

**C2 Preliminary  
Examinations Higher 2**

**CANDIDATE NAME**

**CT GROUP**

**CENTRE NUMBER**

**INDEX NUMBER**

**CHEMISTRY**

**9647/01**

Paper 1 Multiple Choice

**21 September 2016**

**1 hour**

Additional Materials: Optical Mark Sheet (OMS)

Data Booklet

**READ THESE INSTRUCTIONS FIRST**

Write in soft pencil.

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

Complete the information on the optical mark sheet (OMS) as shown below.

1. Enter your **NAME** (as in NRIC). \_\_\_\_\_

2. Enter the **PAPER NUMBER**. \_\_\_\_\_

3. Enter your **CT GROUP**. \_\_\_\_\_

4. Enter your **NRIC NUMBER** or **FIN Number**

5. Now **SHADE** the corresponding circles in the grid for **EACH DIGIT** or **LETTER**

<b>USE PENCIL ONLY</b>							
<b>FOR ALL ENTRIES ON THIS SHEET</b>							
0	1	2	3	4	5	6	7
○	○	○	○	○	○	○	○

NRIC / FIN										
(S)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(A)	(K)	(U)
(F)	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(B)	(L)	(V)
(G)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(C)	(M)	(W)
(T)	(3)	(3)	(3)	(3)	(3)	(3)	(3)	(D)	(N)	(X)

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 OMS.

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.

The use of an approved scientific calculator is expected, where appropriate.

## SECTION A

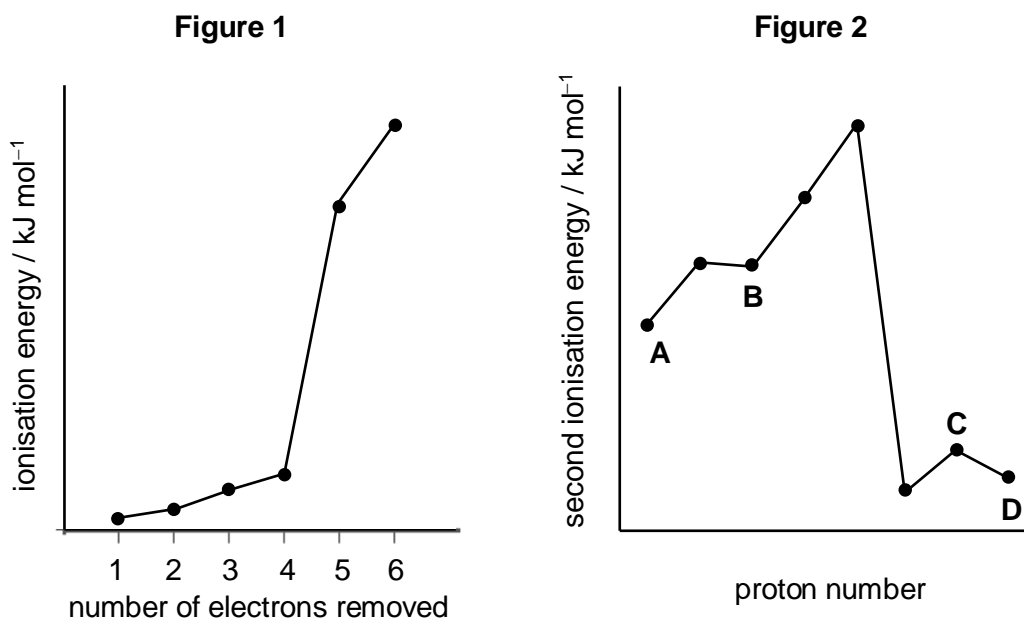
For each question, there are four possible answers **A**, **B**, **C** and **D**. Choose the **one** you consider to be correct.

- 1 Methyl mercaptan,  $\text{CH}_3\text{SH}$ , is one of the substances responsible for bad breath and is often used to impart a smell to natural gas in a pipeline. When a sample of  $10\text{ cm}^3$  of  $\text{CH}_3\text{SH}$  is exploded with  $60\text{ cm}^3$  of oxygen, the final volume of gas after burning is passed into an excess of aqueous alkali. The chemical equation for the combustion process is shown below.



What percentage of the final volume of gas after burning dissolves in the alkali? All gaseous volumes are measured at room temperature and pressure.

- A** 40.0%      **B** 28.5%      **C** 20.0%      **D** 14.3%
- 2 **Figure 1** shows the first six ionisation energies of an element **Q** while **Figure 2** shows the second ionisation energies of eight consecutive elements, including **Q**, in the Periodic Table.



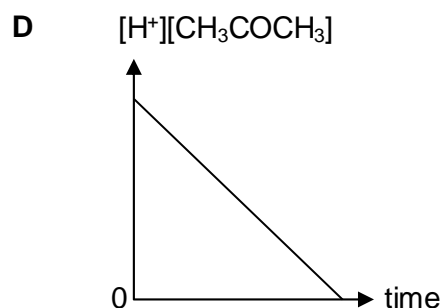
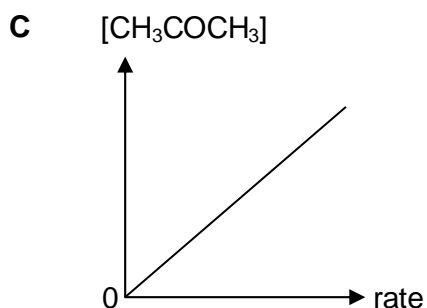
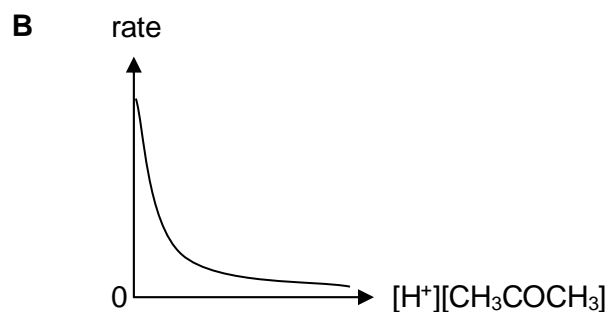
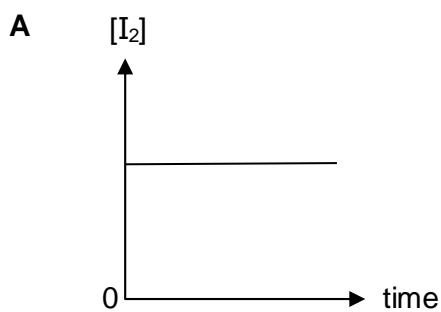
Which of the elements **A**, **B**, **C** or **D** could be the element **Q**?

- 3 Which statement is **not** always true when an ionic solid dissolves in water?
- A** Energy is absorbed to separate the ions in the solid.
- B** Energy is absorbed to break the hydrogen bonding between water molecules.
- C** Energy is released when the ions are hydrated.
- D** Energy is released when the ionic solid dissolves completely.



- 4 Which of the following explains the non-ideal behavior of the gases present in the reaction chamber in the Haber process?
- A the presence of a catalyst
  - B the high temperature of 450 °C
  - C the high pressure of 150 atm
  - D the strong bonds between the atoms in the nitrogen molecules
- 5 Which enthalpy change would best indicate the relative strengths of the intermolecular forces in liquid hydrogen halides?
- A bond dissociation energy
  - B enthalpy change of formation
  - C enthalpy change of solution
  - D enthalpy change of vaporisation
- 6  $\text{CH}_3\text{COCH}_3$  and  $\text{I}_2$  react in the presence of an acid catalyst. The rate of reaction is independent of  $[\text{I}_2]$  but directly proportional to  $[\text{H}^+]$  and to  $[\text{CH}_3\text{COCH}_3]$ .

Which graph is correct?



- 7 When the system  $X_2(g) + 3Y_2(g) = 2XY_3(g)$  is at equilibrium at 500 K and 1 atm, the value of the equilibrium constant,  $K_p$ , is 100. What is the value of  $K_p$  at a pressure of 2 atm at the same temperature?

**A** 25                      **B** 100                      **C** 200                      **D** 400

- 8 The numerical values of the solubility product of  $BaSO_4$ ,  $BaCO_3$  and  $Ba(IO_3)_2$  at 25 °C are given in the table below.

Compound	Solubility product
$BaSO_4$	$1.1 \times 10^{-10}$
$BaCO_3$	$2.6 \times 10^{-9}$
$Ba(IO_3)_2$	$4.0 \times 10^{-9}$

An aqueous solution of  $BaCl_2$  was added slowly, until in excess, to a solution containing  $0.5 \text{ mol dm}^{-3} Na_2SO_4$ ,  $1.0 \text{ mol dm}^{-3} Na_2CO_3$  and  $1.5 \text{ mol dm}^{-3} NaIO_3$  at 25 °C.

What is the correct order of precipitation of the three barium salts?

	First to precipitate	—————>	Last to precipitate
<b>A</b>	$BaSO_4$		$Ba(IO_3)_2$
<b>B</b>	$Ba(IO_3)_2$		$BaSO_4$
<b>C</b>	$BaSO_4$		$BaCO_3$
<b>D</b>	$BaCO_3$		$BaSO_4$

- 9 What is the pH of the final solution formed when  $V \text{ dm}^3$  of dilute hydrochloric acid of pH 1.0 is mixed with  $V \text{ dm}^3$  of dilute sulfuric acid of pH 1.0, followed by the addition of  $2V \text{ dm}^3$  of water?

**A** 1.1                      **B** 1.3                      **C** 2.0                      **D** 4.0

- 10 Stomach juices have a pH of 1.0.

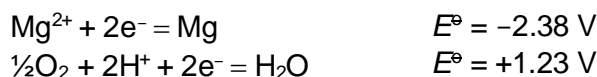
Aspirin is a monobasic acid represented by HA ( $K_a = 10^{-4} \text{ mol dm}^{-3}$ ) which dissociates into  $H^+$  and  $A^-$  ions.

What are the relative concentrations of  $H^+$ ,  $A^-$  and HA when aspirin from a tablet enters the stomach?

**A**  $[H^+] > [HA] > [A^-]$                       **B**  $[H^+] > [A^-] > [HA]$   
**C**  $[HA] > [H^+] = [A^-]$                       **D**  $[H^+] = [A^-] > [HA]$



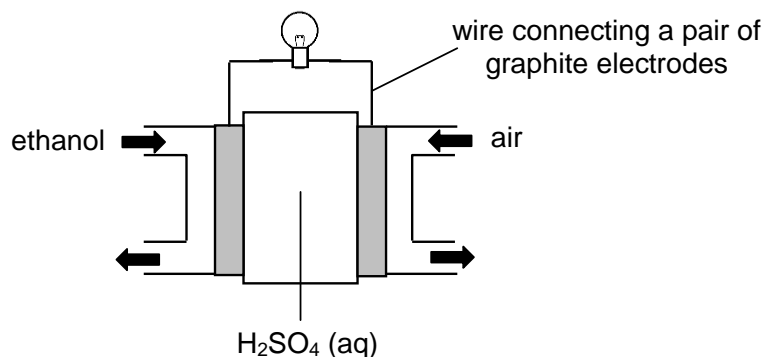
- 11 In the construction of heart 'pacemakers', a tiny magnesium electrode is used which creates an electrochemical cell with the inhaled oxygen. The relevant half-equations are as follows.



Under standard conditions, the cell e.m.f. would be 3.61 V. However, in the body, a potential of 3.25 V is more usual.

Which of the following is an explanation for this lower e.m.f. in the body?

- A the pH of about 7.4 of the body fluid surrounding the electrodes  
 B the low concentration of  $\text{Mg}^{2+}$  ions surrounding the electrodes  
 C the small size of the magnesium electrode  
 D the large amount of oxygen inhaled
- 12 Ethanol fuel cells are more practical than hydrogen fuel cells since ethanol is easier to store and transport than hydrogen. Ethanol is converted to carbon dioxide when the fuel cell is operated.



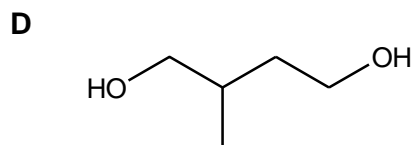
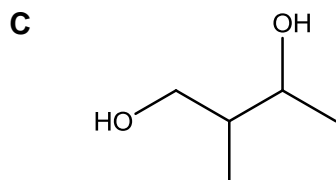
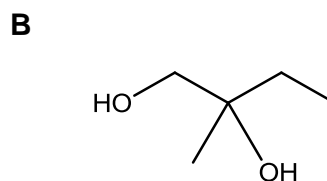
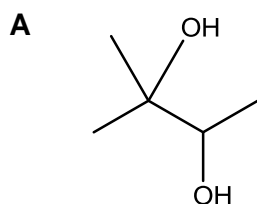
Which statement is correct about ethanol fuel cells?

- A Ethanol fuel cells can work indefinitely as long as there is a supply of ethanol and air.  
 B For every 1 mol of ethanol oxidised, 6 mol of electrons are produced.  
 C  $\text{H}^{+}$  ions react with air to produce water at the anode.  
 D The acid needs to be replenished as hydrogen ions are being used up.

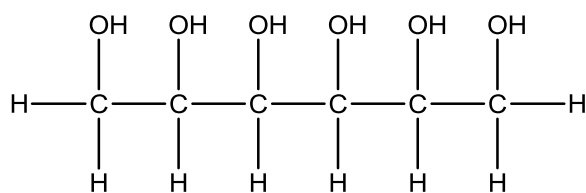
- 13 How many structural isomers of  $C_3H_4Br_2$  contain  $C=C$  and how many do not contain  $C=C$ ?

	structural isomers with $C=C$	structural isomers without $C=C$
<b>A</b>	4	0
<b>B</b>	4	2
<b>C</b>	5	0
<b>D</b>	5	2

- 14 2-methylbuta-1,3-diene,  $CH_2=C(CH_3)-CH=CH_2$ , is used as a monomer in the manufacture of synthetic rubbers. Which compound would **not** produce this monomer on treatment with excess concentrated sulfuric acid at  $170\text{ }^\circ\text{C}$ ?



- 15 Sorbitol is a naturally-occurring compound with a sweet taste. It is often used as a substitute for sucrose by the food industry.



sorbitol

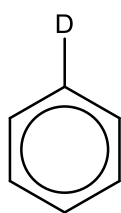
How many chiral centres are present in sorbitol?

- A** 3                      **B** 4                      **C** 5                      **D** 6

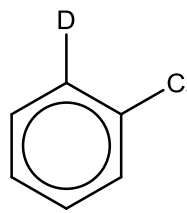


- 16 Deuterium, D, is a heavy isotope of hydrogen. Deuteriobenzene is reacted with chlorine and  $AlCl_3$  under controlled condition so that only monochlorination takes place.

Assuming that the carbon-deuterium bond is broken as easily as a carbon-hydrogen bond, which proportion of the chlorinated products will be 2-chlorodeuteriobenzene?



deuteriobenzene

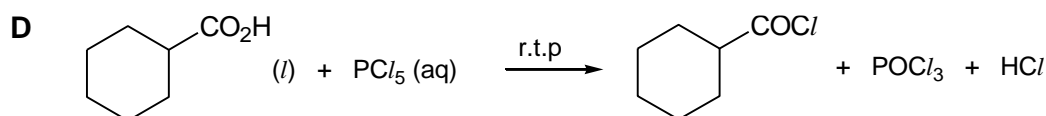
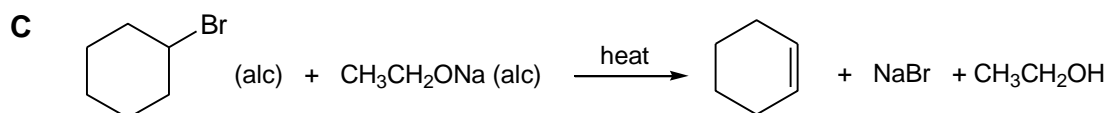
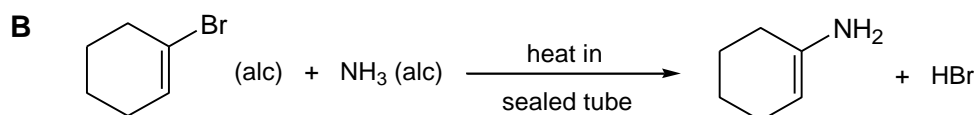
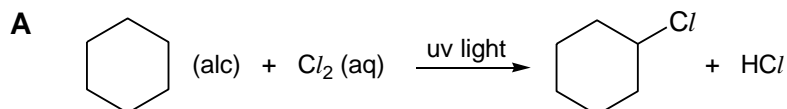


2-chlorodeuteriobenzene

- A 16%                      B 20%                      C 33%                      D 40%
- 17 What is the correct set of reagents and conditions for the conversion of methylbenzene to 2-nitromethylbenzene?

