-8}$ mol dm^{-3}

$[H^+] = (3.16 \times 10^{-8} \times 0.0025)^{1/2} = 8.89 \times 10^{-6}$ mol dm^{-3}

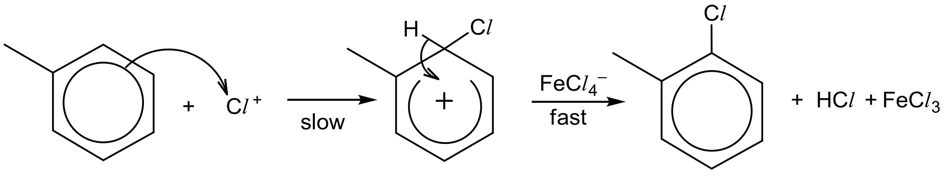
pH = − lg (8.89×10^{-6}) = **5.05**

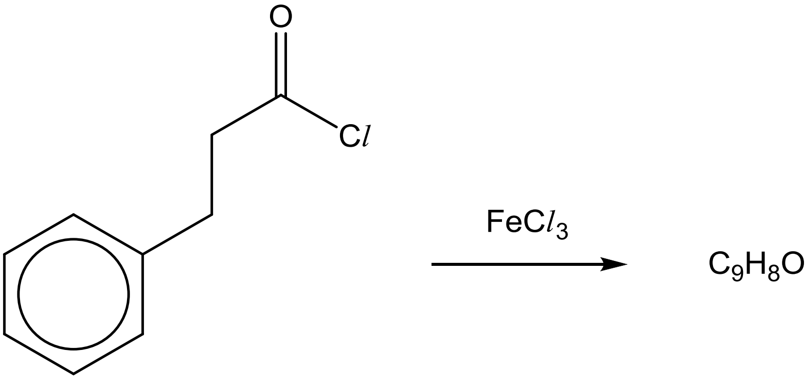
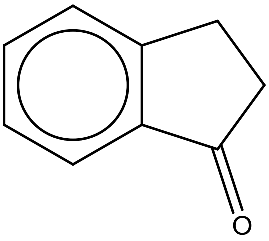
To determine whether the free chlorine in a sample of tap water meets the regulatory limit (4 mg C*l* per litre), $\mathrm{OC}l^-$ is quantitatively reduced to $\mathrm{C}l^-$ by I^- ions, which is in turn oxidised to I_2. The I_2 is titrated with standard sodium thiosulfate. The following reaction takes place during the titration.

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

(iii) Construct a balanced equation between $\mathrm{OC}l^-$(aq) and acidified KI(aq) **[1]**

$2H^+(aq) + 2I^-(aq) + \mathrm{OC}l^-(aq) \rightarrow \mathrm{C}l^-(aq) + I_2(aq) + H_2O(l)$

		(iv)	When 2 dm^3 of tap water was tested, 6.0 cm^3 of 0.00455 mol dm^{-3} sodium thiosulfate was required to discharge the colour of iodine. Calculate the concentration of OCl^{-} in the sample of water.	**[2]**
			Amount of $S_2O_3^{2-}$ = 2.73×10^{-5} mol Amount of iodine produced = 1.37×10^{-5} mol Amount of OCl^{-} present = 1.37×10^{-5} mol Concentration = 6.83×10^{-4} mol dm^{-6}	
		(v)	Suggest why the calculated concentration of OCl^{-} has the same value as the concentration of *free* chlorine.	**[2]**
			In the equilibrium, $HOCl(aq) \rightleftharpoons H^+(aq) + OCl^-(aq)$, as OCl^- is reduced by I^-, $[OCl^-]$ decreases and the equilibrium position shifts right to favour the formation of more OCl^- until all the $HOCl$ completely dissociates.	
		(vi)	Determine if the sample of tap water is safe for consumption.	**[2]**
			Mass concentration of free chlorine = $6.83 \times 10^{-6} \times 35.5 = 0.242$ mg per litre. The tap water is safe for consumption.	
	(d)	Chlorine is also used in organic chemistry to produce the Lewis acid catalyst, $FeCl_3$, for the reaction between methylbenzene and chlorine.		
		(i)	Describe the mechanism of the above reaction.	**[3]**
			$FeCl_3 + Cl_2 \rightarrow FeCl_4^{-} + Cl^{+}$  	
		(ii)	$FeCl_3$ reacts in a similar way with acyl chlorides. Predict the structure of the product of the following reaction.	**[1]**

				
				
			[Total: 20]	

2 **(a)** Nitrous oxide or dinitrogen oxide, N_2O, is commonly known as "laughing gas" due to the euphoric effects of inhaling it. It is used in surgery and dentistry for its anesthetic and analgesic effects. To produce N_2O, ammonium nitrate is decomposed at 170 °C. Water is a by-product of this reaction.

