SERANGOON JUNIOR COLLEGE
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME	
CLASS	

CHEMISTRY
JC2 Preliminary Examination
Paper 1 Multiple Choice

9729/01
22 Sep 2017
1 hour

Additional Materials: Data Booklet
Optical Mark Sheet (OMS)

READ THESE INSTRUCTIONS FIRST

On the separate multiple choice OMS given, write your name, subject title and class in the spaces provided. Shade correctly your FIN/NRIC number.

There are **30** questions in 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 using a **soft pencil** on the separate OMS.
Each correct answer will score one mark.
A mark will not be deducted for a wrong answer.

You are advised to fill in the OMS as you go along; no additional time will be given for the transfer of answers once the examination has ended.

Any rough working should be done in this question paper.

This document consists of **16** printed pages and **0** blank page.

Answer all questions

1 An acidified solution of the salt $KClO_x$ will oxidise Fe^{2+}(aq) to Fe^{3+}(aq) quantitatively, the chlorine being reduced to Cl^-(aq).

When 0.302 g of the salt $KClO_x$ was reacted with 0.540 mol dm^{-3} Fe^{2+}(aq) in the presence of H^+(aq), 21.0 cm^3 of Fe^{2+}(aq) was needed for complete reaction.

Which of the following is the value of x?

A 1

B 2

C 3

D 4

2 A student made up a 0.10 mol dm^{-3} solution of $Ba(OH)_2.8H_2O$ which she found in the laboratory cupboard and left the solution in an open beaker. A week later, she returned to the laboratory, used the solution for titration with 0.10 mol dm^{-3} HC*l* and was surprised to discover that her titres were lower than expected.

Which of the following explains why the values were so low?

A Some of the barium hydroxide has reacted with carbon dioxide in the air to form solid barium carbonate.

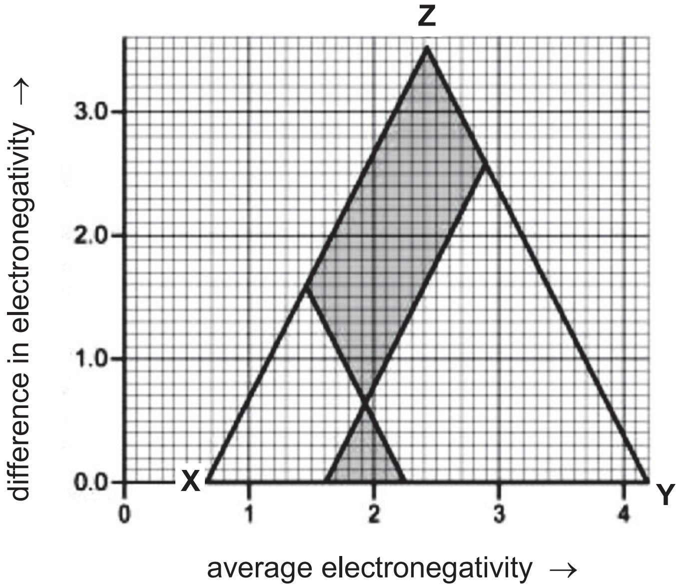
B Some water had evaporated from the barium hydroxide solution.

C The concentration of HC*l* was less than the stated 0.10 mol dm^{-3}.

D The crystals had less water of crystallisation than stated.

3 The type of bonding between two elements can be rationalised and even predicted using a van Arkel triangle. The triangle is based on electronegativity values. Difference in electronegativity is plotted along the y–axis and average electronegativity is plotted along the x–axis.

What is the type of bonding present at each of these bonding extremes, labelled **X**, **Y** and **Z** on the triangle?



	X	**Y**	**Z**
A	metallic	covalent	ionic
B	covalent	metallic	ionic
C	covalent	ionic	metallic
D	ionic	covalent	metallic

4 Equimolar amounts of aqueous ClO_2 and hydroxide ions react according to the equation below.

$$2ClO_2\ (aq) + 2OH^-\ (aq) \rightarrow ClO_3^-\ (aq) + ClO_2^-\ (aq) + H_2O\ (l)$$

Which statement is correct?

A The shape changes from linear in ClO_2 to bent in ClO_2^-.

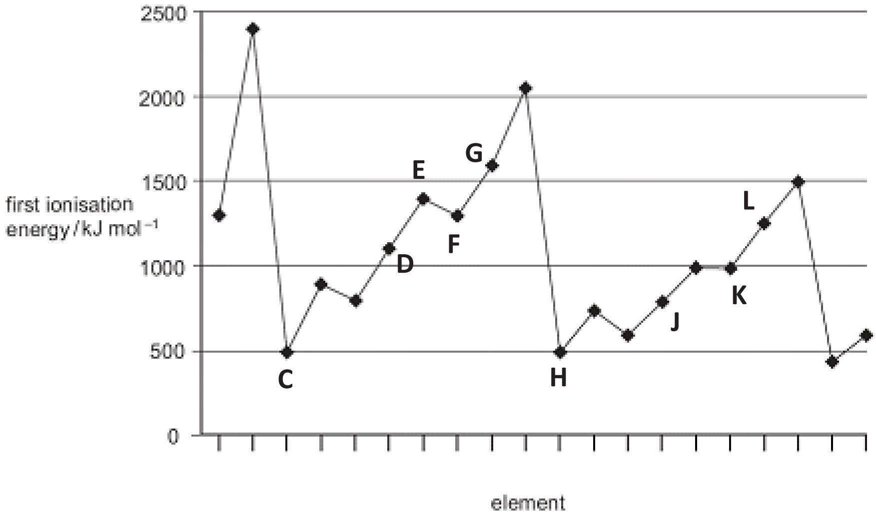
B The shape changes from bent in ClO_2 to trigonal planar in ClO_3^-.

C The bond angle changes from about 120° in ClO_2 to 107° in ClO_3^-.

D The bond angle changes from about 105° in ClO_2 to 107° in ClO_3^-.