- A dilute nitric acid, 100 °C  
 B concentrated  $HNO_3$ , 30 °C  
 C concentrated  $HNO_3$  and concentrated  $H_2SO_4$ , 30 °C  
 D concentrated  $HNO_3$  and concentrated  $H_2SO_4$ , 100 °C

- 18 Which reaction gives the best yield of products? [(alc) indicates an alcoholic solution.]



- 19 Chlorofluorocarbons (CFCs) have been widely used in aerosol sprays, refrigerators and in making foamed plastics, but are now known to destroy ozone in the upper atmosphere.

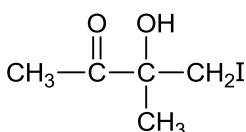
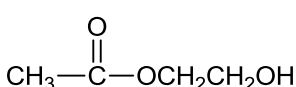
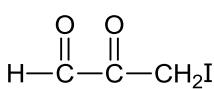
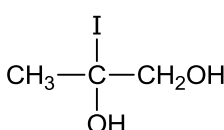
Which compound will **not** destroy ozone, and therefore can be used as a replacement for CFCs?

- A  $\text{CHBr}_3$   
 B  $\text{CCl}_3\text{CBr}_3$   
 C  $\text{CHCl}_3/\text{CF}_2$   
 D  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$

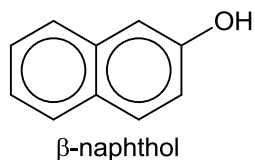
- 20 Compound X has the following properties.

- It changes the colour of acidified sodium dichromate(VI) from orange to green.
- It gives yellow precipitate with alkaline aqueous iodine.

Which compound could be X?

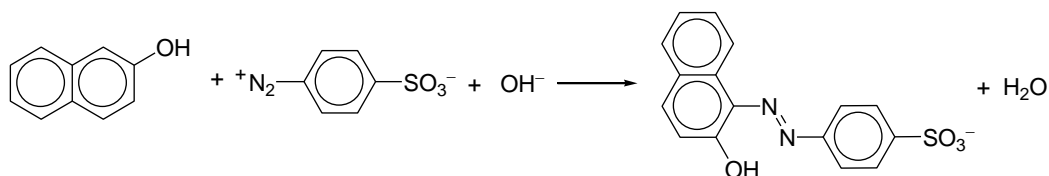
- A  B 
- C  D 

- 21  $\beta$ -naphthol is a crystalline solid that is widely used in the production of dyes.



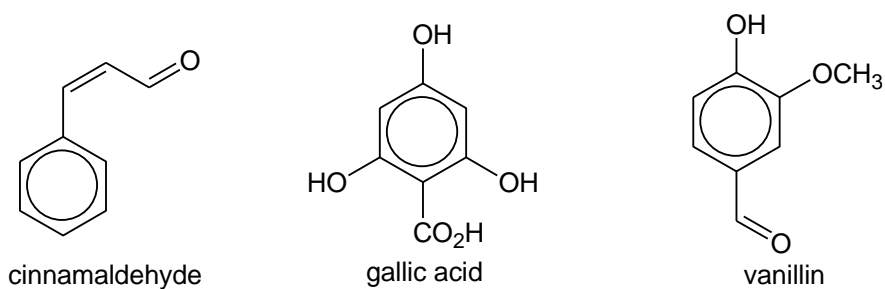
Which of the following is likely to be a property of  $\beta$ -naphthol?

- A Its  $\text{p}K_{\text{a}}$  is lower than that of phenol.  
 B It gives white fumes with  $\text{SOCl}_2$ .  
 C It reacts with carboxylic acid to form ester.  
 D It undergoes nucleophilic substitution in the reaction below.





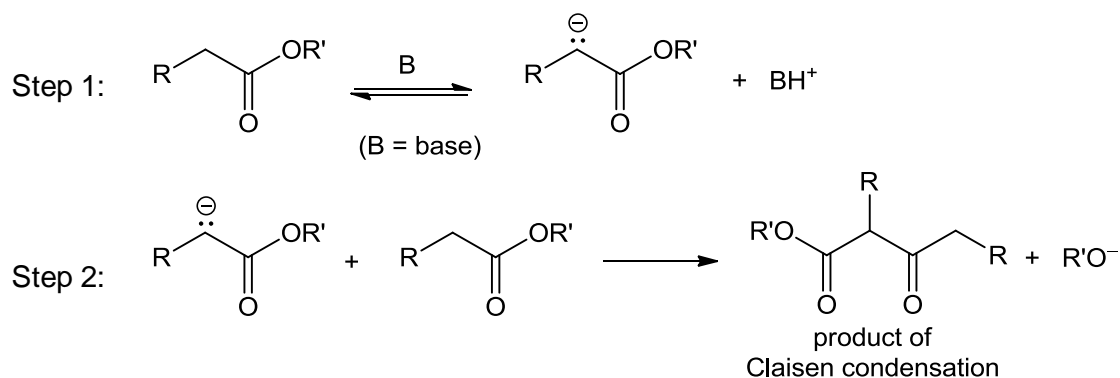
- 22 Cinnamaldehyde, gallic acid and vanillin are naturally occurring organic compounds found in plants.



The CH<sub>3</sub>O group is inert and can be disregarded in this question.

Which set of reagents can be used to distinguish these three compounds?

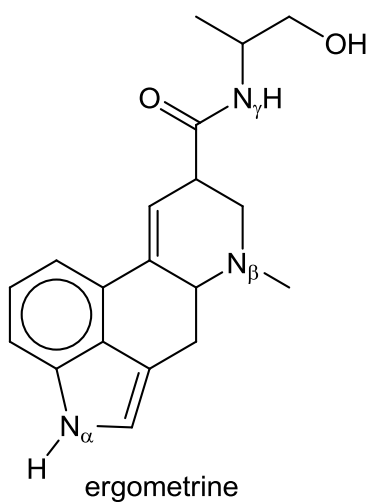
- A** Aqueous bromine and aqueous sodium hydrogencarbonate  
**B** Aqueous bromine and Tollens' reagent  
**C** Fehling's solution and neutral iron(III) chloride  
**D** Fehling's solution and hot acidified potassium manganate(VII)
- 23 Two esters can react via Claisen condensation in the presence of a strong base. The two steps of this reaction are shown below.



Which compound will be formed when CH<sub>3</sub>CH<sub>2</sub>OCOCH<sub>3</sub> undergoes Claisen condensation?

- A** 
$$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{H}}{\underset{\text{CH}_3}{\text{C}}}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$$
- B** 
$$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_2\text{CH}_3$$
- C** 
$$\text{CH}_3\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{H}}{\underset{\text{CH}_3}{\text{C}}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2\text{CH}_3$$
- D** 
$$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OCH}_3$$

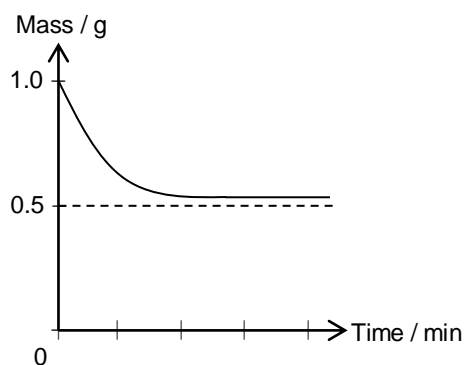
24 Ergometrine is a drug used in obstetrics to treat heavy bleeding after childbirth.



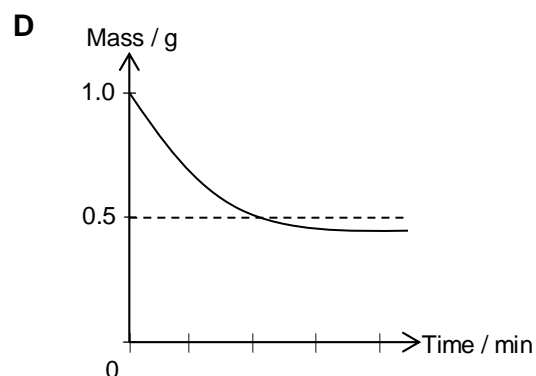
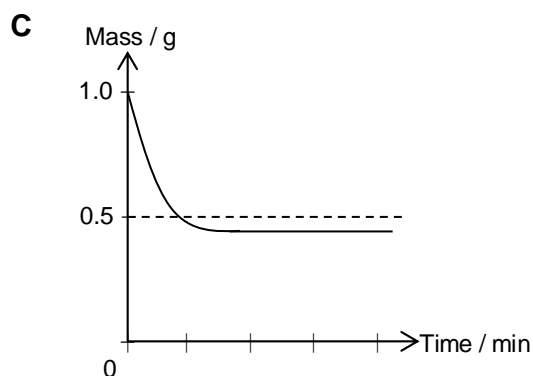
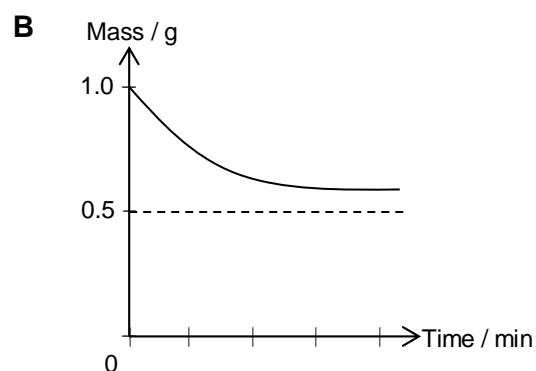
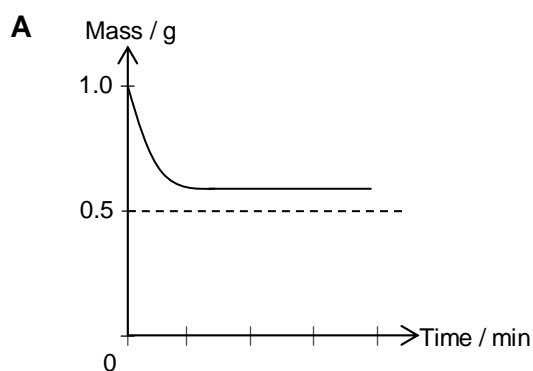
Which statement about ergometrine is correct?

- A  $pK_b$  of the labelled three nitrogen atoms in increasing order is  $N_\beta < N_\alpha < N_\gamma$ .
- B It reacts with both dilute NaOH and dilute HCl at room temperature.
- C It forms orange precipitate with 2,4-dinitrophenylhydrazine.
- D One mole of ergometrine reacts with 3 moles of  $\text{CH}_3\text{COCl}$ .

- 25 The graph represents the change in mass that occurs when 1.0 g of powdered calcium carbonate,  $\text{CaCO}_3$ , is heated at a temperature,  $T$ .



Which graph would be obtained by heating 1.0 g of powdered magnesium carbonate,  $\text{MgCO}_3$ , at the same temperature,  $T$ ?



- 26 What chlorine-containing products are formed when chlorine is bubbled into hot aqueous sodium hydroxide?
- A**  $\text{NaClO}$  only
- B**  $\text{NaClO}_3$  only
- C**  $\text{NaCl}$  and  $\text{NaClO}$
- D**  $\text{NaCl}$  and  $\text{NaClO}_3$

27 Which statement concerning the Period 3 elements, sodium to chlorine, is correct?

- A Chlorine has the largest anion.
- B Aluminium has the highest melting point.
- C Chlorine exhibits the most number of different oxidation states.
- D Phosphorus reacts most vigorously with water.

28 Element **X** is one of the first five elements in Period 3 of the Periodic Table. The following four statements were made about the properties of element **X** or its compounds.

Three statements are correct descriptions and one is false.

Which statement does **not** fit with the other three?

- A The oxide of **X** dissolves in excess dilute NaOH(aq).
- B **X** exhibits only one possible oxidation number in its chloride, which is not a solid at room temperature.
- C The oxide of **X** has a very high melting point.
- D The chloride of **X** reacts with water to give an acidic solution with pH 1.

29 Which property of the first row transition elements does **not** remain relatively constant?

- |                           |                               |
|---------------------------|-------------------------------|
| A atomic radius           | B melting point               |
| C first ionisation energy | D ionic radius of the +2 ions |

30 Aqueous platinum(IV) chloride reacts with ammonia to form compounds in which the coordination number of platinum is 6. When dissolved in water, 1 mol of such compound gave 3 mol of ions.

What is the formula of this compound?

- |   |   |
|---|---|
| A $\text{Pt}(\text{NH}_3)_2\text{Cl}_4$ | B $\text{Pt}(\text{NH}_3)_3\text{Cl}_4$ |
| C $\text{Pt}(\text{NH}_3)_4\text{Cl}_4$ | D $\text{Pt}(\text{NH}_3)_6\text{Cl}_4$ |

## 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.

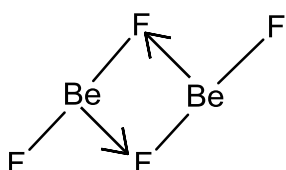
**31** Which statements about one mole of a metal are always correct?

- 1 It contains the same number of atoms as one mole of hydrogen atoms.
- 2 It contains the same number of atoms as that in 12 grams of  $^{12}\text{C}$ .
- 3 It is liberated by one mole of electrons.

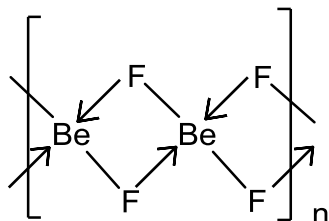
**32** Beryllium is the first member of Group II and forms covalent compounds which are said to be electron deficient. In many ways, beryllium resembles aluminium.

Which of the following are possible?

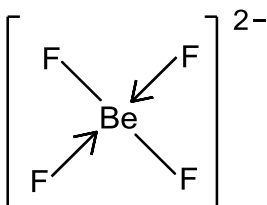
1



2



3



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

<b>A</b>	<b>B</b>	<b>C</b>	<b>D</b>
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.

- 33** When 25.0 cm<sup>3</sup> of a 0.100 mol dm<sup>-3</sup> strong monobasic acid was titrated against 0.200 mol dm<sup>-3</sup> of a weak base **X**, 12.50 cm<sup>3</sup> of the base was required to completely neutralise the acid.

Which statement is correct for this experiment?

- 1 Bromocresol green ( $pK_{in} = 4.7$ ) is a suitable indicator for this titration.
- 2 1 mole of **X** reacts with 1 mole of the monobasic acid.
- 3 A solution of maximum buffering capacity was formed when 6.25 cm<sup>3</sup> of the base was added.

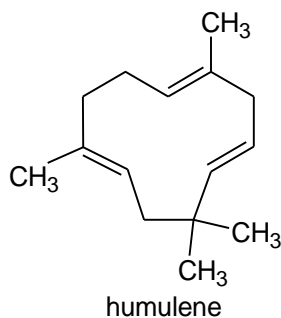
- 34** *The use of the Data Booklet is relevant to this question.*

Electrolysis of a solution of **M**<sup>n+</sup>(aq) led to the deposition of **M** atoms at the cathode. 5.00 × 10<sup>-3</sup> mol of **M** is deposited when 965 C of electricity are passed through the solution.