(i) Write an equation for the production of dinitrogen oxide from ammonium nitrate. **[1]**

$NH_4NO_3\ (s) \rightarrow 2\ H_2O\ (g) + N_2O\ (g)$

(ii) In the manufacturing of N_2O gas, 1 kg of N_2O gas is produced for every 2.1 kg of ammonium nitrate used. Determine the percentage yield of dinitrogen oxide. **[2]**

Amount of NH_4NO_3 used = $\frac{2.1\times1000}{14\times2+4+16\times3}$ = 26.3 mol

Theoretical amt of N_2O produced = 26.3 mol

Theoretical mass of N_2O produced = 26.3 × (14 × 2+ 16) = 1157g

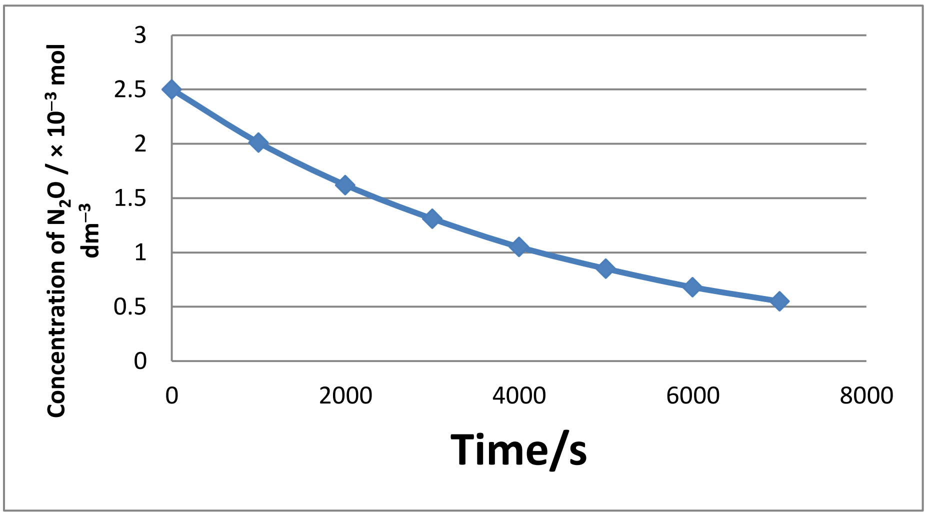
% yield = $\frac{1000}{1157}$ × 100% = 86.4%

(b) At 1200 K, in the presence of gold wire, dinitrogen oxide decomposes as shown:

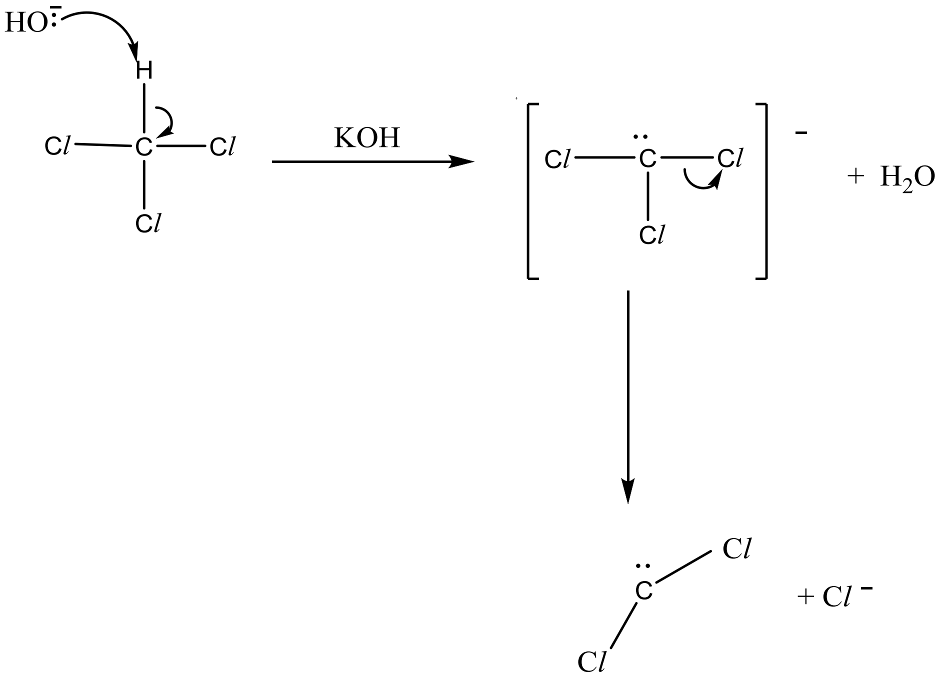
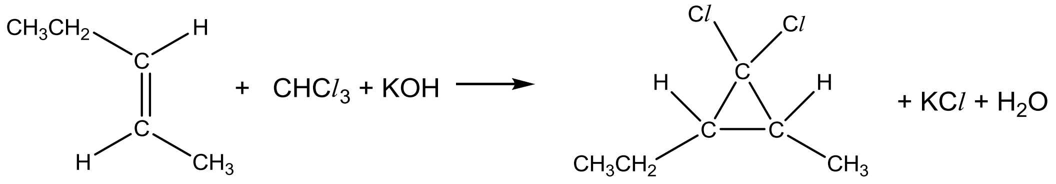
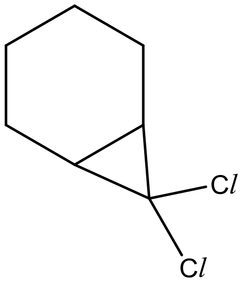
$$2N_2O(g) \longrightarrow 2N_2(g) + O_2(g).$$