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

The first ionisation energies of successive elements in the Periodic Table are represented in the graph.



Which of the following statements about elements **C** to **L** are correct?

1 **E** and **J**$^-$ have half–filled p–orbitals.

2 Chlorides of **D** and **J** undergo hydrolysis.

3 **F** and **K** reacts to form acidic compounds.

4 **D** and **F** forms compounds with formula **DF** and **DF$_2$**.

5 **G** and **L** forms compounds with variable oxidation states from –1 to +7.

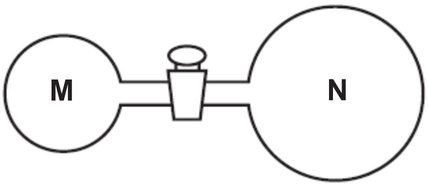
A 1 and 4 only

B 2 and 5 only

C 1, 3 and 4 only

D 2, 3 and 5 only

6 Two glass vessels **M** and **N** are connected by a closed valve.



M contains helium at 25 °C at a pressure of 1×10^5 Pa. **N** has been evacuated, and has three times the volume of **M**. In an experiment, the valve is opened and the whole set-up placed in boiling water.

What is the final pressure in the system?

A 3.13×10^4 Pa

B 3.76×10^4 Pa

C 1.00×10^5 Pa

D 1.33×10^5 Pa

7 Consider the following equilibrium system:

$$\mathrm{Fe_3O_4(s) + CO(g) \rightleftharpoons CO_2(g) + 3FeO(s)} \qquad \Delta H = +\text{ve}$$

Given that $K_p = K_c\,(RT)^{\Delta n}$, where Δn is the sum of gaseous products – sum of gaseous reactants.

Which of the following statements are correct?

1 $K_c = K_p$ for this system.

2 The equilibrium constant, K_c, for this reaction has no units.

3 Adding FeO causes the position of equilibrium to shift to the left.

4 Increasing the temperature causes the position of equilibrium to shift to the right.

A 1 and 2 only

B 1 and 3 only

C 2, 3 and 4 only

D 1, 2 and 4 only

8 In an experiment to measure the enthalpy change of neutralisation, 20 cm^3 of aqueous sulfuric acid containing 0.02 mol of H_2SO_4 is placed in a plastic cup of negligible heat capacity.

A 20 cm^3 sample of aqueous sodium hydroxide containing 0.04 mol of NaOH, at the same initial temperature, is added and the temperature rises by 15 K.

If the heat capacity per unit volume of the final solution is 4.2 J K^{-1} cm^{-3}, what is the enthalpy change of neutralisation?

A $-\left(\dfrac{20\times4.2\times15}{0.04\times1000}\right)$ kJ mol^{-1}

B $-\left(\dfrac{40\times4.2\times15}{0.04\times1000}\right)$ kJ mol^{-1}

C $-\left(\dfrac{20\times4.2\times15}{0.02\times1000}\right)$ kJ mol^{-1}

D $-\left(\dfrac{40\times4.2\times15}{0.02\times1000}\right)$ kJ mol^{-1}

9 The conversion of graphite into diamond is a non–spontaneous reaction at 298 K. The entropy change of this reaction is negative at 298 K.

$$\text{C(graphite)} \rightarrow \text{C(diamond)} \qquad \Delta G = +3.08\ \text{kJ mol}^{-1}\ ,\ \ \Delta S = -3.3\ \text{J mol}^{-1}\ \text{K}^{-1}$$

With reference to the enthalpy change, ΔH, of the reaction above, which statements are correct?

1 Enthalpy change of atomisation of diamond is more endothermic than that of graphite.

2 Enthalpy change of combustion of diamond is more exothermic than that of graphite.

3 Bond energy of carbon–carbon bonds in graphite is greater than that in diamond.

4 The activation energy to convert graphite to diamond is lower than the activation energy for the reverse reaction.

A 1 and 4 only

B 2 and 3 only

C 1, 2 and 3 only

D 2, 3 and 4 only

10 The reaction between acidified KI and aqueous H_2O_2 involves the following steps:

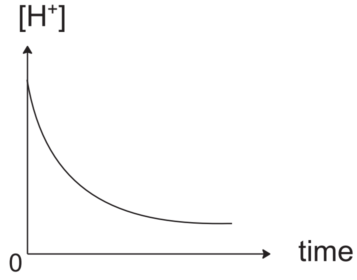
$H_2O_2 + I^- \rightarrow H_2O + OI^-$ slow

$OI^- + H^+ \rightarrow HOI$ fast

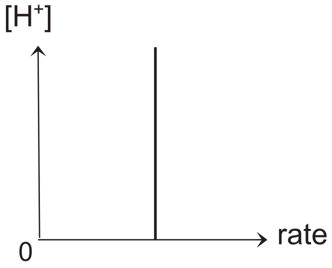
$HOI + H^+ + I^- \rightarrow I_2 + H_2O$ fast

Which graph would be obtained?

A



B



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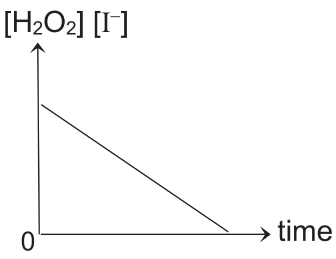
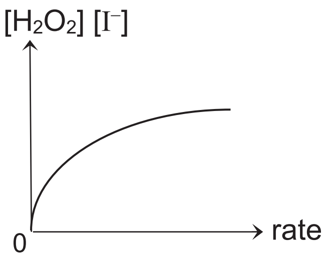


D



11 Compounds of beryllium are amphoteric, like compounds of aluminium.

In which equations is the beryllium-containing reactant acting as a Brønsted-Lowry acid?