What could **M**<sup>n+</sup> be?

- 1 Sn<sup>2+</sup>
- 2 Cr<sup>2+</sup>
- 3 Ag<sup>+</sup>

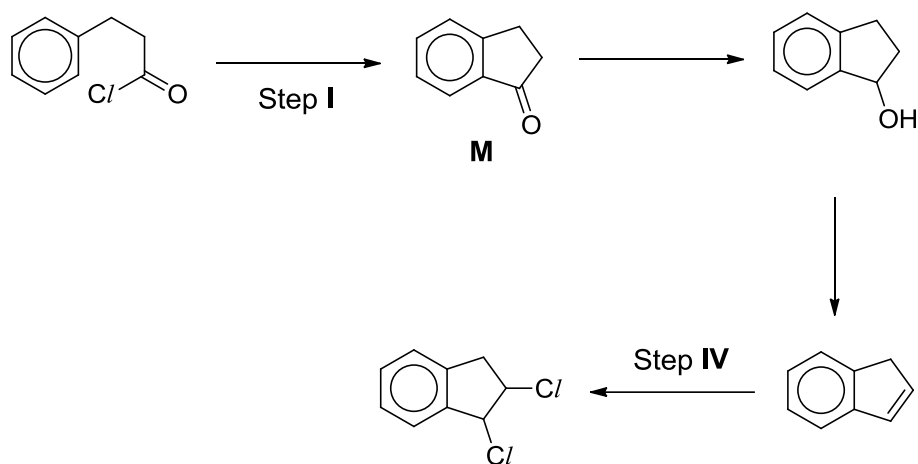
35 Humulene can be extracted from carnation flowers.



Which products are obtained from the reaction of humulene with hot acidified concentrated  $\text{KMnO}_4$ ?

- 1  $\text{CH}_3\text{COCH}_2\text{CH}_2\text{CO}_2\text{H}$
- 2  $\text{CH}_3\text{COCH}_2\text{CO}_2\text{H}$
- 3  $\text{HO}_2\text{CCH}_2\text{C}(\text{CH}_3)_2\text{CO}_2\text{H}$

36 Consider the following reaction scheme.



Which of the following statements about this reaction scheme are correct?

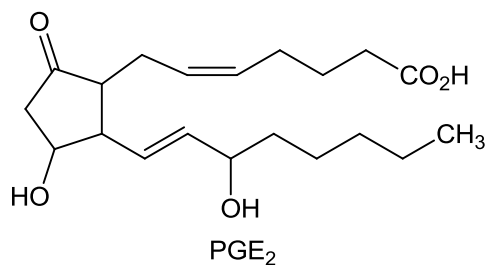
- 1 Step I requires a catalyst.
- 2 Compound **M** is a planar molecule.
- 3 Step IV is a substitution reaction.

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

<b>A</b>	<b>B</b>	<b>C</b>	<b>D</b>
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.

**37** PGE<sub>2</sub> is a prostaglandin that has pharmacological activity.

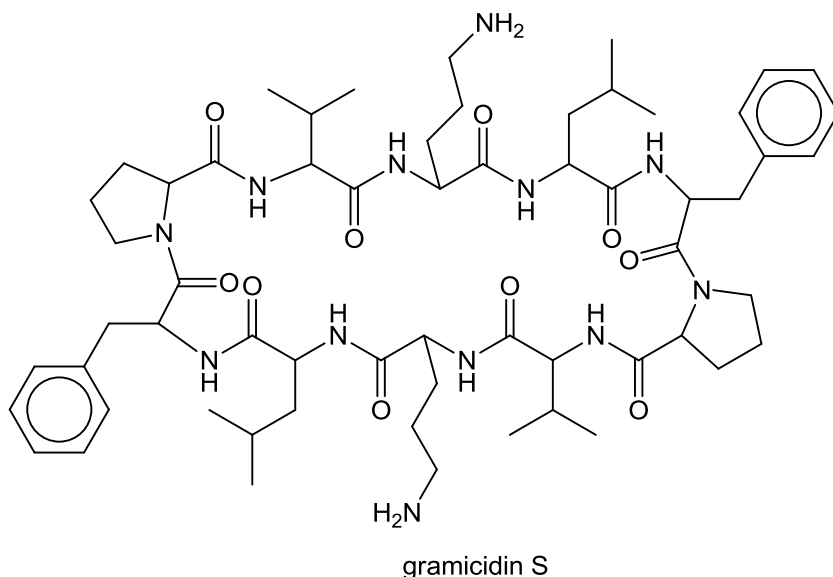


What is the correct number of hydrogen atoms incorporated per molecule of PGE<sub>2</sub> when PGE<sub>2</sub> is reacted with each of the following reducing agents?

	Reducing agent	Number of hydrogen atoms incorporated per molecule of PGE <sub>2</sub>
<b>1</b>	H <sub>2</sub> / Ni	6
<b>2</b>	LiAlH <sub>4</sub> in dry ether	4
<b>3</b>	NaBH <sub>4</sub> in ethanol	4



38 The cyclic peptide gramicidin S can act as an antibiotic.



Which statements about gramicidin S are correct?

- 1 It is made up of 5 different amino acids.
- 2 1 mole of gramicidin S reacts with 10 moles of hot dilute HCl.
- 3 Its three-dimensional structure can be stabilised by ionic interaction.

39 Which of the following are trends across Period 3 of the Periodic Table?

- 1 The electronegativity of the elements increases.
- 2 The oxides of the elements change from ionic to covalent.
- 3 The electrical conductivity of the elements decreases.

40 Prussian blue,  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ , is a dark blue pigment often used in painting and dyeing.

It can be synthesised in the laboratory by mixing iron(III) chloride,  $\text{FeCl}_3$ , with potassium ferrocyanide,  $\text{K}_4[\text{Fe}(\text{CN})_6]$ .

Based on the information given above, which conclusions can be made about Prussian blue?

- 1 The percentage by mass of iron in Prussian blue is 45.5%.
- 2 A redox reaction has taken place in the formation of Prussian blue.
- 3 Prussian blue absorbs blue light strongly.

**The End**

**2016 C2 H2 CHEMISTRY PRELIMINARY  
EXAM  
SUGGESTED SOLUTIONS**

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**Paper 1**

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

**C2 Preliminary  
Examinations Higher 2**

CANDIDATE NAME

CT GROUP

CENTRE NUMBER

INDEX NUMBER

**CHEMISTRY**

**9647/02**

Paper 2 Structured Questions

**30 August 2016**

**2 hours**

Candidates answer on the Question Paper

Additional Materials: Data Booklet

**INSTRUCTIONS TO CANDIDATES**

- 1) Write your **name, CT group, centre number** and **index number** clearly in the spaces at the top of this page.
- 2) Answer **all** questions in the spaces provided in this Question Paper.

**INFORMATION FOR CANDIDATES**

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

A Data Booklet is provided.

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

You may use a calculator.

You are reminded of the need for good English and clear presentation in your answers.

<b>For Examiner's Use</b>	
<b>1</b>	<b>/ 12</b>
<b>2</b>	<b>/ 17</b>
<b>3</b>	<b>/ 14</b>
<b>4</b>	<b>/ 13</b>
<b>5</b>	<b>/ 16</b>
<b>Deductions</b>	
<b>Total</b>	<b>/ 72</b>

Calculator Model:

**1 Planning (P)**

An electrochemical cell is a device that produces an electric current as a result of redox reactions. Any spontaneous redox reaction can be harnessed to produce electrical energy under the right conditions. Electrons are generated at one electrode and driven towards the other by electromotive force, also known as the cell potential, measured in volts.

The Gibbs' Free Energy equation is given as  $\Delta G = \Delta H - T\Delta S$ .  $\Delta G$  may be obtained from the cell potential of an electrochemical cell by the relationship:

$$\Delta G = -nFE$$

where  $n$  = number of moles of electrons transferred in the reaction

$F$  = Faraday's constant

$E$  = cell potential

By constructing an electrochemical cell, the cell potential can be measured over a range of temperatures. The entropy change of a reaction can then be determined by plotting a suitable linear graph using the data obtained.

- (a) (i)** Write an ionic equation for the reaction between Cu and  $\text{Fe}^{3+}$ . You should include state symbols in your equation.

.....[1]

- (ii)** Predict the sign of  $\Delta S$  for the above reaction. Explain your answer.

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

- (b)** Using the information given above, you are required to write a plan for determining the entropy change for the redox reaction between Cu and  $\text{Fe}^{3+}$ . You will measure the cell potential over a 30 °C range of temperature.

You are also required to explain how the data you obtain from this experiment may be used to determine the entropy change of the reaction.

You may assume that the values of  $\Delta H$  and  $\Delta S$  are constant over this measured temperature change.

You may also assume that you are provided with:

0.20 mol dm<sup>-3</sup> aqueous  $\text{FeCl}_3$

0.10 mol dm<sup>-3</sup> aqueous  $\text{CuSO}_4$

0.50 mol dm<sup>-3</sup> aqueous  $\text{H}_2\text{SO}_4$

solid hydrated iron(II) sulfate,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

common electrodes

the apparatus normally found in a school or college laboratory.

Your plan should include:

- a fully-labelled diagram of the set-up of the electrochemical cell you would use to monitor how cell potential varies with temperature;
- details for the preparation of 100 cm<sup>3</sup> of 0.20 mol dm<sup>-3</sup> aqueous acidified FeSO<sub>4</sub>;
- details of the appropriate quantities and concentrations of solutions used;
- the temperatures at which the experiments would be carried out;
- an outline of how the results would be obtained;
- a sketch of the graph you would expect to obtain;
- how the data obtained from the graph would be used to determine the entropy change for the reaction.

For  
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- 2 (a) The transition metals form many complexes. Two examples of complexes formed by  $\text{Fe}^{3+}$  are  $[\text{Fe}(\text{H}_2\text{O})_5(\text{SCN})]^{2+}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$ .

These complexes contain the ligands,  $\text{H}_2\text{O}$ ,  $\text{SCN}^-$ , and  $\text{CN}^-$ , in which the "donor atom" for dative bonding are O, S and C respectively.

- (i) Explain why the atomic radius of oxygen (0.066 nm) is smaller than that of carbon (0.077 nm).

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

- (ii) Explain why the atomic radius of sulfur (0.104 nm) is larger than those of oxygen and carbon.

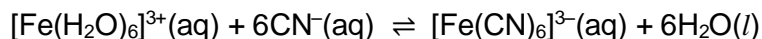
.....  
.....  
.....[1]



- (b) When water ligands in an aqua complex are replaced by other ligands, the equilibrium constant for the reaction is called the stability constant,  $K_{\text{stab}}$ , of the new complex.

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use

For example,



$$K_{\text{stab}} = \frac{[\text{Fe}(\text{CN})_6^{3-}]}{[\text{Fe}(\text{H}_2\text{O})_6^{3+}] [\text{CN}^{-}]^6}$$

The  $K_{\text{stab}}$  value is an indication of the stability of a complex ion with reference to the aqua complex. The table below lists the  $K_{\text{stab}}$  values of some iron complexes.

complex	$K_{\text{stab}}$
$[\text{Fe}(\text{H}_2\text{O})_5(\text{SCN})]^{2+}$	$1 \times 10^2$
$[\text{Fe}(\text{CN})_6]^{3-}$	$1 \times 10^{31}$
$[\text{Fe}(\text{CN})_6]^{4-}$	$1 \times 10^{24}$
$[\text{Fe}(\text{edta})]^{-}$	$1 \times 10^{25}$
$[\text{Fe}(\text{edta})]^{2-}$	$2 \times 10^{14}$



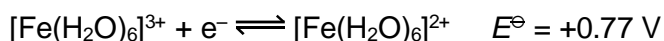
- (i) State the colour of the solution obtained when aqueous potassium thiocyanate, KSCN, is added to aqueous  $\text{Fe}^{3+}$ .

.....[1]

- (ii) Suggest why the colour you stated in (b)(i) is not obtained when aqueous KSCN is added to aqueous  $[\text{Fe}(\text{CN})_6]^{3-}$ .

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

- (iii) Predict whether edta would make the reduction potential for the Fe(III)/Fe(II) system higher or lower than +0.77 V. Explain your answer.



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

(c) A series of tests was conducted as follow:

- I When concentrated hydrochloric acid was added to dissolve black copper(II) oxide, a yellow solution was obtained.
- II Dilution of this yellow solution with water changed its colour to green and then blue.
- III When aqueous ammonia was then added, a pale blue precipitate formed which dissolved in excess aqueous ammonia to give a dark blue solution.

(i) Identify the copper-containing species formed in each test.

Test	Identity of copper-containing species
I	Yellow solution: .....
II	Blue solution: .....
III	Pale blue precipitate: .....
	Dark blue solution: .....

[2]

(ii) Write equations to illustrate the ligand exchange reactions in forming the blue solution in Test II:

.....

the dark blue solution in Test III:

..... [2]

(d) Aluminium is extracted from molten aluminium oxide,  $Al_2O_3$ , by electrolysis.

(i) With reference to  $E^\ominus$  data from the *Data Booklet*, explain why an aqueous solution of  $Al^{3+}$  (from a soluble aluminium salt) would be unsuitable as the electrolyte.

.....

.....

..... [1]

In the industry,  $Al_2O_3$  is dissolved in molten cryolite,  $Na_3AlF_6$  to lower the melting point of  $Al_2O_3$ . The molten mixture is then electrolysed using graphite electrodes.

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- (ii) The electrode reactions are very complicated. In one simplified study, some scientists say that, in molten cryolite,  $Al_2O_3$  ionises into  $Al^{3+}$  ions and  $AlO_2^-$  ions.

At the cathode,  $Al^{3+}$  is converted to  $Al$  metal:  $Al^{3+} + 3e^- \rightarrow Al$

At the anode,  $AlO_2^-$  is converted to  $Al_2O_3$  and oxygen gas.

Write an equation for the anode reaction.

..... [1]

- (iii) A typical cell operates at  $10^4$  A. Calculate the time, in hours, needed to produce 1 tonne of aluminium. (1 tonne = 1000 kg)

[2]

- (e) A saturated solution of  $XeF_2$  ( $M_r = 169$ ) in water at  $0^\circ C$  contains  $25.0 \text{ g dm}^{-3}$  of  $XeF_2$ . The solution is a strong oxidising agent, quantitatively oxidising another solution containing  $0.150 \text{ mol dm}^{-3}$  of a Cr(III) salt.  $XeF_2$  is reduced to  $Xe$  in the reaction.

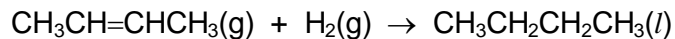
In an experiment,  $15.20 \text{ cm}^3$  of the  $XeF_2$  solution is required to completely react with  $10.0 \text{ cm}^3$  of the Cr(III) solution.

Determine the oxidation state of Cr after the reaction.

[3]

[Total: 17]

- 3 The hydrogenation of but-2-ene is shown in the equation below



- (a) Describe the changes in bond angle and the type of hybridisation involved at the site of the hydrogenation reaction.

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

- (b) Under certain conditions, but-2-ene gives alcohol **A**,  $\text{C}_4\text{H}_{10}\text{O}$ , which exists as a liquid at room temperature.

- (i) State the reagents and conditions required in this reaction. Draw the displayed formula of alcohol **A** formed in this reaction.

Reagents and conditions:

.....  
**A:**

[2]

- (ii) Explain, in terms of structure and bonding, the difference in the physical state of but-2-ene and alcohol **A** at room temperature. Draw a diagram to illustrate your answer for alcohol **A**.

.....  
 .....  
 .....  
 .....  
 .....

Diagram:

[3]

- (iii) Ester **C** is used in synthetic fruit flavours. Alcohol **A** reacts with compound **B** at room temperature to give a good yield of ester **C** with relative molecular mass of 116.