To follow the rate of reaction, the change in concentration of a sample of N_2O is measure against time. The results are shown below:

Time, t / s	**Concentration of N_2O / × 10^{-3} mol dm^{-3}**
0	2.50
1000	2.01
2000	1.62
3000	1.31
4000	1.05
5000	0.85
6000	0.68
7000	0.55

		(i)	What do you understand by the term *half-life* of N_2O?	**[1]**
			Half-life is time taken for the concentration of N_2O to be halved.	
		(ii)	Plot the above data on a graph paper. Use the following scale: • 2 cm to represent 1000 s on the x-axis; and • 2 cm to represent to represent 0.25×10^{-3} mol dm^{-3} on the y-axis.	**[2]**
				
		(iii)	From your graph, deduce the order of the reaction with respect to N_2O.	**[2]**
			When concentration decreases from 2.5×10^{-3} to 1.25×10^{-3}, time taken is 3300 s. When concentration decreases from 1.25×10^{-3} to 0.7×10^{-3}, time taken is 3100 s. (to be shown on the graph) Since half-life is approximately constant, the <u>order of reaction with respect to N_2O is 1</u>. Show on graph that half time constant	
		(iv)	Calculate the rate constant for the reaction and state its units.	**[2]**
			Rate constant = $\frac{\ln 2}{t_{1/2}}$ = 2.17×10^{-4} s^{-1} Correct answer Correct units	
		(v)	The gold wire acts as a *heterogeneous catalyst* in this reaction.	**[3]**

			Explain the terms *in italics* and outline the mode of action of the catalyst.	
			A catalyst is a substance that provides an alternative pathway with lower activation energy, remaining chemically unchanged at the end of reaction. A heterogeneous catalyst is one that is in a different phases as the reactants. Adsorption The gold wire provides active sites whereby N_2O molecules may be adsorbed. The adsorption weakens N–O bonds so that the N_2O molecules are more reactive. Reaction The N_2O molecules on the gold surface are in close proximit and the correct orientation so that they can readily react together. Desorption The products, N_2 and O_2, formed diffuse away from the surface of the catalyst and the active sites become available again.	
	(c)	Alkenes react with carbenes R_2C**:** to yield cyclopropanes. One way to generate a substituted carbene is by reacting chloroform, $CHCl_3$, with a strong base. The mechanism to generate a carbene is described below. 1. Potassium hydroxide, KOH, removes the proton from $CHCl_3$, leaving behind the electron pair. An anionic intermediate is formed. 2. Cl^- is lost and a neutral dichlorocarbene is formed.		
		(i)	Based on the description above, draw a mechanism to show the generation of dichlorocarbene. Show relevant lone pairs and use curly arrows to indicate the movement of electron pairs.	**[3]**

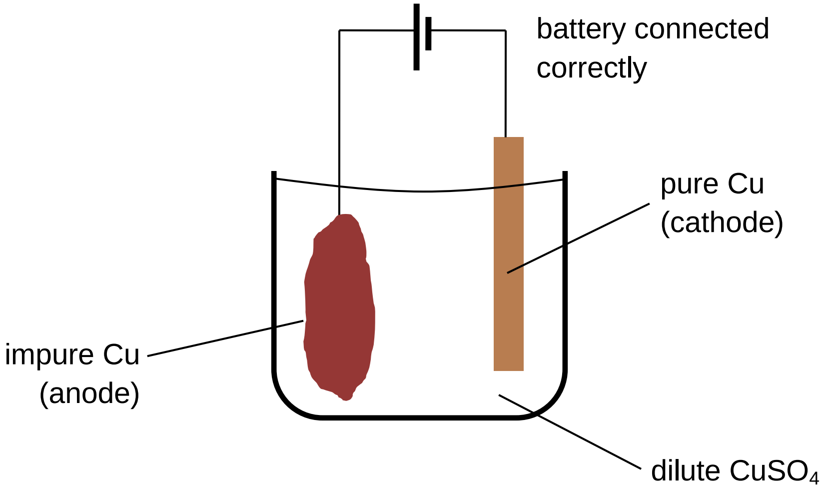
				
		An example of a reaction between an alkene and a carbene is as shown: 		
		(ii)	Suggest the structure of the product formed when cyclohexene reacts with chloroform in the presence of KOH.	**[1]**
				