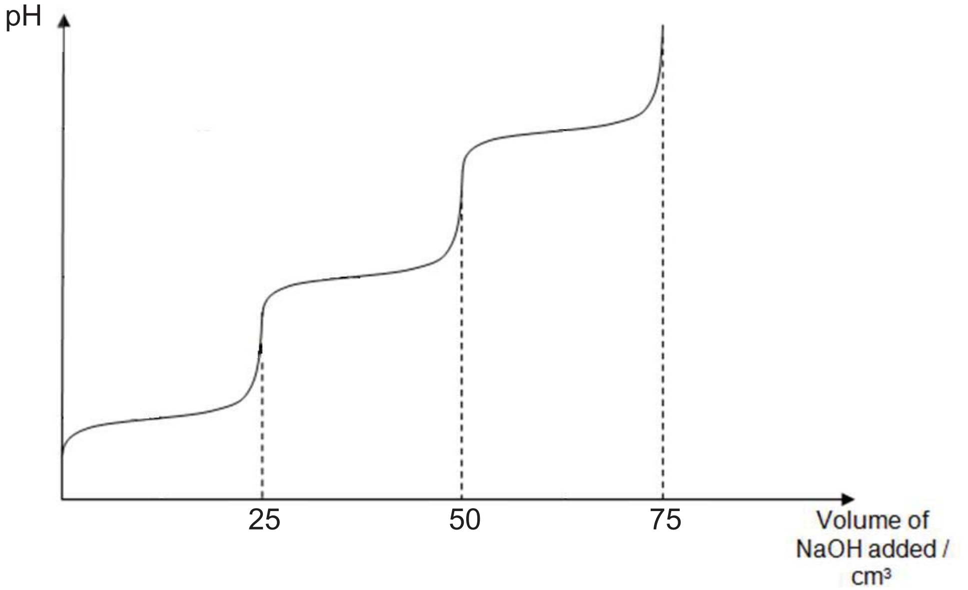
A $BeO(s) + 2OH^-(aq) + H_2O(l) \rightarrow [Be(OH)_4]^{2-}(aq)$

B $BeCl_2 + 4H_2O \rightarrow Be(H_2O)_4^{2+} + 2Cl^-$

C $2Be + O_2 \rightarrow 2BeO$

D $Be(H_2O)_2(OH)_2 + 2OH^- \rightarrow Be(OH)_4^{2-} + 2H_2O$

12 25 cm^3 of 1 mol dm^{-3} of the fully protonated form of compound **L** was titrated against a standard sodium hydroxide solution of a similar concentration and the following titration curve was obtained.



Which of the following compounds is a possible identity of compound **L**?

A $NH_2CH(CH_2CH_2CONH_2)COOH$

B $NH_2CH(CH_2CH_2CH_2OH)COOH$

C $NH_2CH(CH_2CH_2CH_2NH_2)COOH$

D $NH_2CH(CH_2CH_2CHO)COOH$

13 A sparingly soluble calcium salt dissociates in solution according to the equation:

$$Ca_3\mathbf{Q}_2\text{ (s)} \rightleftharpoons 3Ca^{2+}\text{ (aq)} + 2\mathbf{Q}^{3-}\text{ (aq)}$$

If the solubility product of $Ca_3\mathbf{Q}_2$ is p, what is the concentration of $\mathbf{Q}^{3-}$ at equilibrium in a saturated solution of $Ca_3\mathbf{Q}_2$ (aq)?

A $2p^{\frac{1}{5}}$

B $2(\frac{p}{36})^{\frac{1}{5}}$

C $2(\frac{p}{72})^{\frac{1}{5}}$

D $2(\frac{p}{108})^{\frac{1}{5}}$

14 A transition metal cation can exist in a 'high spin' or 'low spin' state while exposed to different ligands in an octahedral complex.

A 'high-spin' state has the electrons occupying all the d-orbitals singly first, before pairing in the lower energy d-orbitals.

A 'low-spin' state has the lower energy d-orbitals filled first, pairing up if necessary, before the higher energy d-orbitals are filled.

Which cation would have the largest number of unpaired electrons?

A 'High-spin' Mn^{3+}

B 'High-spin' Fe^{3+}

C 'Low-spin' Co^{2+}

D 'Low-spin' Ni^{4+}

15 Which of the following is **not** a result of the small energy gap between 3d and 4s orbitals?

A Transition metals have higher electrical conductivity than aluminium.

B Transition metals can exhibit variable oxidation states.

C Transition metals have higher melting point than calcium.

D Transition metals ions are usually coloured.

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

Two catalysed reactions and their respective catalysts are shown below.

Reaction	**Equation**	**Catalyst**
I	$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$	Fe^{3+}
II	$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$	Mn^{2+}

Which statements about the reactions and the catalysts are correct?

1 Mn^{2+} is an auto-catalyst in reaction **II**.

2 Fe^{2+} could replace Fe^{3+} as a heterogeneous catalyst in reaction **I**.

3 Mn^{2+} could replace Fe^{3+} as a homogeneous catalyst in reaction **I**.

4 Both catalysts increase the energetic feasibility of their respective reactions.

A 1 and 3 only

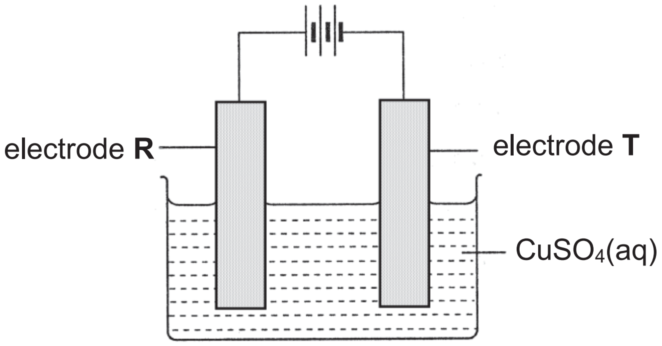
B 2 and 3 only

C 1, 2 and 4 only

D 2, 3 and 4 only

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

Impure copper obtained from copper ores can be purified by electrolysis as shown below. The cell potential is adjusted such that copper of the impure copper electrode dissolves and impurities such as silver, iron and zinc can be removed through this process.