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Draw the structures of compounds **B** and **C**.

**B:**

**C:**

[2]

- (c) (i) In a separate reaction, butane is treated with a small quantity of bromine in the presence of ultraviolet light to give 1-bromobutane and 2-bromobutane. It is found experimentally that the hydrogen atom is substituted by bromine at different rates, as shown in the table below.

Type of H atom	Relative rate of substitution
Primary hydrogen	1
Secondary hydrogen	4.5

Using this information, and considering the number and types of hydrogen within butane, determine the mole ratio of the two monobrominated products.

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

- (ii) Name and outline the mechanism for the formation of 2-bromobutane in this reaction.

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use*

[3]

[Total: 14]



- (ii) The dissociation equilibrium of a solute in a solvent can be significantly shifted by the addition of a suitable substance into the solution. Suggest an inorganic reagent which can be added to increase the dissociation of HF in water. Explain your choice.

.....

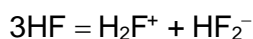
.....

.....

.....

.....[2]

- (d) Similar to water, pure liquid hydrogen fluoride also undergoes auto-ionisation according to the following equilibrium:



The ionic product of HF is  $8.0 \times 10^{-12} \text{ mol}^2 \text{ dm}^{-6}$ .

- (i) Draw the structures of both the cationic and anionic species in liquid HF. Label the types of bonding within the anionic species.

[2]

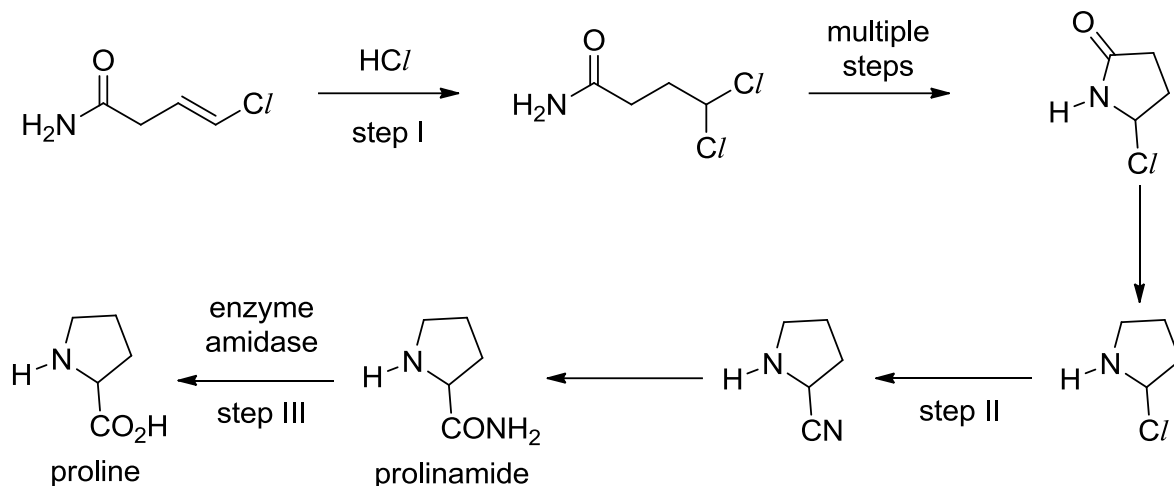
- (ii) Calculate the fraction of  $\text{H}_2\text{F}^+$  in liquid HF (density =  $1.002 \text{ g cm}^{-3}$ ), supposing that only these three species are present in the system.

[2]

[Total: 13]



- 5 The following reaction scheme is proposed for the synthesis of the amino acid proline.



- (a) (i) Draw structures of two possible intermediates formed in step I. Hence, explain why the yield of the product in step I is low.

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

- (ii) With the aid of a sketch of the Boltzmann distribution, explain how an increase in temperature affects the rate of reaction in step II.



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

- (iii) It was found that only 50% of prolinamide synthesised by the method above could be converted to proline by enzyme amidase in step III. Suggest an explanation for this observation.

For  
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use

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

- (b) The enzyme amidase used in step III contains amino acids listed in the following table.

name	abbreviation	structural formula
aspartic acid	asp	$\text{HO}_2\text{CCH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$
asparagine	asn	$\text{H}_2\text{NCOCH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$
cysteine	cys	$\text{HSCH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$
glycine	gly	$\text{CH}_2(\text{NH}_2)\text{CO}_2\text{H}$
isoleucine	ile	$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$
lysine	lys	$\text{H}_2\text{N}(\text{CH}_2)_4\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$
phenylalanine	phe	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$
serine	ser	$\text{HOCH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$

- (i) There are three  $\text{p}K_a$  values associated with aspartic acid: 2.1, 3.7 and 9.8. In the boxes below, draw the structures of the major species present in solutions of aspartic acid at pH 3 and pH 8.

pH 3	pH 8

[2]

- (ii) Complete the following table by indicating the type of interaction between each pair of amino acid residues that stabilises the tertiary structure of enzyme amidase at pH 7.

amino acid residue 1	amino acid residue 2	type of interaction
aspartic acid	lysine	
isoleucine	phenylalanine	
serine	asparagine	

[2]

- (iii) Explain how mercury ion,  $\text{Hg}^{2+}(\text{aq})$ , affects the activity of the enzyme amidase through denaturation.

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

- (c) A section of the polypeptide chain in enzyme amidase was partially hydrolysed and the following peptide fragments are produced.

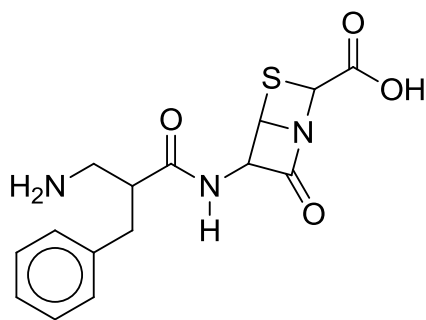
lys-gly, asp-lys-ser, cys-asn-phe, gly-cys-asn, ser-phe-lys

State the **smallest** possible sequence of amino acids in this section of the polypeptide chain using the 3-letter abbreviations.

..... [1]

- (d) A scientist extracted a new compound **D** from microorganisms. He proposed the following structure for **D**.

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use



**D**

- (i) **D** was postulated to be synthesised from amino acids.

Identify from the list in (b), **two**  $\alpha$ -amino acids that could be used in the synthesis.

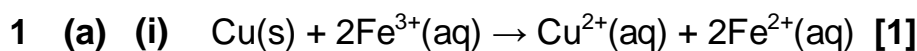
.....[1]

- (ii) Assuming that the S–C bond is inert, draw the organic products if **D** was heated in aqueous H<sub>2</sub>SO<sub>4</sub>.

[2]

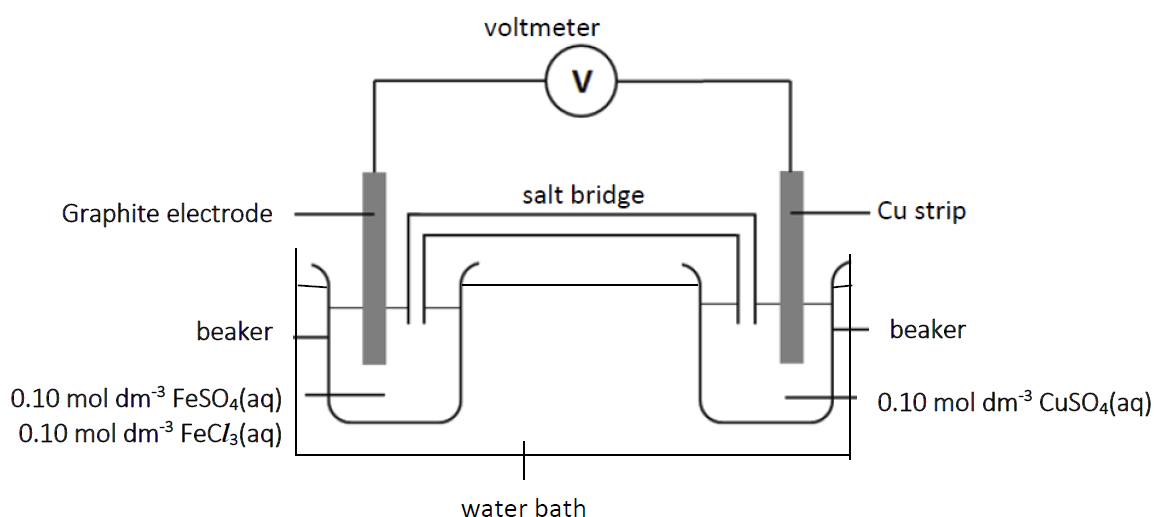
[Total: 16]

**Paper 2**



(ii) Positive. More aqueous ions produced and thus more ways that energy can be distributed in the system through the motion of ions. [1]

1 (b)



<b>M1</b>	[1/2] voltmeter and salt bridge
	[1/2] a single water bath or hot plate (not separate)
<b>M2</b>	Correct $\text{Fe}^{3+}/\text{Fe}^{2+}$ half cell: [1/2] electrode + [1/2] solutions (with correct concentration)
<b>M3</b>	Correct $\text{Cu}^{2+}/\text{Cu}$ half cell: [1/2] electrode + [1/2] solution (with correct concentration)
<b>M4</b>	[1/2] 5.56 g of solid  [1/2] details for weighing – electronic balance, weighing bottle/beaker, reweigh <u>or</u> tare and rinse out all solid
<b>M5</b>	<u>Preparation of acidified <math>\text{FeSO}_4</math> solution:</u> [1/2] adding acid <u>before</u> topping up to $100 \text{ cm}^3$ mark  [1/2] $100 \text{ cm}^3$ volumetric flask
<b>M6</b>	<u>Preparation of <math>\text{FeSO}_4</math> solution:</u> <ul style="list-style-type: none"> <li>• Transfer solid to beaker</li> <li>• Dissolve solid in beaker</li> <li>• Transfer solution to volumetric flask</li> </ul>

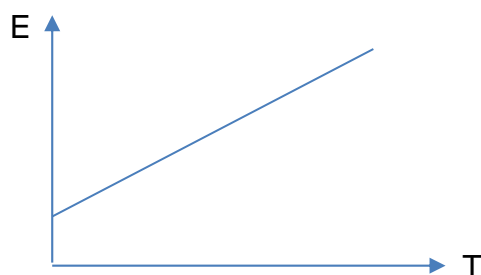
	<ul style="list-style-type: none"> <li>• Transfer washings to volumetric flask</li> <li>• Top up volumetric flask</li> <li>• Shake</li> </ul> <p><b>[1/2]</b> any 3 – 5 points <b>[1]</b> all 6 points</p>
<b>M7</b>	<p><b>[1/2]</b> measure volumes of solutions used for both half-cells (minimum volume of electrolyte in each half-cell: 20 cm<sup>3</sup>)</p> <p><b>[1/2]</b> use appropriate apparatus e.g. measuring cylinder for measurement of solutions for both half-cells</p>
<b>M8</b>	<p><b>[1/2]</b> measure temperature using thermometer or set temperature of thermostatically controlled water bath</p> <p><b>[1/2]</b> range of temperature used at least 30 °C – should have at least 5 readings with at least 5 °C intervals (lowest temperature should not be below 20 °C)</p>
<b>M9</b>	<p>Sketch of graph:</p> <p><b>[1/2]</b> Correct choice of axes – E vs T (ignore units)</p> <p><b>[1/2]</b> Linear graph with positive gradient</p> <p>Allow a plot of <math>\Delta G</math> vs T. In this case, a linear graph with negative gradient would be obtained. Candidate needs to explain clearly how <math>\Delta G</math> can be obtained.</p>
<b>M10</b>	<p><b>[1]</b> explain how entropy change could be obtained from the graph – e.g. Gradient = <math>\Delta S/nF</math> (for E vs T graph)</p> <p>Gradient = <math>-\Delta S</math> (for <math>\Delta G</math> vs T graph)</p>

### Sample procedure

1. Using an electronic weighing balance, weigh accurately 5.56g of FeSO<sub>4</sub>.7H<sub>2</sub>O in a weighing bottle.
2. Transfer this solid into a 100 cm<sup>3</sup> beaker. Reweigh the weighing bottle to account for any residual solid. Record the mass of the solid used.
3. Dissolve the solid using about 20 cm<sup>3</sup> of 0.50 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>(aq).
4. Transfer this solution into a 100 cm<sup>3</sup> volumetric flask. Rinse the beaker thoroughly and transfer all washings into the flask. Top up to the mark with deionised water/H<sub>2</sub>SO<sub>4</sub>(aq) and shake well to obtain a homogeneous solution. Label this solution as FA1.

5. Transfer 15 cm<sup>3</sup> of FA1 and 15 cm<sup>3</sup> of 0.20 mol dm<sup>-3</sup> FeCl<sub>3</sub> into a 100 cm<sup>3</sup> beaker using separate burettes.
6. Transfer 30 cm<sup>3</sup> of 0.10 mol dm<sup>-3</sup> CuSO<sub>4</sub> into a 100 cm<sup>3</sup> beaker using a burette.
7. Set up the apparatus as shown in the diagram above.
8. Ensure that the water bath is maintained at 25°C by measuring the temperature with a thermometer.
9. Record the cell potential using a voltmeter.
10. Record the cell potential at different temperatures: 30°C, 35°C, 40°C, 45°C, 50°C, 55°C.

Plot a graph of E against T.



$\Delta S = \text{gradient of the graph} \times F \times n$

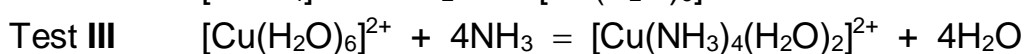
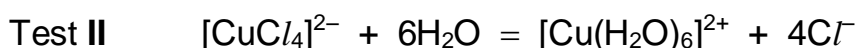
- 2 (a) (i) ½m each:
- ✓ O atom has more protons (or higher nuclear charge than C atom)
  - ✓ shielding effect is similar (or almost the same)
  - ✓ O has higher effective nuclear charge
  - ✓ its outer electrons are pulled (or attracted) more closely to the nucleus
- (ii) 1m: S atom has 1 more occupied quantum shell than O and C.
- 2 (b) (i) 1m: blood red
- (ii) ½m each:
- ✓ [Fe(CN)<sub>6</sub>]<sup>3-</sup> has (much) higher  $K_{\text{stab}}$  than [Fe(H<sub>2</sub>O)<sub>5</sub>(SCN)]<sup>2+</sup>
  - ✓ SCN<sup>-</sup> (and H<sub>2</sub>O) unable to replace CN<sup>-</sup> as the ligands attached to Fe<sup>3+</sup> i.e. no ligand exchange
- (iii) 1m:
- [Fe(edta)]<sup>-</sup> has (much) higher  $K_{\text{stab}}$  than [Fe(edta)]<sup>2-</sup>.  
 So [Fe(edta)]<sup>-</sup> is less likely to be reduced to [Fe(edta)]<sup>2-</sup>.  
 OR reduction equilibrium [Fe(edta)]<sup>-</sup> + e<sup>-</sup> ⇌ [Fe(edta)]<sup>2-</sup> lies more to the left.

OR edta ligand stabilises +3 oxidation state of Fe relative to +2 state.  
 $\therefore$  reduction potential for Fe(III)/Fe(II) with edta as ligands or for  $[\text{Fe}(\text{edta})]^-/[\text{Fe}(\text{edta})]^{2-}$  would be lower than +0.77 V.