		(iii)	Suggest the role of carbene in its reaction with an alkene. Explain your answer.	**[2]**
			Carbene acts as an electrophile. Carbon in carbene is electron deficient as it is bonded to two electronegative chlorine atoms/it has only 6 valence electrons, hence it acts as an electrophile.	
		(iv)	Suggest the type of reaction when carbene reacts with an alkene.	**[1]**

			Addition	
			[Total: 20]	

3 Copper is a rare element, constituting only 6.8×10^{-3} percent of the Earth's crust by mass. However, it has a wide range of uses such as in alloys, plumbing and in electrical cables. The common oxidation states of copper are +2 and +1.

(a) Copper can be obtained by roasting a copper ore, $CuFeS_2$, to give Cu_2S, which is further oxidised to form metallic copper. This impure copper can be purified by electrolysis.

(i) Draw a diagram to illustrate the electrolytic cell used in the purification of copper, using $CuSO_4$(aq) as the electrolyte. **[2]**



(ii) If a current of 0.8 A was passed through the cell, calculate the time required for 0.25 g of pure copper to be collected. **[2]**

Amt of Cu = 0.25 / 63.5 = 3.94×10^{-3} mol

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Amt of e^- required = $2(3.94 \times 10^{-3}) = 7.88 \times 10^{-3}$ mol

Quantity of charge required = nF = $7.88 \times 10^{-3} \times 96500 = 760$ C

Time required = Q / I = 760 / 0.8 = <u>**950 s**</u> (or 15.8 min)

(b) Anhydrous copper(II) sulfate, $CuSO_4$(s), is a white powder. It dissolves in water to form a pale blue solution.

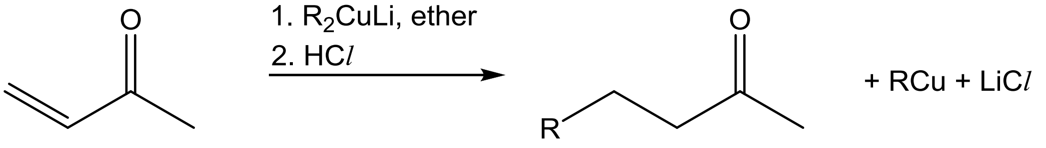
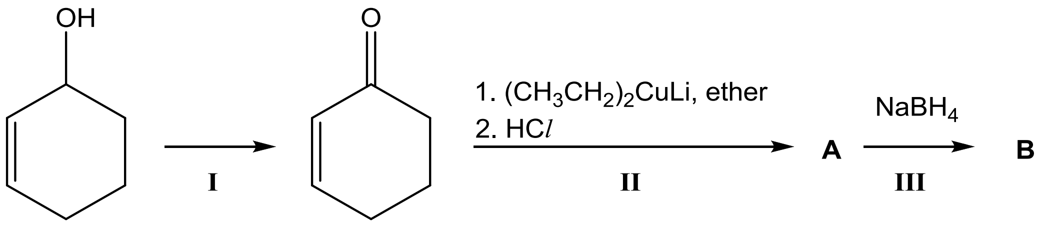
(i) State the species responsible for the pale blue colour of the solution. **[1]**

$[Cu(H_2O)_6]^{2+}$

(ii) Explain why the solution is pale blue in colour. **[3]**

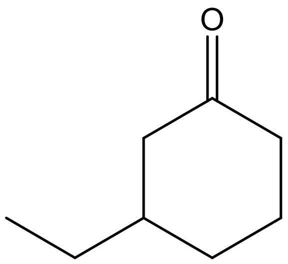
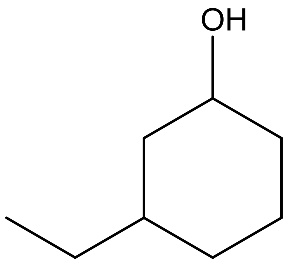
Cu^{2+} has a <u>partially filled 3d subshell</u> (electronic configuration $1s^22s^22p^63s^23p^63d^9$). In the presence of H_2O ligands in