Which statement is **not** correct regarding the above electrolytic process?

A Reduction occurs at electrode **T**.

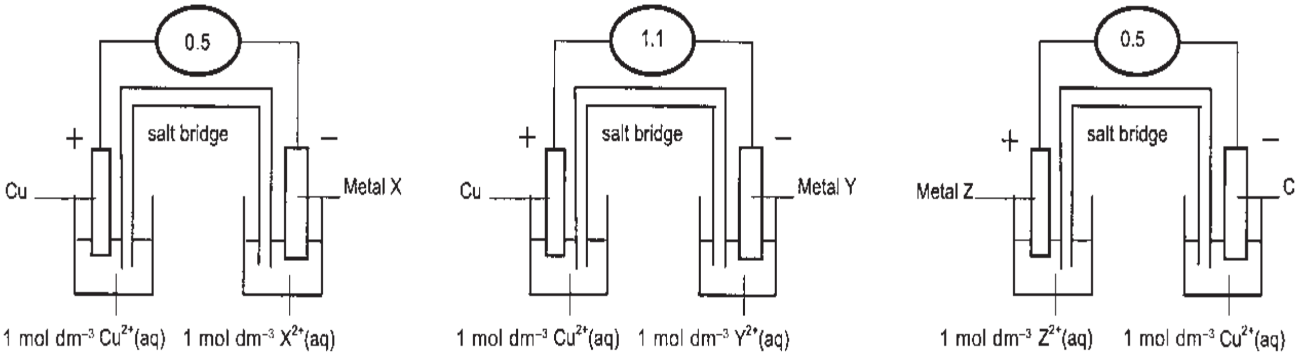
B Electrode **R** contains impure copper.

C Zinc impurity goes into the solution as Zn^{2+} ions.

D Iron and silver impurities fall to the bottom as sludge.

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

Three electrochemical cells are set up as shown below. The *e.m.f* in volts is shown on each voltmeter.



These *e.m.f* indicate the order of reactivity of the metals. The order of the weakest to the strongest reducing agent is

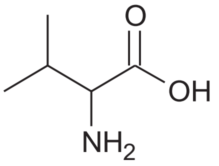
A **X**, **Y**, Cu, **Z**

B Cu, **Z**, **X**, **Y**

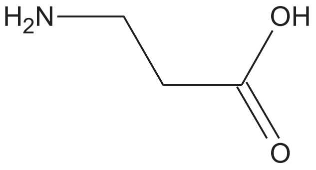
C **Z**, Cu, **X**, **Y**

D **Y**, **X**, **Z**, Cu

19 Valine is a naturally occurring amino acid.



Valine



3-aminopropanoic acid

Which statement about valine and 3-aminopropanoic acid is correct?

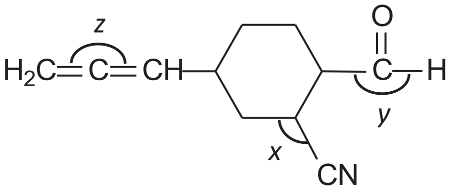
A Both compounds are able to form zwitterions.

B Both compounds are able to react with ethanoic acid to give amide.

C Both compounds are able to react with $NaBH_4$ in methanol to give alcohol.

D Both compounds are soluble in water due to the formation of intermolecular hydrogen bonding.

20 Which of the following statements are correct about compound **U**?



compound **U**

1 The bond angles in compound **U** increase in the order ***x*** < ***y*** < ***z***.

2 There is only one sp hybridised carbon atom in compound **U**.

3 There are 26 σ and 5 π bonds.

4 Compound **U** is planar.

A 1 and 2 only

B 1 and 3 only

C 1, 2 and 4 only

D 2, 3 and 4 only

21 Deuterium (D or ^2H) is a heavy isotope of hydrogen. A deutero-hydrocarbon has the part structural formula shown below.

$$CDH{=}CH{-}CH{=}C(C_3H_7)_2$$

What is the total number of isomers with the above part-structural formula?

A 2

B 4

C 8

D 10

22 The molecule of benzene, C_6H_6 is a regular hexagon in which the π electrons are described as delocalised.

Which of the following statements support this structure?

1 Benzene is a good conductor of electricity.

2 Addition reactions of benzene take place more easily than substitution.

3 All C–C bonds lengths in benzene are intermediate between C–C bond in an alkane and C=C bond in an alkene.

4 The enthalpy change of hydrogenation of benzene is less exothermic than that predicted for cyclohexatriene.

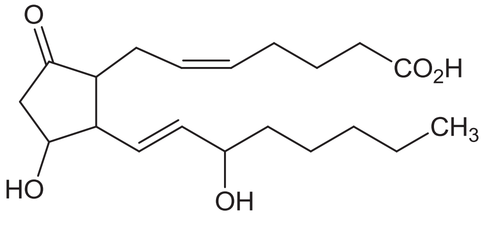
A 1 and 3 only

B 3 and 4 only

C 1, 2 and 3 only

D 1, 2 and 4 only

23 PGE_2 is a prostaglandin that has pharmacological activity.

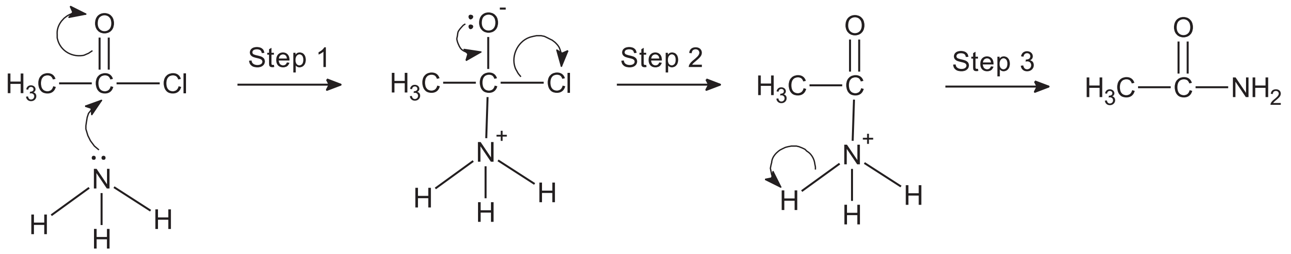


PGE_2

Which of the following is incorrect?