2 (c) (i)  $\frac{1}{2}$ m each:

- ✓ yellow solution:  $[\text{CuCl}_4]^{2-}$
- ✓ blue solution:  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$
- ✓ pale blue ppt:  $\text{Cu}(\text{OH})_2$  or  $[\text{Cu}(\text{OH})_2(\text{H}_2\text{O})_4]$
- ✓ dark blue solution:  $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$

(ii) 1m each:



Accept  $\rightarrow$

2 (d) (i)  $\frac{1}{2}$ m each:

- ✓  $E^\ominus(\text{H}_2\text{O}/\text{H}_2) = -0.83 \text{ V}$  and  $E^\ominus(\text{Al}^{3+}/\text{Al}) = -1.66 \text{ V}$   
 or  $E^\ominus(\text{H}^+/\text{H}_2) = 0 \text{ V}$  and  $E^\ominus(\text{Al}^{3+}/\text{Al}) = -1.66 \text{ V}$
- ✓  $E^\ominus(\text{H}_2\text{O}/\text{H}_2)$  is higher or less negative, so  $\text{H}_2\text{O}$  would be preferentially reduced to  $\text{H}_2$ ,  $\text{Al}^{3+}$  would not be reduced to give  $\text{Al}$ .  
 or  $E^\ominus(\text{H}^+/\text{H}_2)$  is higher or less negative, so  $\text{H}^+$  would be preferentially reduced to  $\text{H}_2$ ,  $\text{Al}^{3+}$  would not be reduced to give  $\text{Al}$ .

(ii) 1m:  $2\text{AlO}_2^- \rightarrow \text{Al}_2\text{O}_3 + \frac{1}{2}\text{O}_2 + 2\text{e}^-$   
 or  $4\text{AlO}_2^- \rightarrow 2\text{Al}_2\text{O}_3 + \text{O}_2 + 4\text{e}^-$

(iii) 1m: calculates no. of moles of electrons  
 1m: calculates time in hours

$$\text{Amount of Al deposited} = \frac{1000 \times 10^3}{27} = 3.704 \times 10^4 \text{ mol}$$

$$\text{Amount of electrons passed} = 3 \times 3.704 \times 10^4 = 1.111 \times 10^5 \text{ mol}$$

$$Q = It = 1.111 \times 10^5 \times 96500 = 1.072 \times 10^{10} \text{ C}$$

$$t = \frac{1.072 \times 10^{10}}{10^4} = 1.072 \times 10^6 \text{ s} = 298 \text{ h} \quad (\text{or } 297.8 \text{ h})$$

2 (e) 1m: concludes +6

1m: calculates 0.00225 mol  $\text{XeF}_2$  and 0.00150 mol Cr(III)

1m: explains how to conclude +6, e.g. 1 mol Cr(III) loses 3 mol electrons

Sample working:



$$\text{Amount of XeF}_2 = \frac{15.2}{1000} \times \frac{25}{169} = 0.002249 \text{ mol}$$

XeF<sub>2</sub> reduced to Xe, oxidation state of Xe changes from +2 to 0

$$\text{Amount of electrons transferred} = 2 \times 0.002249 = 0.004497 \text{ mol}$$

$$\text{Amount of Cr(III)} = \frac{10}{1000} \times 0.150 = 0.00150 \text{ mol}$$

$$\frac{0.004497}{0.00150} = 3 \text{ mol of electrons lost from 1 mol of Cr(III)}$$

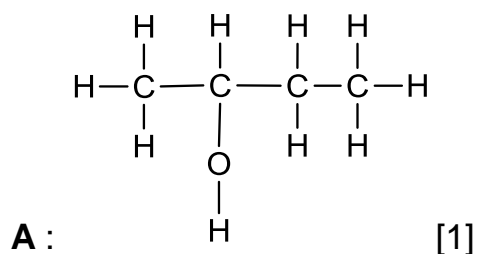
∴ oxidation state of Cr increases by 3 units

∴ oxidation state of Cr is +6 after reaction

- 3 (a) The carbon atom of the reactant (but-2-ene) in the C=C bond is sp<sup>2</sup> hybridised [1/2] and the bond angle around the carbon atom is 120° [1/2].

The carbon atom of the product (butane) in the C–C bond is sp<sup>3</sup> hybridised [1/2], and the bond angle around the carbon atom is 109.5° (accept 109°) [1/2]

- (b) (i) Steam, 300°C, 70 atm (or 60 atm), (conc) H<sub>3</sub>PO<sub>4</sub> [1]  
OR conc H<sub>2</sub>SO<sub>4</sub> followed by warming with water.



- (ii) Both but-2-ene and alcohol are simple covalent compounds /simple, discrete molecules /have simple molecular structure. [1/2]

For but-2-ene, there are weak dispersion forces between its molecules. For alcohol **A** (butan-2-ol) with polar O–H bond, there are strong intermolecular hydrogen bonding between its molecules. [1/2]

More energy is required to overcome the stronger intermolecular hydrogen bonding in alcohol **A** than the weak dispersion forces in but-2-ene which is therefore in gaseous state. [1/2]

OR

the energy provided by room temperature is insufficient to overcome the strong hydrogen bonds between alcohol **A** molecules,

Hence alcohol **A** exists as a liquid at room temperature and but-2-ene exists as gas. [1/2]

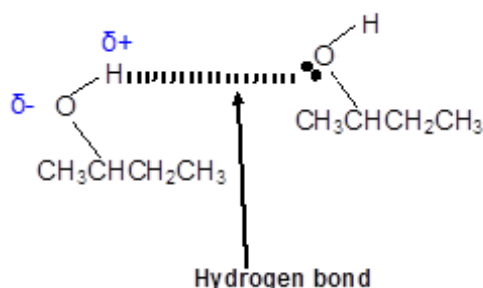
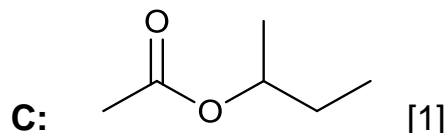
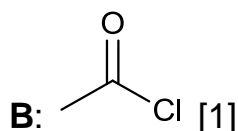


Diagram [1]

- showing correct hydrogen bond (must be oxygen atom and the H atom from the OH group)
- labelling hydrogen bond
- showing lone pair of electrons on oxygen
- labelling  $\delta+$  and  $\delta-$  for the O–H group forming H bond.

Each mistake minus 1/2 mark

(iii)

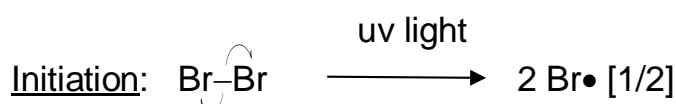


3 (c) (i) Ratio of 1-bromobutane : 2-bromobutane = 1 : 3 [1]

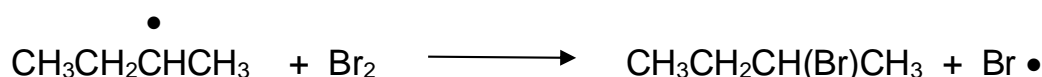
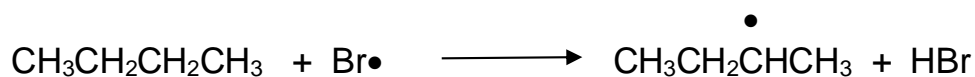
In 1-bromobutane: there are 6 possible primary ( $1^\circ$ ) H atoms for substitution and in 2-bromobutane: there are only 4 secondary ( $2^\circ$ ) H atoms for substitution [1/2]

Relative rate of substitution suggests that the mole ratio of 1-bromobutane : 2-bromobutane =  $1 \times 6 : 4.5 \times 4 = 6 : 18$  [1/2] for working

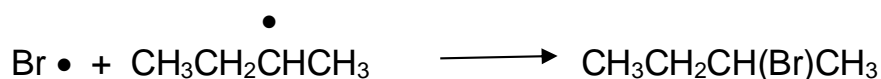
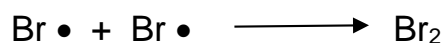
(ii) Type of mechanism: Free radical substitution [1]

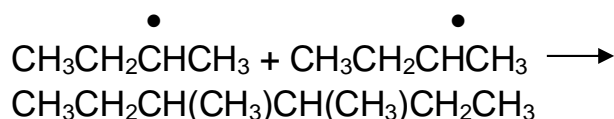


Propagation: [1]



Termination [1/2]





- 4 (a) The thermal stability of the hydrogen halides **decreases** down the group [1/2] as the **bond energy of H-X** decreases accordingly from +562 (HF) to +431 (HCl) to +366 (HBr) to +299 kJ mol<sup>-1</sup> (HI) [1/2].

Down the group, **less energy is required** to break the bond [1/2] as the **bond strength decreases** [1/2].

- (b) Step 1: To 1 cm<sup>3</sup> of each reagent in separate test tubes, add a few drops of **aqueous lead(II) nitrate** and shake. [1/2]  
If yellow ppt (of PbI<sub>2</sub>) is obtained, the test tube contains NaI. If white ppt is obtained, the test tube contains KBr or KCl. [1]

Step 2: To 1 cm<sup>3</sup> of each reagent that gave white ppt in step 1, add a few drops of **acidified sodium chlorate(I) OR Cl<sub>2</sub>(aq)** and shake. [1/2]  
If the solution turned yellow-orange, the test tube contains KBr. If the solution remained colourless, the test tube contains KCl. [1]

OR

Step 1: To 1 cm<sup>3</sup> of each reagent in separate test tubes, add a few drops of **acidified sodium chlorate(I) OR Cl<sub>2</sub>(aq)**, followed by 1 cm<sup>3</sup> of **hexane**. Shake well and leave to stand. [1]

If both layers remained colourless, the test tube contains KCl.

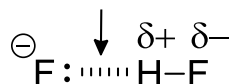
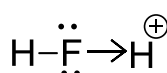
If the aqueous layer turned yellow-orange, while the organic layer turned reddish-brown, the test tube contains KBr.

If the aqueous layer turned brown, while the organic layer turned violet, the test tube contains KI. [3 obs correct:2m; 2 obs correct:1m]

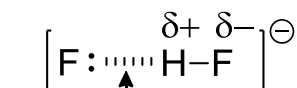
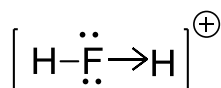
- 4 (c) (i)  $2\text{HF} + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{HF}_2^-$  [1]  
 $K = K_1 \times K_2 = (1.1 \times 10^{-3})(2.6 \times 10^{-1}) = 2.86 \times 10^{-4}$  [1]

- (ii) NaOH, Na<sub>2</sub>CO<sub>3</sub>, etc. Base reacts with acid, lowers [H<sub>3</sub>O<sup>+</sup>] and shifts position of equilibrium forward. [2]

- (d) (i) hydrogen bonding



OR



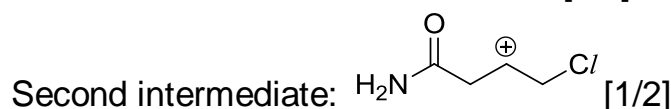
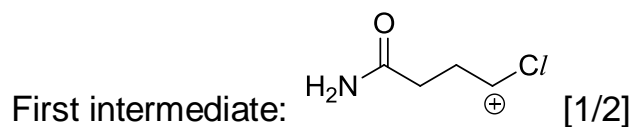
hydrogen bonding [1] x 2

(ii)  $[H_2F^+] = [HF_2^-] = \sqrt{(8.0 \times 10^{-12})} = 2.83 \times 10^{-6} \text{ mol dm}^{-3}$  [1]  
 $[HF] = \frac{1.002 \times 10^3}{1.0 + 19.0} = 50.1 \text{ mol dm}^{-3}$

The auto-dissociation causes a negligible change in [HF], hence the

requested fraction is  $\frac{[H_2F^+]}{[HF]} = \frac{2.83 \times 10^{-6}}{50.1} = 5.65 \times 10^{-8}$  [1]

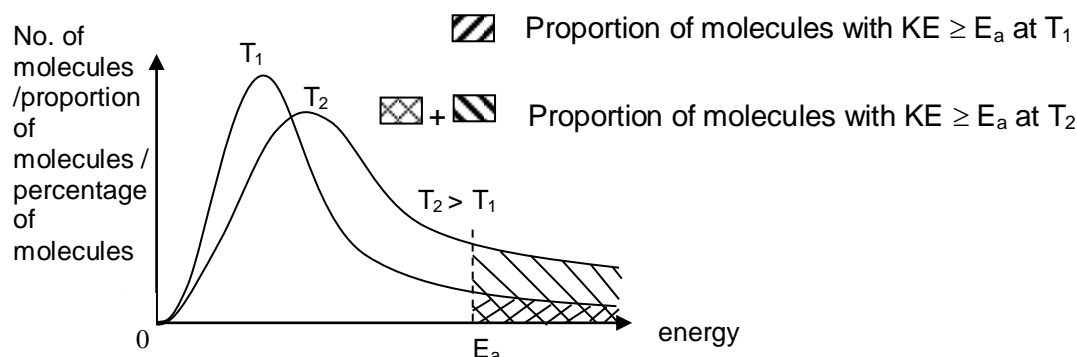
5 (a) (i)



Product formed is from the first intermediate which is less stable than second intermediate. [1/2]

This is because the positive charge is intensified by electron withdrawing chlorine through inductive effect. [1/2]

(ii) Boltzmann distribution diagram: [1]



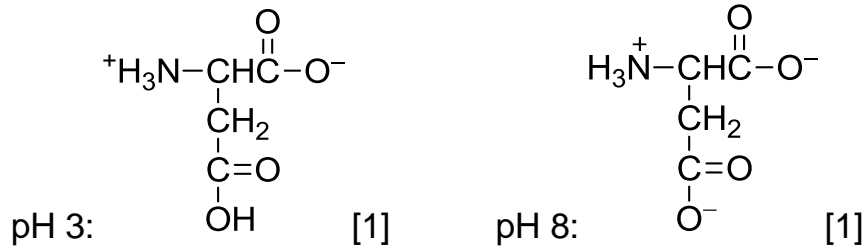
At higher temperatures, the proportion of molecules with kinetic energy greater than or equal to activation energy increases [1].

Thus, frequency of effective collision increases [0.5], reaction rate increases [0.5]

(iii) The prolinamide is synthesised as a racemic mixture containing equal proportions of two enantiomers. [1/2]

Hence only 50% of the synthesised prolinamide can fit into / would possess the correct 3D shape to bind to the active site of the enzyme. [1/2]

5 (b) (i)



(ii)

aspartic acid	lysine	<b>Ionic interaction</b>
isoleucine	phenylalanine	<b>dispersion forces / van der Waals interaction</b>
serine	asparagine	<b>Hydrogen bond</b>

3 correct = [2], 2 correct = [1], 1 correct = [1/2]

(iii) Mercury ion disrupts the disulfide bridge by binding tightly with -SH of cysteine residue

OR

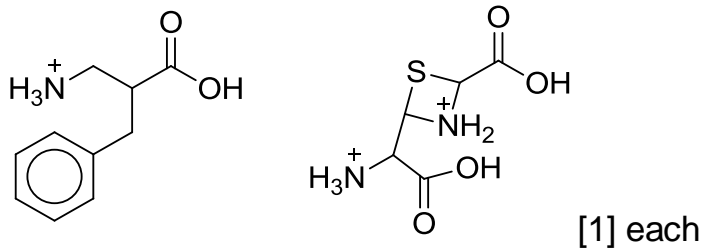
Mercury ion disrupts the ionic interaction by forming ionic interaction with -CO<sub>2</sub><sup>-</sup> side chain of aspartic acid. [1]

The tertiary structure / shape of the enzyme is altered, and hence its function is lost. [1]

5 (c) Asp-lys-ser-phe-lys-gly-cys-asn-phe [1]

(d) (i) Glycine [1/2], cysteine [1/2]

(d) (ii)



**C2 Preliminary Examinations  
Higher 2**

CANDIDATE  
NAME

CT GROUP

15S

CENTRE  
NUMBER

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INDEX  
NUMBER

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**CHEMISTRY**

**9647/03**

Paper 3 Free Response

**19 September 2016**

**2 hours**

Candidates answer on separate paper.