			$[Cu(H_2O)_6]^{2+}$, the 3d orbitals of Cu^{2+} are split into 2 sets of orbitals with different energies/become non-degenerate. The difference in energies (ΔE) between these 2 sets of non-degenerate 3d orbitals is small and radiation from the visible region of the electromagnetic spectrum is absorbed when an electron is promoted from a lower energy d-orbital to another unfilled/partially-filled *d* orbital of higher energy. The (blue) colour observed corresponds to the complement of the (orange) light absorbed.	
		(iii)	Describe the colour changes observed when the following solutions are added to the pale blue solution, giving the formulae of all relevant species. **I.** Dilute NH_3(aq), until in excess; **II.** KI(aq).	**[4]**
			I. A **(pale) blue precipitate** of **$Cu(OH)_2$** is formed, which is soluble in excess NH_3(aq) to form a **dark blue solution** of **$[Cu(NH_3)_4(H_2O)_2]^{2+}$**. **II.** An **off-white/cream precipitate** of **CuI** **(Accept: Cu_2I_2)** is formed in a **brown solution** of **I_2**.	
	(c)	When Na_2CO_3 is added to a solution of $CuSO_4$ and the resultant mixture is filtered, a green solid, cupric carbonate, is obtained. The formula of this solid is $Cu_2(OH)_a(CO_3)_b$. 0.10 mol of $Cu_2(OH)_a(CO_3)_b$ required 0.40 mol of hydrochloric acid for complete reaction. The products of this reaction include copper(II) chloride, carbon dioxide and water.		
		(i)	Given that 2.4 dm³ of CO_2 was formed at room temperature and pressure, determine the values of ***a*** and ***b***.	**[2]**
			$Cu_2(OH)_a(CO_3)_b + (a + 2b)H^+ \rightarrow 2Cu^{2+} + bCO_2 + (a + b)H_2O$ Amt of CO_2 formed = 2.4 / 24 = 0.10 mol $\frac{1}{b} = \frac{0.10}{0.10} \Rightarrow b = \underline{1}$ $\frac{1}{a+2b} = \frac{0.10}{0.40} \Rightarrow a + 2b = 4 \Rightarrow a = \underline{2}$	
		(ii)	Hence, write an equation for the reaction of cupric carbonate with	**[1]**

			hydrochloric acid.	
			$Cu_2(OH)_2CO_3 + 4HCl \rightarrow 2CuCl_2 + CO_2 + 3H_2O$	
	(d)	Cu_2O, a brick red solid, is a compound where copper is in the oxidation state of +1. It can be formed by reacting an alkaline solution of complexed Cu^{2+} with a particular organic functional group.		
		(i)	State the functional group that will produce Cu_2O with the alkaline solution of complexed Cu^{2+}.	**[1]**
			Aliphatic/Non-aromatic aldehyde	
		(ii)	Name the type of reaction undergone by the functional group in **(i)**.	**[1]**
			Oxidation	
	(e)	Organocopper compounds are useful reagents in organic synthesis. One such class of compounds is the Gilman reagents, with the general formula R_2CuLi, where R represents an alkyl group. Gilman reagents are effective nucleophiles used in conjugate addition reactions. Conjugate addition involves the addition of a nucleophile across a C=C bond instead of across a C=O bond. This is illustrated in the example below:  The Gilman reagent can be seen as providing the "R^-" nucleophile while a mineral acid (e.g. HCl) provides the proton that is added to one of the carbon atoms in the C=C bond.		
		The following synthesis involves a Gilman reagent for one of the steps:  Suggest the reagent and conditions for Step **I** and the structures of compounds **A** and **B**.		**[3]**
		Reagents and conditions for Step **I**:		

acidified **$K_2Cr_2O_7$(aq)**, **heat** (under reflux)

Structures:

	
A	**B**

[Total: 20]

4 **(a)** Copper(I) chloride is used as a precursor of a fungicide and a catalyst for a variety of organic reactions. It is sparingly soluble in water.

(i) Define the standard enthalpy change of hydration of an ion. **[1]**

The standard enthalpy change of hydration of an ion is the enthalpy change when **one mole of *gaseous ions* is hydrated** under standard conditions.

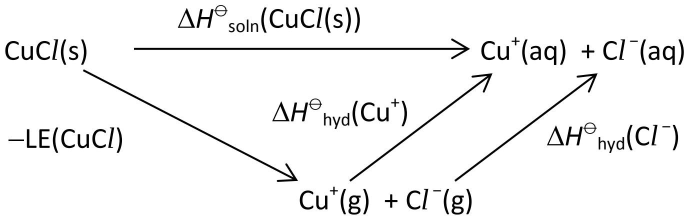
(ii) Using the data given in the following table, draw an appropriate energy cycle and calculate the standard enthalpy change of solution for copper(I) chloride.