	Reducing agent	**Number of hydrogen atoms incorporated per molecule of PGE_2**
A	H_2 / Ni	6
B	Na in ethanol	8
C	$NaBH_4$ in methanol	6
D	$LiAlH_4$ in dry ether	4

24 A mechanism for the reaction between ammonia and ethanoyl chloride is given below.



Which of the following statements are correct?

1 The ammonia behaves as a nucleophile.

2 The loss of proton in **step 3** is shown incorrectly.

3 The ammonia attacks an electron-deficient carbon atom.

4 The rate of reaction will increase if ethanoyl bromide is used.

A 1, 2, 3 and 4

B 1, 3 and 4 only

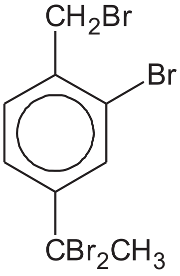
C 1 and 3 only

D 2 and 4 only

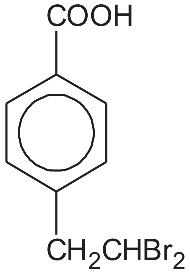
25 Diols formed on the same carbon atom are generally unstable and will undergo the following reaction.

$$RCR'(OH)_2 \rightarrow RCOR' + H_2O$$

Compounds **V** and **W** are both reacted with hot aqueous NaOH followed by dilute HC*l* at room temperature.



Compound **V**



Compound **W**

Which reagents could be used to distinguish the final products of **V** and **W**?

1 2,4−DNPH
2 Fehling's solution
3 Sodium carbonate
4 Hot acidified $K_2Cr_2O_7$
5 Iodine in aqueous NaOH

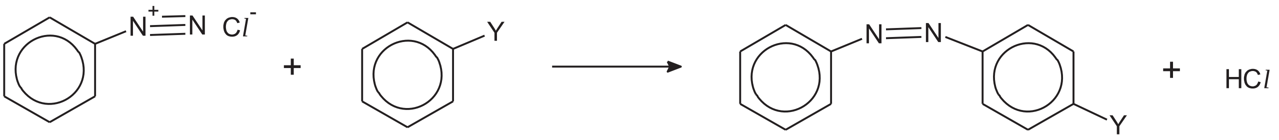
A 1 and 2 only
B 3 and 4 only
C 1, 4 and 5 only
D 2, 3 and 5 only

26 The ozone depletion potential (ODP) of a chemical compound is the relative amount of degradation to the ozone layer it can cause, with trichlorofluoromethane being fixed at an ODP of 1.0.

Which of the following compounds has an ODP of greater than 1.0?

A methane
B dichlorodifluoromethane
C chlorotrifluoromethane
D bromotrifluoromethane

27 Azo coupling is an organic reaction between a diazonium compound and another aromatic compound that produces an azo compound.



diazonium

Which of the following correctly represents the type of reaction and the role of diazonium compound?

	Type of reaction	**Role of diazonium**
A	nucleophilic substitution	nucleophile
B	electrophilic substitution	electrophile
C	nucleophilic substitution	electrophile
D	electrophilic substitution	nucleophile

28 What is the order of increasing pH of 1 mol dm^{-3} of each organic compound?

A CH_3CO_2Na, CH_3CO_2H, CF_3CO_2H, $HOCH_2CHO$

B CH_3CO_2Na, $HOCH_2CHO$, CH_3CO_2H, CF_3CO_2H

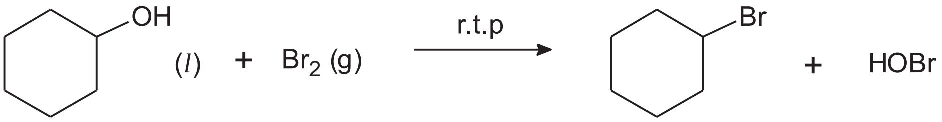
C CF_3CO_2H, CH_3CO_2H, $HOCH_2CHO$, CH_3CO_2Na

D CF_3CO_2H, CH_3CO_2H, CH_3CO_2Na, $HOCH_2CHO$

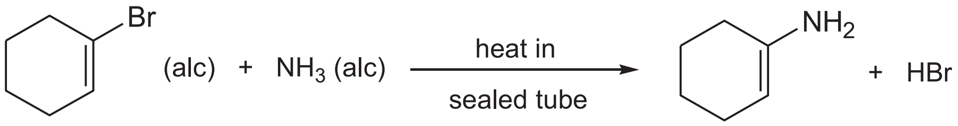
29 Which reaction gives the best yield of products?

[(*alc*) indicates an alcoholic solution.]