Additional Materials: Answer Paper

Data Booklet

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**INSTRUCTIONS TO CANDIDATES**

Write your name and class on all the work you hand in.

Write in dark blue or black pen.

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 **new** piece of paper.

A Data Booklet is provided.

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.

**Write down the question numbers for the questions attempted on the cover page provided.**

Answer any **four** questions.

- 1 (a) Suggest and explain how the boiling points of 1-chlorobutane and 1-bromobutane differ from each other. [2]

- (b) (i) Define the term *standard enthalpy change of combustion*. [1]

- (ii) Use of the *Data Booklet* is relevant to this question.

In an experiment to determine the enthalpy change of combustion of bromobutane, a quantity of the fuel was burnt underneath a copper can containing 200 g of water. It was found that the temperature rose by 45.0 °C after 2.35 g of bromobutane had been burnt. The heat transfer was known to be only 80% efficient.

Calculate the enthalpy change of combustion of the bromobutane. Ignore the heat capacity of the copper can. [2]

- (c) An experiment was set up to study the reaction between 2-bromo-3-methylbutane and sodium hydroxide. The reagents used were **FA1**, containing 0.0100 mol dm<sup>-3</sup> of 2-bromo-3-methylbutane and **FA2**, containing 0.0100 mol dm<sup>-3</sup> NaOH. In each experiment, the reagents were dissolved in a suitable solvent to ensure good mixing. The results are recorded in the table below.

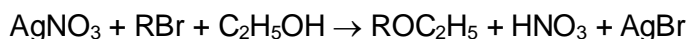
Expt	Volume of <b>FA1</b> / cm <sup>3</sup>	Volume of <b>FA2</b> / cm <sup>3</sup>	Volume of solvent / cm <sup>3</sup>	Rate / mol dm <sup>-3</sup> s <sup>-1</sup>
1	10.0	30.0	60.0	7.40 x 10 <sup>-7</sup>
2	5.0	20.0	25.0	9.86 x 10 <sup>-7</sup>
3	10.0	5.0	35.0	4.93 x 10 <sup>-7</sup>

- (i) Use the data in the table to deduce the order of reaction with respect to 2-bromo-3-methylbutane and sodium hydroxide. Hence, write a rate equation for this reaction. [3]
- (ii) With reference to your answer to (c)(i), describe the mechanism for the reaction between 2-bromo-3-methylbutane and sodium hydroxide. [3]
- (iii) Calculate the rate constant for the reaction, stating the units. [2]

- (d) In a separate experiment, a student performed the following qualitative analysis tests on three different bromoalkanes: 1-bromobutane, 2-bromobutane and 2-bromo-2-methylpropane. Different solvents were used for **Test 1** and **Test 2** and it was observed that the choice of solvents did have an effect on the type of reaction mechanisms undergone by the bromoalkanes.

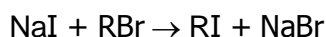
**Test 1:**

When silver nitrate was added to the bromoalkanes using ethanol as the solvent, silver bromide was precipitated for all three bromoalkanes at different rates.



**Test 2:**

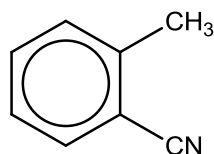
When sodium iodide in propanone solvent was added to the bromoalkanes, sodium bromide was precipitated for 1-bromobutane and 2-bromobutane at different rates, but not 2-bromo-2-methylpropane.



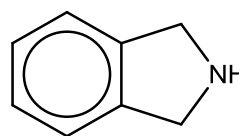
The observations for each test were recorded in the following table.

	Time taken for precipitate to appear	
	Test 1	Test 2
1-bromobutane	5 min	Almost immediately
2-bromobutane	3 min	5 min
2-bromo-2-methylpropane	Almost immediately	No precipitate

- (i) Different nucleophilic substitution mechanisms have been proposed for the reactions in the two tests.
- Considering the information provided, suggest the predominant mechanism undergone in each test. [1]
- (ii) Considering the structure of the bromoalkane, explain why the test results support your answer in (d)(i). [2]
- (iii) Considering the interactions involved with the solvent, explain why the suggested mechanism for **Test 1** occurs predominantly. [1]
- (e) 2-methylbenzotrile can be used as a starting reagent to form compound **A**. Propose a synthesis route for the formation of compound **A** in no more than 3 steps, showing clearly the reagents, conditions and structures of the intermediates formed.



2-methylbenzotrile



Compound **A**

[3]

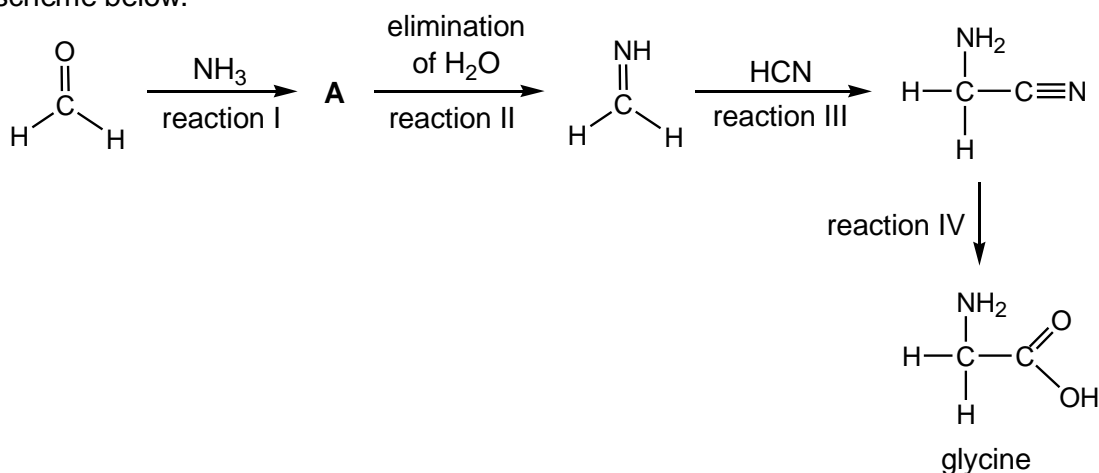
[Total: 20]



- 2 Ethanoic acid behaves as a weak acid in water, with  $K_a = 1.8 \times 10^{-5} \text{ mol dm}^{-3}$ .  
In contrast, ethanoate ion behaves as a weak base in water, with  $K_b = 5.6 \times 10^{-10} \text{ mol dm}^{-3}$ .

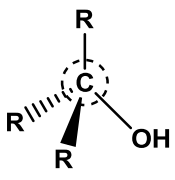
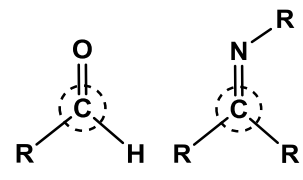
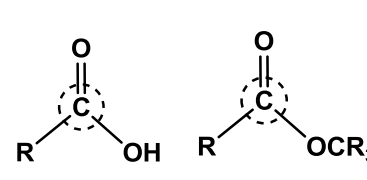
- (a) (i) Write the expressions for  $K_a$  and  $K_b$  of ethanoic acid and ethanoate ion respectively, and use these expressions to show that the product  $K_a \times K_b$  has a constant value at a fixed temperature. [2]
- (ii) Compare the relative strength of ethanoate ion and water as bases, and explain with the aid of an equation, whether a solution of sodium ethanoate is acidic, alkaline, or neutral. [2]
- (iii) Calculate the pH of a solution which contains  $0.50 \text{ mol dm}^{-3}$  ethanoic acid and  $0.50 \text{ mol dm}^{-3}$  sodium ethanoate. [1]

- (b) The Strecker synthesis is a route to prepare amino acids. Glycine (2-aminoethanoic acid) can be prepared from methanal as shown in the reaction scheme below.



- (i) Suggest a structure for compound **A**. [1]
- (ii) The product of **reaction II** is an imine, which has a C=N bond. Methanal undergoes reaction with another compound **B** to form an orange solid **C** which also has a C=N bond. Name compound **B** and draw the structure of the orange solid **C**. [2]
- (iii) What *type of reaction* is occurring during **reaction III**? [1]
- (iv) State the reagents and conditions for **reaction IV**. [1]
- (v) Compound **D** is an isomer of glycine. Upon warming **D** with dilute sodium hydroxide, a gas which turns litmus blue is evolved. Draw the structure of **D**. [1]
- (vi) A carbonyl compound **E** can be used as the starting material to prepare another amino acid, alanine (2-aminopropanoic acid) using the Strecker synthesis. Draw the structure of **E**. [1]
- (vii) The synthesis of alanine in (b)(vi) produces a mixture of two optical isomers. State which one of the reactions, **I** to **IV**, gives rise to this mixture, and explain your choice briefly. [2]

- (c) In organic chemistry, the number of bonds that a given carbon atom has with electronegative atoms like O or N is called the functional group level of that carbon atom. Some examples are shown below, but there are many other possibilities.

Functional group level		
1	2	3
		

(R = alkyl or aryl group or H atom)

- (i) State the functional group level of the carbon atom in methane and in carbon dioxide. [1]

Keeping track of the functional group level can be used to understand a large number of organic reactions.

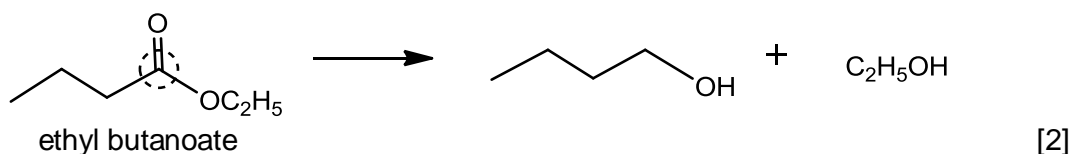
During **oxidation reactions**, the functional group level increases as C–H bonds are converted into new C–O bonds.

During **reduction reactions**, the functional group level decreases as C–O bonds are converted into new C–H bonds.

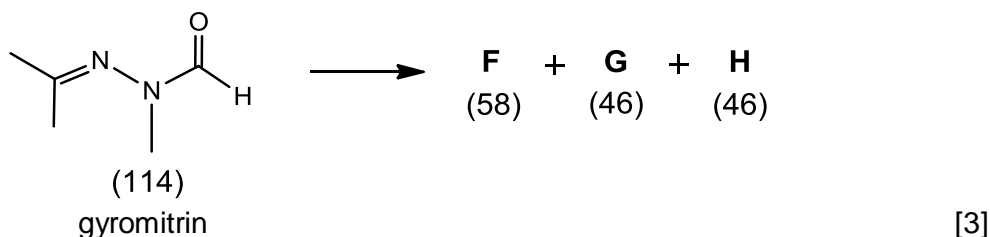
During **hydrolysis reactions**, the functional group level of every carbon remains the same.

In each of the reactions in (c)(ii) and (c)(iii), no carbon-carbon bonds are broken or formed.

- (ii) Ethyl butanoate undergoes the following reaction to form two products. State the functional group level of the *circled* carbon atom at the start and end of the reaction, and hence deduce whether the reaction is an oxidation, a reduction, or a hydrolysis reaction.



- (iii) Gyromitrin, a toxin found in fungi, undergoes hydrolysis to give three different products, **F**, **G**, and **H**. Suggest structures for these products using their relative molecular masses (shown in brackets) and the functional group levels of the carbon atoms.



[Total: 20]

3 Use of the Data Booklet is relevant to this question.

In 2016, 4 new elements were added to the Periodic Table. Part of the Periodic Table showing information about the 4 new elements is shown below.

– Nh nihonium 113		– Mc moscovium 115		– Ts tennessine 117	– Og oganeson 118	<b>Key</b> relative atomic mass atomic symbol name proton number
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Mc, Ts, and Og were synthesised by accelerating calcium ions into atoms of heavier elements. Once in every few billion collisions, the nuclei of the 2 particles would fuse and give rise to the new element. For example, Ts was synthesised using berkelium ( $_{97}\text{Bk}$ ).

- (a) (i) State the heavy element used in the synthesis of Mc. [1]
- (ii) Based on the relative position of Ts in the Periodic Table, predict the physical state of Ts at room temperature. Give a brief explanation for your answer. [2]
- (iii) Scientists have predicted the existence of superheavy elements above proton number 120 that are stable under standard conditions. One such element, if successfully synthesised in large quantities, would give rapid effervescence of a colourless gas in water, and its oxide would be basic in nature. The sulfate compound of the element would be insoluble in water.

State, with reasons, the group of the Periodic Table that this element is likely to belong. [2]

- (b) Scientists are already working on the next element of proton number 119 using berkelium and titanium.
- (i) Explain, using relevant electronic configurations, why titanium is considered a transition element but not zinc. [2]
- (ii) Tetrahydrofuran (THF),  $M_r = 72.1$ , is a simple covalent molecule that behaves as a monodentate ligand. Titanium forms a complex with zero net charge with THF and chloride ligands. A 1.00 g sample of the complex was completely hydrolysed in water and filtered. The residue contained  $2.99 \times 10^{-3}$  mol of  $\text{TiO}_2$ . The filtrate yields 1.72 g of silver chloride after treating with aqueous silver nitrate. Determine the coordination number of the central titanium of the complex. [3]

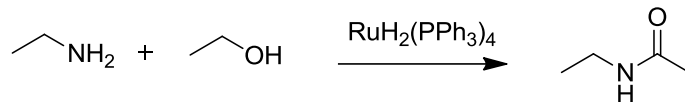
Calcium and titanium are both metals but differ in their chemical and physical properties.

- (c) (i) Compounds of calcium contain the  $\text{Ca}^{2+}$  ion. The corresponding ion of titanium is  $\text{Ti}^{3+}$ . Use relevant data from the *Data Booklet* to explain why  $\text{Ca}^{3+}$  compounds do not exist and  $\text{Ti}^{3+}$  compounds do. [3]
- (ii) Draw labelled diagrams to show the shapes of the orbitals in the **outermost** occupied quantum shell of a  $\text{Ca}^{2+}$  ion. [2]
- (iii) Explain why the melting point of titanium is higher than that of calcium. [2]
- (iv) Describe the observations when calcium is burned in air, and excess water is added to the resulting oxide. Write equations where appropriate and suggest the pH value of the aqueous solution formed. [3]

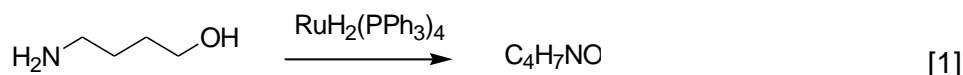
[Total: 20]

4 Transition metal catalysed reactions have emerged in recent years as powerful tools for preparing organic compounds from previously unavailable routes. Ruthenium-based catalysts have been at the heart of these advances.

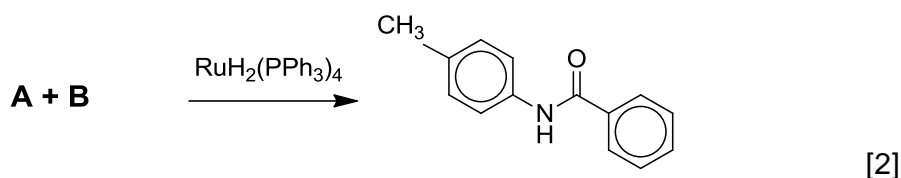
(a) The ruthenium(II) based catalyst  $\text{RuH}_2(\text{PPh}_3)_4$ , where  $\text{PPh}_3 = \text{P}(\text{C}_6\text{H}_5)_3$ , is able to catalyse the formation of an amide under suitable conditions, as shown in the scheme below.



(i) Draw the structure of the product for the reaction below.



(ii)  $\text{RuH}_2(\text{PPh}_3)_4$  also catalyses the formation of the amide shown in the reaction scheme below. Draw the structures of compounds **A** and **B**.