$\Delta H^{\ominus}_{hyd}(Cu^+)$	–593 kJ mol^{-1}
$\Delta H^{\ominus}_{hyd}(Cl^-)$	–378 kJ mol^{-1}
Lattice Energy of CuC*l*	–979 kJ mol^{-1}

[3]

$\Delta H^{\ominus}_{soln}(CuCl(s)) = \Delta H^{\ominus}_{hyd}(Cu^+) + \Delta H^{\ominus}_{hyd}(Cl^-) - LE(CuCl)$

$= (–593) + (–378) – (–979) = +8$ kJ mol^{-1}



(b) **(i)** Explain what is meant by the term *entropy* of a chemical system. **[1]**

Entropy is a measure of the **disorder** in a system. (The more disordered a system, the greater the number of ways for particles and energy to be dispersed, therefore the larger its entropy.)

Describe and explain how the entropy of the following systems will change during the stated process. Assume the pressure of each system remains at 1 atm throughout.

(ii) 1 mol of Cl_2(g) at 298 K is heated to 500 K. **[1]**

Entropy increases/$\Delta S > 0$. There is an increase in disorder as the particles have **more kinetic energy on average** and there are **more ways to distribute** the **larger number of quanta** of energy.

4 **(iii)** 1 mol of Cl_2(g) at 298 K is reacted with copper according to the following equation. **[1]**

$Cu(s) + Cl_2(g) \rightarrow CuCl_2(s)$

Entropy decreases/ΔS < 0. There is an decrease in disorder as the **number of gaseous molecules decreases** from 1 to 0.

(c) Copper(II) ions are pollutants found in water. One method of purification is via precipitation of $Cu(OH)_2$ and CuS.

	K_{sp} (298 K)
CuS	6.3×10^{-36}
$Cu(OH)_2$	2.0×10^{-19}

Using the above data, calculate:

(i) the minimum concentration of Cu^{2+} for a precipitate of CuS to form in 10 ppm S^{2-} solution;

(1 ppm = 1 mg dm^{-3}) **[2]**

$[S^{2-}] = (0.01 / 32.1) = 3.12 \times 10^{-4}$ mol dm^{-3}

$[Cu^{2+}] = (6.3 \times 10^{-36}) / (3.12 \times 10^{-4})$ = **2.02×10^{-32} mol dm^{-3}**

(ii) the maximum pH of a solution containing 0.100 mol dm^{-3} Cu^{2+} ions. **[3]**

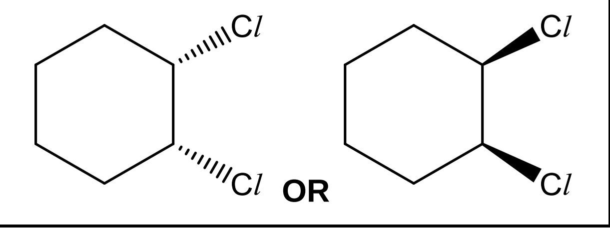
$K_{sp}(Cu(OH)_2) = [Cu^{2+}][OH^-]^2$
$2.0 \times 10^{-19} = (0.1)(x)^2$
$[OH^-] = 1.41 \times 10^{-9}$ mol dm^{-3}

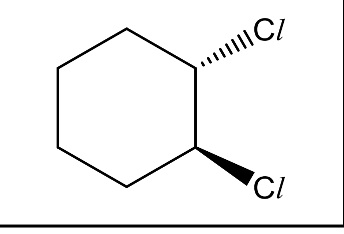
pOH = $-\lg(1.41 \times 10^{-9}) = 8.85$
pH= 14 – pOH = 14 – 8.85 = **5.15**

(d) Many organic compounds also contain chlorine. An example would be 1,2-dichlorocyclohexane, which exhibits both geometrical and optical isomerism.

(i) Explain why 1,2-dichlorocyclohexane can exhibit geometrical isomerism. **[1]**

There is **restricted rotation** about the carbon-carbon bond in the ring structure, resulting in cis- and trans-1,2-dichlorocyclohexane **[1]**.