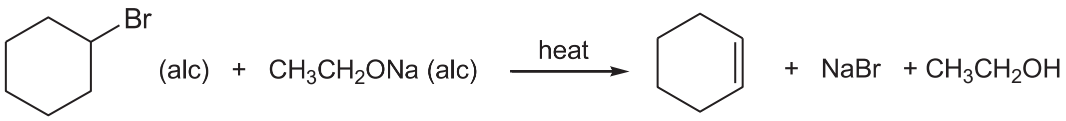
A



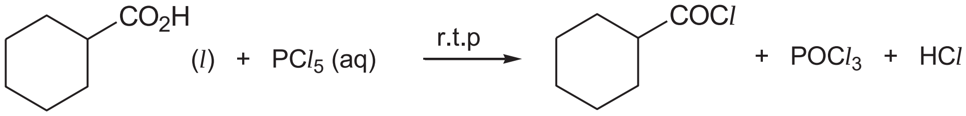
B



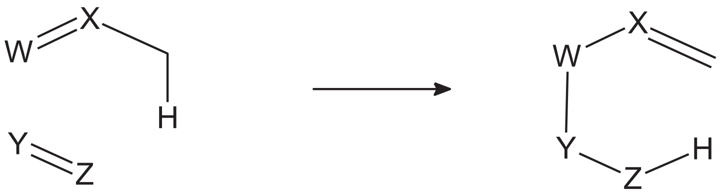
C



D



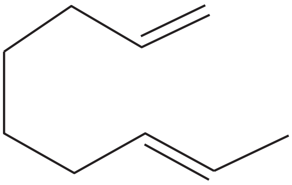
30 The Alder-ene reaction is a reaction between two alkenes and is capable of forming new carbon-carbon bonds. An example of the Alder-ene reaction is given below:



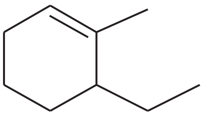
Note: W, X, Y & Z are carbon atoms and other hydrogens are not sho

The Alder-ene reaction typically produces many products as the roles of the two alkenes can be exchanged.

Which compound will **not** be formed when the following compound undergoes Alder-ene reaction?



A



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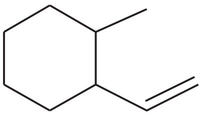
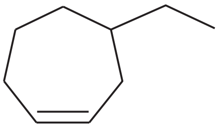
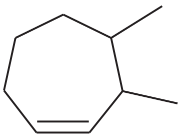


C



D



SERANGOON JUNIOR COLLEGE
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME	
CLASS	

CHEMISTRY 9729/02

JC2 Preliminary Examination **13 Sept 2017**
Paper 2 Structured Questions **2 hours**

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

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

For Examiner's Use	
1	/ 8
2	/ 18
3	/ 25
4	/ 24
TOTAL	/ **75**

This document consists of 24 printed pages

1 The size of an atom can be measured using the distance between the nuclei of two atoms.

For example, the ‘metallic radius’ of the Na atom is half the distance between two Na atoms in the crystal lattice of the metal. The ‘covalent radius’ of the C*l* atom is taken to be half the distance between the nuclei in a Cl_2 molecule. Finally, the ‘van der Waals’ radius’ of the A_r atom is assumed to be half the distance between two atoms in the solid state.

These three types of radius are commonly known as ‘atomic radii’ and the corresponding values for Period 3 elements can be found in the Data Booklet.

(a) **(i)** Explain the general trend in atomic radius across Period 3.

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[2]

(ii) Suggest a reason for the anomaly in the measurement of atomic radius for argon.

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[1]

(b) **(i)** State the general relationship between atomic radius and first ionisation energy across Period 3.

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[1]

(ii) Explain why the relationship does not hold from P to S**.**

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[1]

(c) Across period 3, the elements changes from metallic to non-metallic nature. Correspondingly, the difference in electronegativity between the elements and the oxide decreases, giving rise to different types of oxides.

A, **B** and **C** are Period 3 elements, from Na to S, inclusive.

- **A** has the highest melting point among Period 3 elements.
- **B** has the highest electrical conductivity in Period 3.
- **C** burns in air with a coloured flame.
- **B** and **C** can show the same oxidation state in their compounds.

Identify **A**, **B** and **C** and hence, write equations, including state symbols, to show the acid-base properties of their oxides.

[Give the chemical formulae for only the highest oxide formed.]

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[Total : 8]

2 Benzoic acid occurs naturally in many plants and it has many uses. It is an important precursor for the industrial synthesis of many organic substances.

(a) The benzoic acid and sodium benzoate buffer is commonly used as food preservatives in many acidic foods such as salad dressings and carbonated drinks.

(i) With the aid of relevant chemical equations, explain how the system can control pH when a small amount of base is added.

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[1]

(ii) Given that the acid dissociation constant for benzoic acid is 6.3 x 10^{-5} mol dm^{-3}, calculate the mass of solid sodium benzoate required to be added to 250 cm^3 of 0.50 mol dm^{-3} of benzoic acid to form a buffer solution with an initial pH 4.

[2]

(iii) To achieve the optimal buffering capacity of a 25 cm^3 sample of the buffer prepared in **(a)(ii),** a standard solution of 1.5 mol dm^{-3} sodium hydroxide was added. Calculate the volume of sodium hydroxide needed.

[3]

(b) The presence of benzoic acid in plant extracts can be confirmed using neutral iron(III) chloride according to the following equation.

$$Fe^{3+}(aq) + 3C_6H_5COOH(aq) \longrightarrow Fe(C_6H_5CO_2)_3(s) + 3H^+(aq)$$

When 50 cm^3 iron(III) chloride is added to an equal volume of the plant extract, 0.0532 g of iron(III) benzoate, $Fe(C_6H_5CO_2)_3$ precipitate is formed.

The resultant mixture has a pH value of 2.33.

(i) Calculate the amount of benzoic acid that has reacted with neutral iron(III) chloride solution and H$^+$ in the mixture.