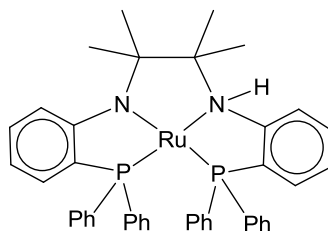


(iii) Propose a synthetic route for the formation of compounds **A** and **B**, using only methylbenzene as the starting compound in each case. [3]

(b) The catalyst  $\text{RuH}_2(\text{PPh}_3)_4$  exhibits geometric isomerism. In the cis configuration, the H-Ru-H angle is  $90^\circ$ , while in the trans configuration, the H-Ru-H angle is  $180^\circ$ .

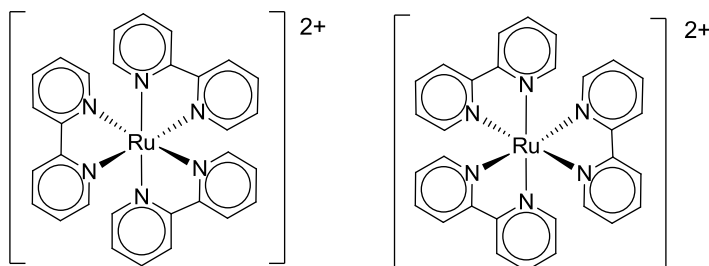
Draw labelled diagrams showing the structures of the two isomers. [2]

(c) In addition to  $\text{RuH}_2(\text{PPh}_3)_4$ , other ruthenium complexes like the one shown below, also proved to be effective in organic synthesis.

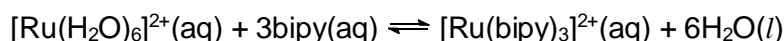


State the oxidation number of ruthenium in the complex above. [1]

- (d) The complex ion tris(bipyridine)ruthenium(II) is a catalyst which has received much attention because of its ability to exhibit optical isomerism. Two of its isomers are shown below.



- (i) Explain why the complex above exhibits optical isomerism. [1]
- (ii) Tris(bipyridine)ruthenium(II) cation contains three bipyridine rings, which can be represented by the symbol, bipy. The formation of tris(bipyridine)ruthenium(II) from aqueous ruthenium(II) ions is shown in the equation below. The enthalpy change for this reaction is approximately zero.



Deduce the sign of the entropy change,  $\Delta S$ , and hence the sign of the free energy change,  $\Delta G$ , in this reaction. [3]

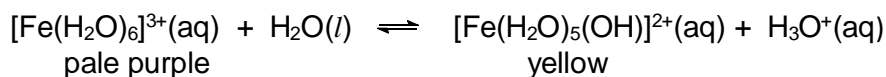
Iron is directly above ruthenium in the transition metal block of the Periodic Table.

- (e) Ligands are able to modify the difference in energy between the non-degenerate d-orbitals in an octahedral crystal field.

The following table lists the different colours of visible light and their corresponding wavelengths. The energy of light is inversely proportional to its wavelength.

Colour	violet	blue	green	yellow	red
Wavelength / nm	400	450	500	600	650

The equation below represents the hydrolysis of Fe(III) ions in water. The pale yellow colour of Fe(III) solutions observed commonly is actually due to the presence of the complex ion  $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$ , while unhydrolysed  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  is pale purple in color.

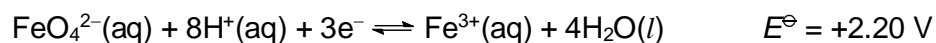


- (i) With reference to the colours of the two complexes above, explain which complex ion has a larger energy gap between their d-orbitals. [2]
- (ii) Electrons in both  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$  exhibit a 'high spin' state, where electrons occupy the d-orbitals singly before starting to pair up in the lower energy d-orbitals.

Draw a suitable diagram to show the electron distribution in the 3d subshell of a  $\text{Fe}^{3+}$  ion in a 'high spin' **excited** state, where an electron from a lower energy d-orbital has been promoted to a higher energy d-orbital by absorbing light of a certain wavelength.

[1]

(f)  $\text{K}_2\text{FeO}_4$  is a strong oxidising reagent which is dark red in colour.



Using relevant data from the *Data Booklet*, describe and explain the observations when the following solutions are mixed together in **I** and in **II** respectively. Calculate the  $E^\ominus_{\text{cell}}$  and write a balanced equation for any reaction occurred.

**I**  $\text{K}_2\text{FeO}_4$  and  $\text{H}_2\text{O}_2$

**II**  $\text{KMnO}_4$  and  $\text{Fe}(\text{NO}_3)_3$

[4]

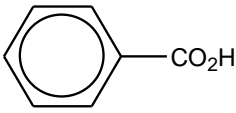
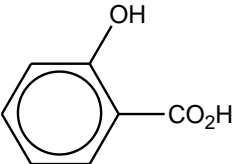
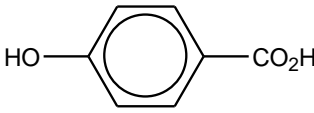
[Total: 20]

- 5 (a)  $\text{Ag}_2\text{CO}_3$  is a sparingly soluble salt. A  $100 \text{ cm}^3$  saturated solution of  $\text{Ag}_2\text{CO}_3$  in water was found to contain  $2.57 \times 10^{-4} \text{ mol dm}^{-3}$  of  $\text{Ag}^+$  ions.

(i) Calculate the  $K_{\text{sp}}$  of  $\text{Ag}_2\text{CO}_3$  and state its units. [2]

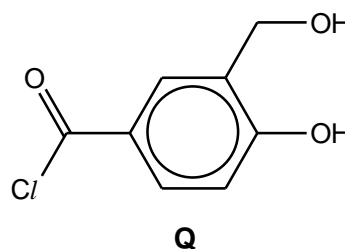
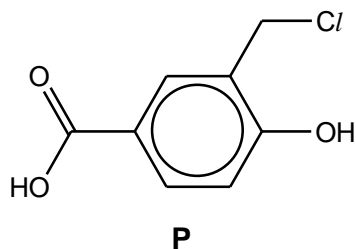
(ii) Hence, calculate the solubility of  $\text{Ag}_2\text{CO}_3$  when  $2.50 \text{ g}$  of  $\text{Na}_2\text{CO}_3$  solid was added to the solution above. [2]

- (b) The table below shows the  $\text{p}K_{\text{a}}$  values of benzoic acid and its derivatives.

Acid	benzoic acid	2-hydroxybenzoic acid	4-hydroxybenzoic acid
Structure			
$\text{p}K_{\text{a}}$	4.20	2.98	4.58

Rank the three compounds in order of **increasing** acid strength and account for the trend. [3]

- (c) Compounds **P** and **Q** can be synthesised from 4-hydroxybenzoic acid.



Suggest the reagents and conditions for a reaction that could be used to distinguish between **P** and **Q**. You need to state how **each** of **P** and **Q** react. [2]

- (d) Heating compound **A**,  $\text{C}_{13}\text{H}_{14}\text{O}_3$ , under reflux with dilute  $\text{H}_2\text{SO}_4$  produces compound **B**,  $\text{C}_8\text{H}_8\text{O}$ , and compound **C**,  $\text{C}_5\text{H}_8\text{O}_3$ .

**B** reacts with aqueous bromine to give compound **D**,  $\text{C}_8\text{H}_7\text{O}_2\text{Br}_3$ . On heating **B** with acidified  $\text{KMnO}_4$ , 4-hydroxybenzoic acid and carbon dioxide gas are formed.

When **C** is heated with acidified  $\text{KMnO}_4$ , compound **E** is the only organic product formed. Both **C** and **E** gave yellow precipitate when warmed with alkaline aqueous iodine. Treatment of **E** with aqueous  $\text{Na}_2\text{CO}_3$  liberates carbon dioxide gas.

- (i) When vaporised in a suitable apparatus,  $0.219 \text{ g}$  of **E** occupied a volume of  $70 \text{ cm}^3$  at  $150 \text{ }^\circ\text{C}$  and a pressure of  $125 \text{ kPa}$ .

Calculate the relative molecular mass of **E** and hence suggest a molecular formula for **E**, given that it contains 3 carbon atoms. [2]

- (ii) Suggest structures for **A** to **E**, explain your reasoning. [9]

[Total: 20]



### Paper 3

1 (a) 1-bromobutane has a higher boiling than 1-chlorobutane. Both 1-bromobutane and 1-chlorobutane are simple molecular. Since 1-bromobutane has a larger electron cloud size [1], there is stronger dispersion forces between its molecules as compared to 1-chlorobutane. Hence, more energy [1] is needed to break the stronger dispersion forces for 1-bromobutane.

(b) (i) Standard enthalpy change of combustion is the heat evolved when one mole of the substance is completely burnt in excess oxygen at 298 K and 1 atm. [1]

(ii) Heat absorbed by water  $q = (200)(4.18)(45.0) = 37620 \text{ J}$   
 $= 37.6 \text{ kJ [1]}$

Enthalpy change of combustion =  $[100/80 \times 37.62] / (2.35/136.9)$   
 $= -2.74 \times 10^3 \text{ kJ mol}^{-1}$  [1]

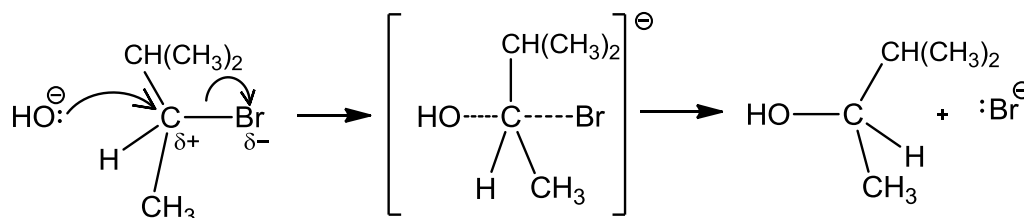
(c) (i) Comparing Expt 1 and 2,  
(Total volume in Expt 2 is half that of Expt 1.)  
Concentration of 2-bromo-3-methylbutane is constant, when concentration of NaOH increases 4/3 times, rate increases 4/3 times. Hence, the reaction is 1<sup>st</sup> order with respect to NaOH [1]

Comparing Expt 2 & 3,  
(Total volume in Expt 2 and 3 are the same)  
When concentration of 2-bromo-3-methylbutane increases 2 times and concentration of NaOH decreases 4 times, the rate decreases 2 times. Since the reaction is first order with respect to NaOH, the reaction is thus 1<sup>st</sup> order with respect to 2-bromo-3-methylbutane [1]

**[Calculation method also accepted]**

Rate =  $k$  [2-bromo-3-methylpentane][NaOH] [1] ecf

(ii) S<sub>N</sub>2 Nucleophilic substitution [1]



2 m for mechanism

(iii) Rate =  $k$  [2-bromo-3-methylbutane][NaOH]

To obtain the numerical value for  $k$ , substitute the rate and the respective concentrations into the rate equation.

$$7.40 \times 10^{-7} = k \left[ \frac{\left(\frac{10}{1000}\right)(0.0100)}{\left(\frac{10.0+30.0+60.0}{1000}\right)} \right] \left[ \frac{\left(\frac{30}{1000}\right)(0.0100)}{\left(\frac{10.0+30.0+60.0}{1000}\right)} \right]$$

$$k = 0.247 \quad \text{[1] Calculation}$$

To derive the units,

$$\text{mol dm}^{-3} \text{ s}^{-1} = k (\text{mol dm}^{-3})^2$$

$$k = \text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1} \quad \text{[1] Units}$$

(d) (i) Test 1: **S<sub>N</sub>1** mechanism

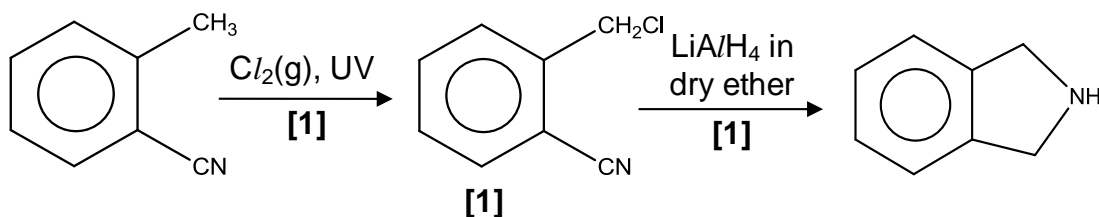
Test 2: **S<sub>N</sub>2** mechanism [1]

(ii) In Test 1, the rate of reaction is the fastest for the tertiary bromoalkane. The carbocation formed from the tertiary bromoalkane is stabilised by three electron-donating alkyl groups, hence it undergoes S<sub>N</sub>1 rapidly. [1]

In Test 2, the rate of reaction is the fastest for the primary bromoalkane as there is least steric hindrance when the nucleophile attacks the electron deficient carbon atom of the primary bromoalkane, hence it undergoes S<sub>N</sub>2 rapidly. [1]

(iii) The carbocation formation is favoured as ethanol can form ion-dipole interactions with the carbocation intermediate thereby stabilising it [1].

(e)



For the second step, accept H<sub>2</sub>, Ni, high temp and high pressure. Also accept if split up last step to show reduction followed by nucleophilic substitution with heat for last step.

2 (a) (i)

$$K_a = \frac{[\text{CH}_3\text{CO}_2^-][\text{H}^+]}{[\text{CH}_3\text{CO}_2\text{H}]}$$

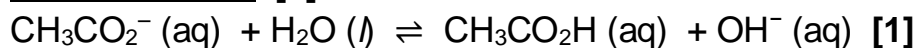
$$K_b = \frac{[\text{CH}_3\text{CO}_2\text{H}][\text{OH}^-]}{[\text{CH}_3\text{CO}_2^-]}$$

[1]

$$\begin{aligned} K_a \times K_b &= \frac{[\text{CH}_3\text{CO}_2^-][\text{H}^+]}{[\text{CH}_3\text{CO}_2\text{H}]} \times \frac{[\text{CH}_3\text{CO}_2\text{H}][\text{OH}^-]}{[\text{CH}_3\text{CO}_2^-]} \\ &= [\text{H}^+][\text{OH}^-] \\ &= K_w \text{ (ionic product of water), which is a constant. } \end{aligned} \quad [1]$$

(ii) CH<sub>3</sub>CO<sub>2</sub>H is a weak acid so its conjugate base CH<sub>3</sub>CO<sub>2</sub><sup>-</sup> is a stronger base than water.

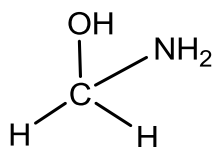
So CH<sub>3</sub>CO<sub>2</sub><sup>-</sup> undergoes hydrolysis forming OH<sup>-</sup> ions, forming an alkaline solution. [1]



(iii) As [CH<sub>3</sub>CO<sub>2</sub>H] = [CH<sub>3</sub>CO<sub>2</sub><sup>-</sup>], this is a maximum capacity buffer;

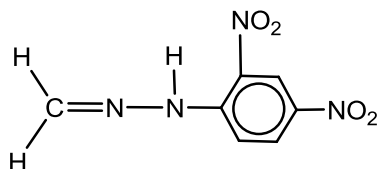
$$\begin{aligned} \text{so pH} &= \text{p}K_a \\ &= -\log(1.8 \times 10^{-5}) \\ &= 4.74 \end{aligned} \quad [1]$$

(b) (i) A [1]



(ii) B = 2,4-dinitrophenylhydrazine [1]

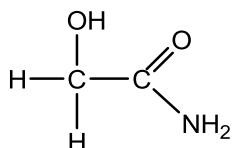
**C [1]**



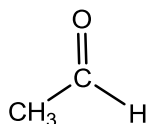
**(iii) addition [1]**

**(iv) Dilute  $H_2SO_4$  /  $HNO_3$  /  $HCl$ , heat [1]**

**(v) D [1]**



**(vi) E [1]**



**(vii) Reaction III [1]**

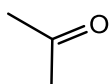
The imine is trigonal planar about the imine carbon atom. The nucleophile can thus attack this  $\delta+$  carbon atom in equal probability from the top as well as the bottom [1], resulting in forming equal proportions of the two optical isomers / racemic mixture.