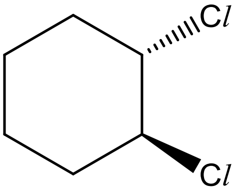
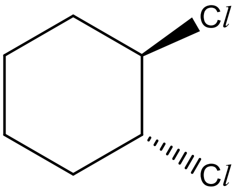
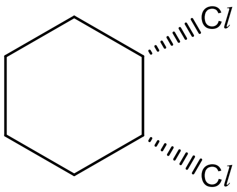
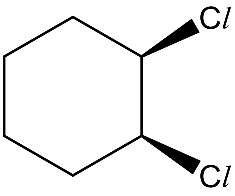


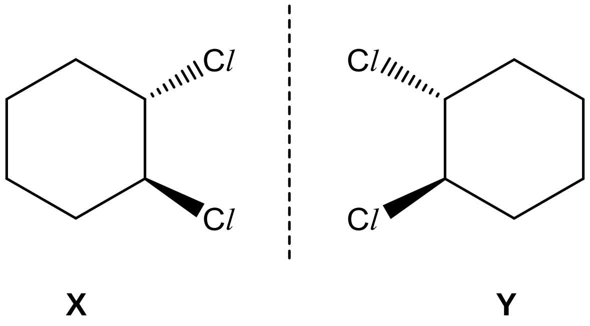
cis isomer	trans isomer

(ii) The effect of plane polarised light on 1,2-dichlorocyclohexane was investigated. Three different types of 1,2-dichlorocyclohexane was identified:

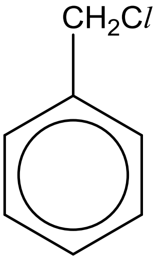
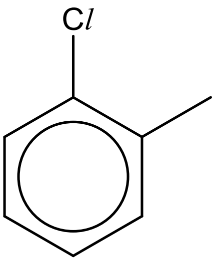
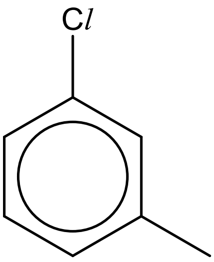
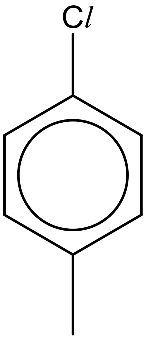
- Molecule **X** rotated plane polarised light to the left
- Molecule **Y** rotated plane polarised light to the right
- Molecule **Z** had no effect on plane polarised light

Suggest an explanation for these observations. **[3]**

Molecule	**Explanation**	
X		Molecules possess **two chiral carbons** and **no plane of symmetry**. Hence, they are mirror images of each other that are non-superimposable (i.e. enantiomers of each other) Structure of **X** and **Y** can be interchanged.
Y		
Z	 **OR** 	Although the molecule has two chiral carbons, there is a **plane of symmetry present**. Hence, the mirror images are **superimposable.**



	(e)	Compounds **C** and **D** both have the molecular formula C_7H_7Cl. In an experiment, both compounds are separately heated under reflux for some time with aqueous sodium hydroxide. The resulting solutions are cooled and acidified with dilute nitric acid. When aqueous silver nitrate is added subsequently, a white precipitate is formed with **C** while no precipitate is formed with **D**. Suggest the structures of **C** and **D**. Explain your reasoning for **each** compound.	**[4]**

C	
	C undergoes **<u>nucleophilic substitution</u>** when heated with NaOH. **<u>Free chloride ion then combines with Ag^+</u>** to form white precipitate of AgCl.
D	 **OR**  **OR** 
	C–Cl bond in **D** has **<u>partial double bond character</u>** due to the **<u>delocalisation of a lone pair of electrons of chlorine into the benzene ring</u>**. Hence, **D** does not undergo nucleophilic substitution with NaOH.

[Total: 20]

5	**(a)**	The electrical conductivities of some Period 3 elements are shown below.	

Element	Na	Mg	Al	P	S	Cl
Electrical conductivity at 298 K / $\times 10^7$ S m^{-1}	2.1	2.3	3.5	Non-conductors		

		(i)	With reference to the data above, describe and explain the difference in electrical conductivities of the elements above.	**[3]**
			Na, Mg & $\mathrm{A}l$ They are metals / have giant metallic structure. Presence of delocalised valence electrons which act as mobile charge carriers thus making them good conductors. Electrical conductivity increases from Na (2.1×10^{7} S m^{-1}) to Mg (2.3×10^{7} S m^{-1}) to $\mathrm{A}l$ (3.5×10^{7} S m^{-1}) as the number of valence electrons increases. P_4, S_8 & $\mathrm{C}l_2$ They are non-metals / have simple covalent structure. Absence of mobile charge carriers thus they are non-conductors.	
		(ii)	Silicon carbide (SiC), also known as carborundum and moissanite, is used in abrasive and cutting tools. Suggest the structure and bonding of SiC.	**[2]**
			Giant covalent structure with strong electrostatic forces of attraction between the Si and C nuclei and the shared pair of electrons.	
	(b)	Chlorides of Period 3 elements dissolve in water to give solutions of varying pH. Explain the following pH values and write the chemical equations for any reactions that occur:		
		(i)	$\mathrm{A}l\mathrm{C}l_3$ dissolves readily in water to form an acidic solution (pH = 3).	**[3]**
			Both hydration of ions and substantial hydrolysis of $\mathrm{A}l^{3+}$(aq) occurs. Due to its high charge density, $\mathrm{A}l^{3+}$ is **highly polarising** and **weakens the O–H bonds** in the water molecules of the complex, causing the O–H bonds to break and hence release the hydrogen ions. $\mathrm{A}l\mathrm{C}l_3(s) + 6H_2O(l) \rightarrow [\mathrm{A}l(H_2O)_6]^{3+}(aq) + 3\mathrm{C}l^{-}(aq)$ $[\mathrm{A}l(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [\mathrm{A}l(H_2O)_5(OH)]^{2+}(aq) + H_3O^{+}(aq)$	
		(ii)	$\mathrm{SiC}l_4(l)$ dissolves in water to form a strongly acidic solution (pH = 2)	**[2]**
			$\mathrm{SiC}l_4$ undergoes hydrolysis in water. This is because Si atom in $\mathrm{SiC}l_4$ has **energetically accessible vacant 3d orbital for dative bonding** with water molecules.	

$SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl(aq)$

(c) Caffeic acid is an organic compound found in all plants as it is a key intermediate in the biosynthesis of lignin, one of the principal components of plant biomass.

Caffeic acid has the molecular formula $C_9H_8O_4$. Caffeic acid reacts with $Br_2(l)$ to give $C_9H_8O_4Br_2$. When treated with hot $KMnO_4$ and H_2SO_4, caffeic acid reacts to give **F**, $C_7H_6O_4$, and a colourless gas that produces a white solid with $Ca(OH)_2(aq)$. **F** reacts with PCl_5 to give **G**, $C_7H_5O_3Cl$, with the production of steamy white fumes. **G** reacts with water to form an acidic solution. When added to neutral $FeCl_3(aq)$, **G** also forms a violet colouration. **G** reacts with $Br_2(aq)$ to give **H**, $C_7H_3O_4Br_3$.

Use the information above to deduce the structures of caffeic acid and compounds **F** to **H**, explaining all the reactions involved. **[10]**

Caffeic acid C:H ratio ≈ 1:1 which suggests presence of benzene ring.

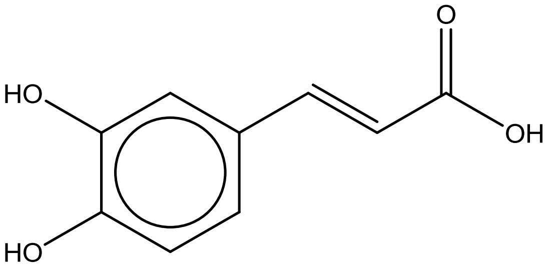
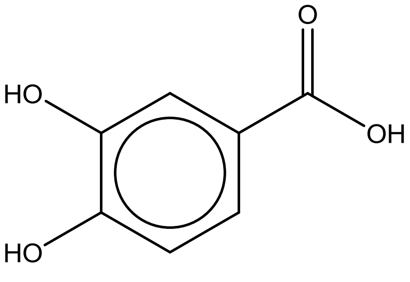
Caffeic acid has a C=C double bond/has an alkene group as it undergoes electrophilic addition with Br_2.

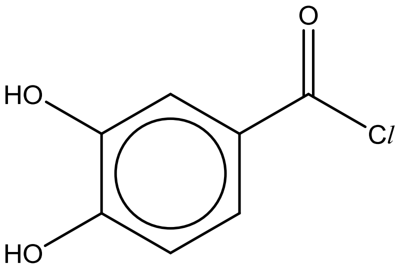
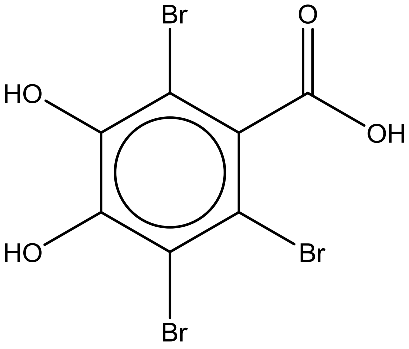
Caffeic acid undergoes oxidation/oxidative cleavage with hot $KMnO_4$ to give carbon dioxide gas. Loss of 2 carbons as CO_2 suggests formation of ethanedioic acid/HO_2CCO_2H after oxidative cleavage.

F contains a carboxylic functional group as it undergoes (nucleophilic) substitution with PCl_5 to give **G**, an acid chloride that hydrolyses in water, and fumes of HCl.

G contains phenol functional group as it forms a complex with $FeCl_3(aq)$.

G undergoes electrophilic substitution with $Br_2(aq)$. Substitution of 3 Br atoms suggests 3 positions on benzene ring that are available for substitution.

Caffeic acid	
F	

		G		
		H		
			[Total: 20]	

– End of Paper –