[1]

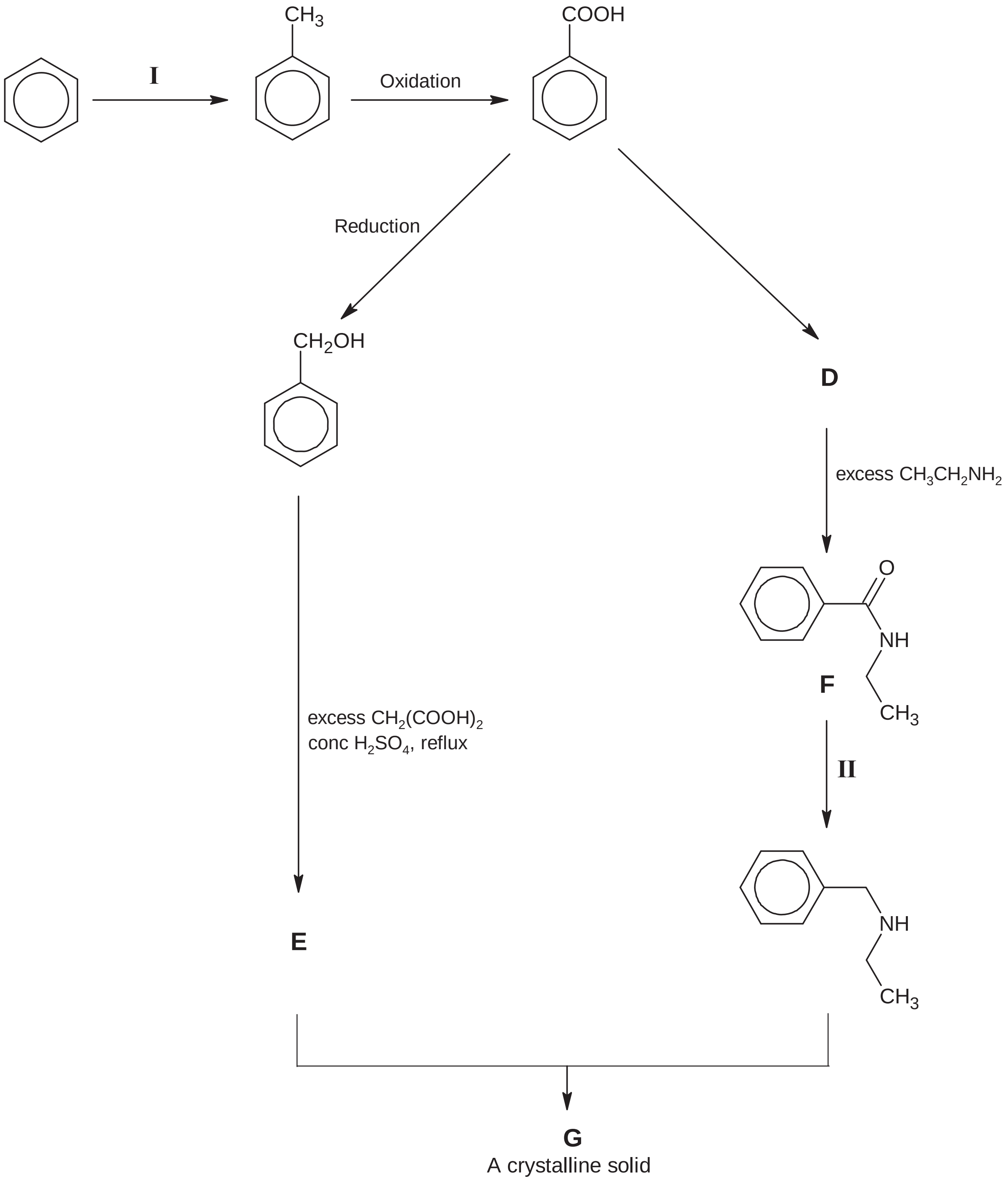
(ii) Assuming that the H^+ ions in solution are formed from the dissociation of benzoic acid and the reaction of benzoic acid with iron(III) chloride, calculate the concentration of benzoate ions in the equilibrium mixture.

[2]

(iii) Calculate the K_{sp} of iron(III) benzoate, given that the concentration of iron(III) ions in the mixture is 1.83×10^{-3} mol dm^{-3} at equilibrium.

[1]

(c) Benzoic acid is involved in the reaction scheme below:



(i) Draw the structures for **D**, **E** and **G** in the boxes below.

D	**E**
G	

[3]

(ii) Suggest the reagents and conditions for reactions **I** and **II**.

Reaction **I**: ……………………………………………………………

Reaction **II**: ……………………………………………………………

[2]

(iii) Compound **F** was heated with aqueous sodium hydroxide and excess carbon dioxide was bubbled through the solution.

Given the acid dissociation constants below, suggest the products that would be formed after the introduction of carbon dioxide.

acid	**formula**	**K_a / mol dm^{-3}**
carbonic acid	H_2CO_3	4.5×10^{-7}
benzoic acid	C_6H_5COOH	6.3×10^{-5}
ethylamine salt	$CH_3CH_2NH_3^+$	1.6×10^{-11}

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……………………………………………………………………………………………

[3]

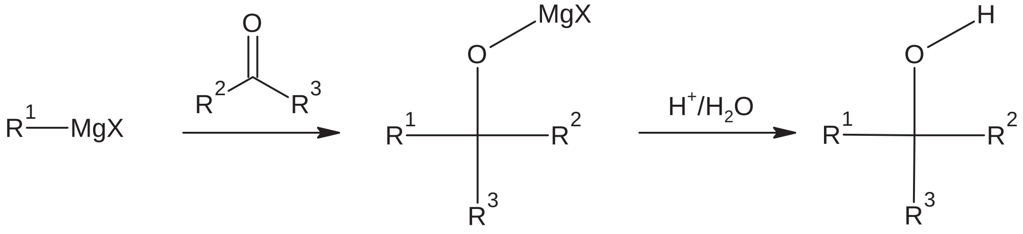
[Total : 18]

3 Grignard reagents are organomagnesium halides, RMgX commonly used in organic synthesis. The R in RMgX behaves like an anion, R^- and is a strong Lewis base. It can be made by the reaction between halogenoalkane and magnesium under anhydrous conditions, using ether as a solvent.

$$R^1\text{—}X \quad + \quad Mg \longrightarrow R^1\text{—}MgX$$

where R= alkyl group, X= C*l*, Br, I

In a Grignard reaction, the Grignard reagent behaves as a nucleophile and may be added to a carbonyl compound for the formation of an alcohol. This reaction is useful for the formation of carbon–carbon bonds.