**(c) (i) Functional group level of C in  $CH_4 = 0$ ; in  $CO_2 = 4$  [1]**

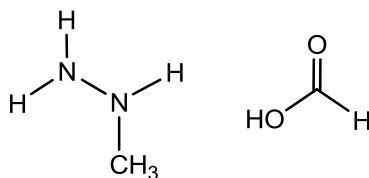
**(ii) Functional group level of circled C at the start = 3; at the end = 1 [1]**

As the functional group level decreases, the reaction is reduction. [1]

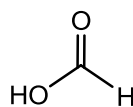
**(iii)**



**F**  
**1m each**



**G / H**



3 (a) (i) [1] Americium (Am)

(ii) Ts lies below astatine in Group VII, following the trend of increasing melting point down the group [1], it should be a solid [1] like iodine or astatine.

(iii) [1] Group II.

[0.5]: Effervescence of hydrogen gas with water => Group I or II metal or

Basic oxide hydrolyses to give metal hydroxide in water => Group I or II metal

[0.5]: Sulfate insoluble => Group II metal as Group I sulfates all soluble. Or Group II sulfate solubility decreases down the group.

(b) (i) Titanium is able to form ions with incomplete d-subshell, Ti<sup>2+</sup>: 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup>3p<sup>6</sup>3d<sup>2</sup> or Ti<sup>3+</sup>: 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup>3p<sup>6</sup>3d<sup>1</sup> [1]

but

zinc forms only the Zn<sup>2+</sup> ion which has 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup>3p<sup>6</sup>3d<sup>10</sup> configuration with a fully filled d-subshell [1].

(ii) No. of moles of titanium = no. of moles of TiO<sub>2</sub> = 2.99 × 10<sup>-3</sup> mol

No. of moles of chloride = 1.72 / 143.5 = 0.0120 mol

Ratio of chloride ions to titanium = 0.0120 / 2.99 × 10<sup>-3</sup> = 4.01 = 4 [1]

1<sup>st</sup> mark can be awarded if student is able to provide an answer that clearly recognises from TiO<sub>2</sub> that the complex is formed from a Ti(IV) center [0.5] and since complex is electrically neutral, there must be 4 chloride ions [0.5]

Mass of titanium and chloride in 1 g sample = 2.99 × 10<sup>-3</sup> × 189.9 = 0.568 g

Mass of coordinated THF molecules in 1 g sample = 0.432 g

0.432 / (72.1 × n) = 2.99 × 10<sup>-3</sup>

No. of THF molecules coordinated = 0.432 / (2.99 × 10<sup>-3</sup> × 72.1) = 2.00 = 2 [1] (*working for no. of THF ligands must be shown*)

Coordination number = 6 [1] (*this answer must be based on an actual no. of chloride and THF ligands stated earlier*)

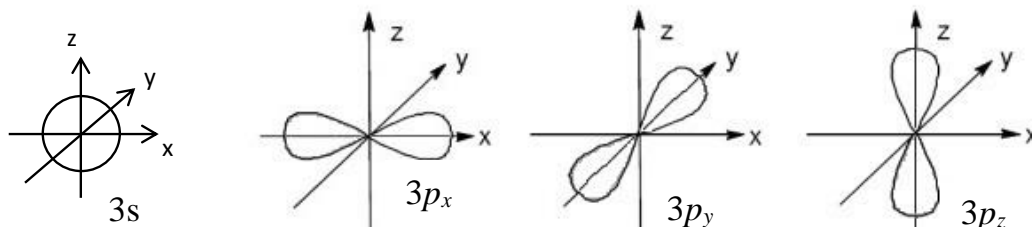
Allow ecf from errors in number or chloride and THF ligands calculated, rounded up to whole numbers.

(c) (i) The 3<sup>rd</sup> ionization energy of Ca (+4940 kJ mol<sup>-1</sup>) is much higher than the 2<sup>nd</sup> (+1150 kJ mol<sup>-1</sup>) as the 3<sup>rd</sup> electron in Ca is removed from an inner quantum shell [1] which requires a lot of energy. Thus, Ca<sup>3+</sup> compounds do not exist.

For Ti, the 2<sup>nd</sup> and 3<sup>rd</sup> ionisation energies (+1310, +2720 kJ mol<sup>-1</sup>) do not differ greatly as 4s and 3d electrons are close in energy [1]. Thus, Ti<sup>3+</sup> can be formed.

[1]: some comparison/discussion of ionisation energies for Ca and Ti pertaining to the high 3<sup>rd</sup> ionisation energy for Ca compared to Ti.

(ii)

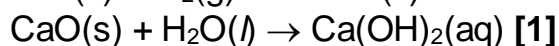
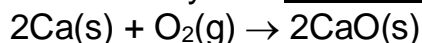


[2]

(iii) In calcium, only the 4s electrons are donated to the sea of delocalised electrons, while in titanium, both the 4s and 3d electrons are involved (idea of more electrons contributed towards metallic bonding). **OR** Titanium cations have higher charge/ smaller ionic radius / greater charge density than calcium cations. [1]

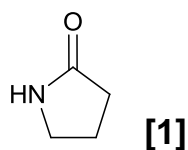
This leads to titanium having stronger metallic bond strength and more energy is needed to overcome the metallic bonds [1] and hence a higher melting point.

(iv) Burns slowly with brick-red flame, leaving a white residue [1]

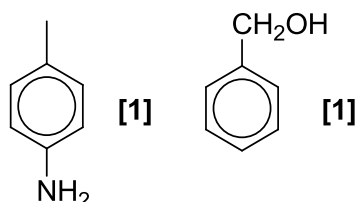


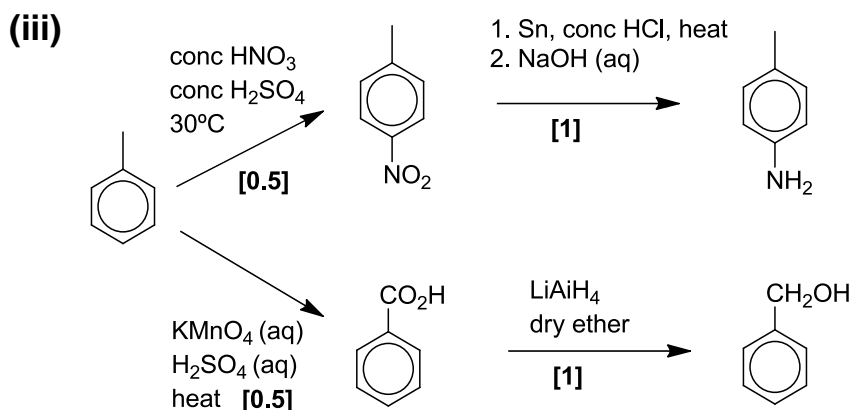
Ca(OH)<sub>2</sub> dissolves / gives a colorless solution in water to give an alkaline solution of pH = 12 [1] (Accept any value above 7)

4 (a) (i)

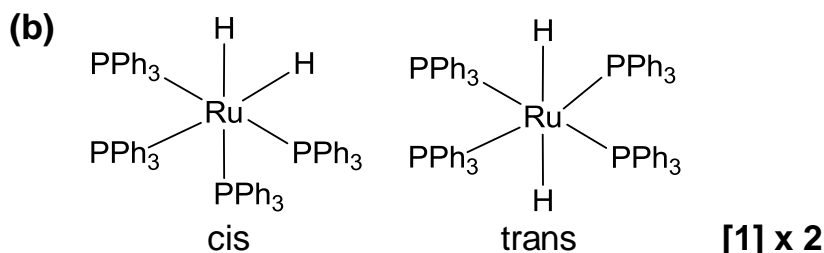


(ii)





accept  $\text{Cl}_2$  (g), UV or heat, followed  $\text{NaOH}$  (aq), heat to get phenylmethanol.



(c) +1 [1]

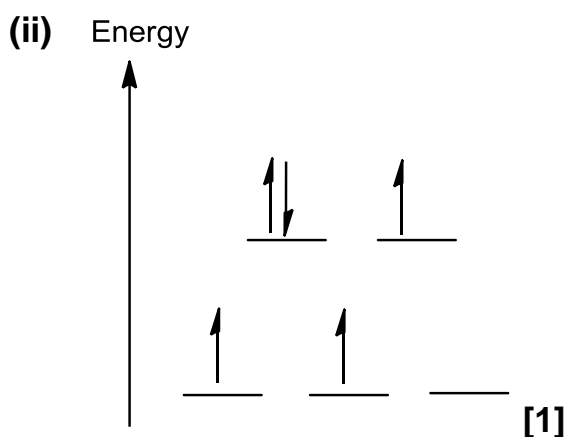
(d) (i) The complex is chiral as the two optical isomers are non-superimposable mirror images of each other. [1]

(ii)  $\Delta S$  is positive [0.5] as the number of product particles is greater than the number of reactant particles therefore the number of ways to distribute energy in the system increases. [1]

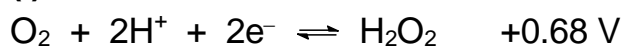
$$\Delta G = \Delta H - T\Delta S.$$

As  $\Delta H = 0$  and  $\Delta G = -T\Delta S$  [1]. Thus,  $\Delta G$  is negative [0.5]

(e) (i) The wavelength of light (complementary of yellow) absorbed by  $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$  is of a lower wavelength than that for  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  [1]. Therefore, the energy gap between the d-orbitals must be larger in  $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$  [1].

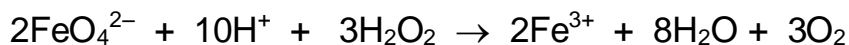


(f) (I)



$$E^\ominus_{\text{cell}} = +2.20 - (0.68)$$

$$= +1.52 \text{ V} > 0 \quad \text{reaction is feasible}$$



Observations: Red solution turns pale yellow, as  $\text{FeO}_4^{2-}$  is reduced to  $\text{Fe}^{3+}$ . Effervescence of  $\text{O}_2$  OR effervescence of a colourless and odourless gas that rekindles a glowing splint. [3]

(II)



$$E^\ominus_{\text{cell}} = +1.52 - (2.20) < 0 \quad \text{reaction is not feasible}$$

Solution remains purple [1]

5 (a) (i)  $K_{\text{sp}} = [\text{Ag}^+]^2[\text{CO}_3^{2-}]$   
 $= (2.57 \times 10^{-4})^2(2.57 \times 10^{-4}/2) = 8.49 \times 10^{-12} \text{ mol}^3 \text{ dm}^{-9}$

[1m for numerical answer; 1m for units]

(ii)  $K_{\text{sp}} = [\text{Ag}^+]^2[\text{CO}_3^{2-}]$   
 $8.49 \times 10^{-12} = [\text{Ag}^+]^2 \times (2.50 \div (23 \times 2 + 12 + 16 \times 3) \div (100/1000))$   
 $[\text{Ag}^+] = 6.00 \times 10^{-6} \text{ mol dm}^{-3}$  [1]  
Solubility of  $\text{Ag}_2\text{CO}_3 = \frac{1}{2} \times 6.00 \times 10^{-6} = 3.00 \times 10^{-6} \text{ mol dm}^{-3}$  [1]

(b) 4-hydroxybenzoic acid, benzoic acid, 2-hydroxybenzoic acid [1]

4-hydroxybenzoic acid is a weaker acid than benzoic acid because the –OH group attached to the benzene ring is electron-donating (lone pair of electrons on O atom is delocalised into the benzene ring), hence intensifying the negative charge on the carboxylate anion and reducing its stability. [1]

2-hydroxybenzoic acid is a stronger acid than benzoic acid because its conjugate base can be stabilised by intramolecular hydrogen bonding/ion-dipole interactions. [1]

(c) Add  $\text{AgNO}_3(\text{aq})$  at room temperature [1]  
Q : White ppt of  $\text{AgCl}$  formed immediately  
P: No white ppt formed [1]

OR

Add  $\text{K}_2\text{Cr}_2\text{O}_7$ , dilute  $\text{H}_2\text{SO}_4$ , heat [1]  
Q : Orange  $\text{K}_2\text{Cr}_2\text{O}_7$  turns green  
P: Orange  $\text{K}_2\text{Cr}_2\text{O}_7$  remains orange [1]

OR



Add water [1]

Q: Dense white fumes evolved

P: No white fumes evolved [1]

- (d) (i)  $PV = nRT$   
 $Mr = (\text{mass} \times R \times T) / PV$   
 $(0.219 \times 8.31 \times 423) / (125 \times 10^3 \times 70 \times 10^{-6}) = 88.0$  [1]  
 $C_3H_4O_3$  [1]

- (ii) **A**,  $C_{13}H_{14}O_3$ , and **B**,  $C_8H_8O$  have high C:H ratio  $\Rightarrow$  Benzene ring present in **A** and **B**

**A** undergoes acidic hydrolysis with dilute  $H_2SO_4$  to form **B** and **C**  $\Rightarrow$  **A** contains an ester group

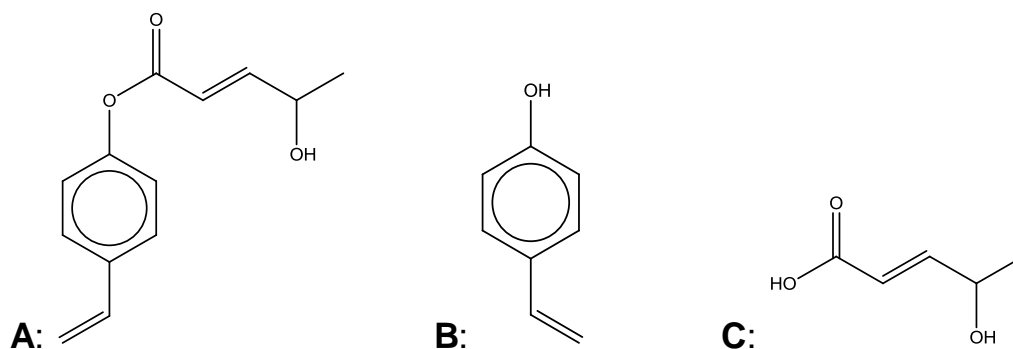
**B** undergoes electrophilic substitution and electrophilic addition with aqueous bromine to form **D**,  $C_8H_7O_2Br_3$   $\Rightarrow$  **B** contains phenol and alkene respectively.

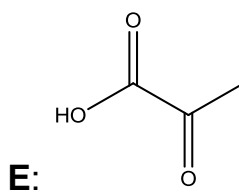
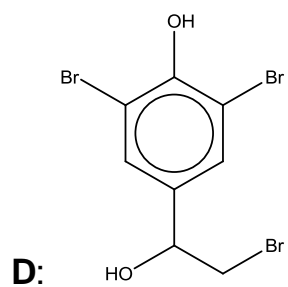
**B** undergoes oxidative cleavage with acidified  $KMnO_4$  to form 4-hydroxybenzoic acid and  $CO_2$  in a 1:1 mole ratio  $\Rightarrow$  **B** contains a terminal alkene

**C** undergoes oxidative cleavage with acidified  $KMnO_4$  to form **E**,  $C_3H_4O_3$ , and carbon dioxide gas in a 1:2 mole ratio  $\Rightarrow$  **C** contains alkene and possibly forms ethanedioic acid (further oxidised to form 2  $CO_2$ ) upon oxidation

**C** and **E** undergo oxidation / forms  $CHI_3$  yellow ppt / gave positive iodoform test with warm aqueous alkaline iodine  
 $\Rightarrow$  **C** contains  $-CO(CH_3)$  or  $-CH(CH_3)(OH)$  group or **E** contains  $-CO(CH_3)$  group

**E** undergoes acid-base reaction with  $Na_2CO_3$   
 $\Rightarrow$  **E** contains a carboxylic acid group





**4m max for explanations  
1m for each structure**

[9m]