(a) **(i)** Suggest, with an equation, why the synthesis of Grignard reagent has to be done under anhydrous conditions.

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[2]

(ii) Besides organomagnesium compounds, organolithium compounds can be formed between lithium and relevant organic substances. Account for the similarity in the reactions involving lithium and magnesium.

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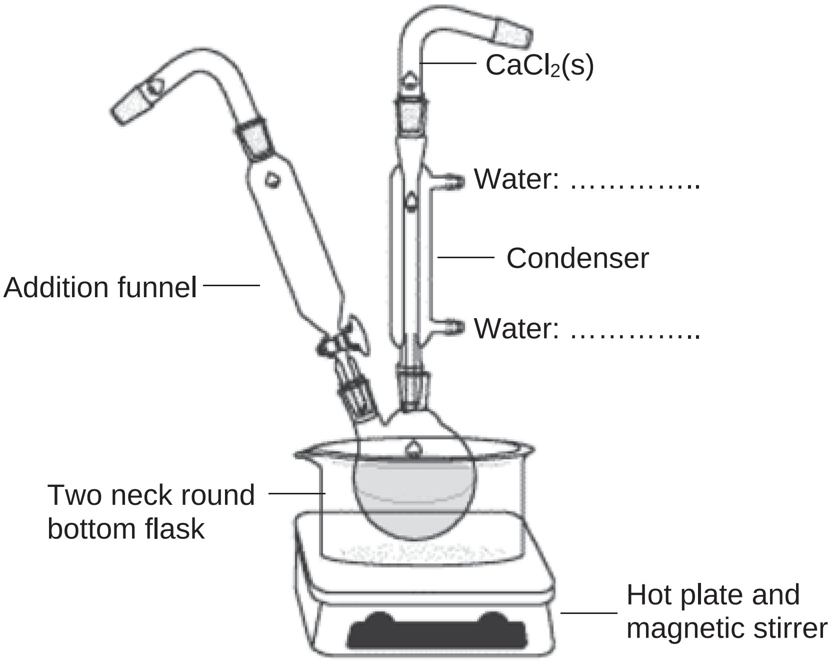
[2]

The preparation and set up of Grignard synthesis of 2-methylhexan-2-ol is described below:

Table 3.1

Compound	**Melting pt / °C**	**Boiling pt / °C**	**Molar mass / g mol^{-1}**	**Density / g cm^{-3}**	**Solubility in water**
1-bromobutane	−11.2	101.4	136.9	1.27	Insoluble
Magnesium	651	1100	24.3	1.74	Insoluble
Diethyl ether	−116.3	34.6	74.0	0.713	Insoluble
Propanone	−94.7	56.1	58.0	0.785	Soluble
Sulfuric acid	10.3	337	98.1	1.84	Soluble
2-methylhexan-2-ol	−	143	116.0	0.82	Soluble



<u>Preparation of Grignard reagent, RMgX</u>

1. Add 15 g of 1-bromobutane and 3 g of magnesium into the 250 cm^3 two-neck round bottom flask.

2. Add 50 cm^3 of anhydrous diethyl ether using the addition funnel. Gently stir the mixture under reflux for 30 minutes. The reaction is exothermic and will boil without external heat.

3. When the reaction is complete, cool the reaction mixture using an ice bath.

(b) **(i)** With reference to Table 3.1, suggest why a reflux set up is necessary in this organic synthesis.

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[1]

(ii) On the diagram on page 10, label and account for the direction of water flow.

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…………………………………………………………………………………………

[1]

(iii) Some heating may be required at the beginning as the initial rate of formation of RMgX is slow. Magnesium metal has to be scrapped or sliced into smaller pieces to increase the reaction rate.

Write an equation to suggest why magnesium may not be as reactive as expected.

…………………………………………………………………………………………

[1]

(iv) Excess diethyl ether is added to keep the Grignard reagent at a low concentration. This will prevent the Grignard reagent from reacting with unreacted 1-bromobutane. Draw the structure of the organic by-product.

[1]

Synthesis of alcohol

4. Using the addition funnel, add 6.5 g (dissolved in 15 cm^3 of diethyl ether) of propanone to the Grignard reagent.

5. To a separate 250 cm^3 beaker, add 100 cm^3 of ice water and 4 cm^3 of concentrated sulfuric acid and mix well.

6. When the reaction with propanone is completed, add the reaction mixture into a 250 cm^3 beaker, sitting in an ice bath. Carefully transfer sulfuric acid solution from step 5 into reaction mixture. Stir gently to mix well.

(c) **(i)** Using Table 3.1, calculate the theoretical mass of 2-methylhexan-2-ol.

[2]

(ii) The actual yield for 2-methylhexan-2-ol is 4 g. Calculate the percentage yield for this reaction.

[1]

(iii) Suggest why the addition of sulfuric acid has to be carried out in an ice bath in step 6.

…………………………………………………………………………………………

[1]

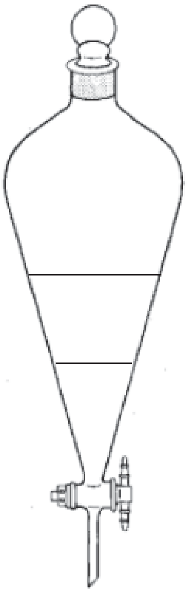
<u>Solvent extraction</u>

7. Add the mixture from step 6 into a 500 cm^3 separation funnel and add 10 cm^3 of diethyl ether. Shake the separation funnel, releasing any gas formed. Allow the layers to separate and collect both layers separately.

8. Repeat step 7 with the aqueous layer and a fresh sample of 10 cm^3 diethyl ether. Collect and combine each ether layer.

9. The combined ether layer is poured back to the separation funnel and mixed with several 20 cm^3 portions of 5 % sodium bicarbonate solution until no more carbon dioxide is generated.

(d) **(i)** After step 7, there are two layers in the separation funnel. Identify the ether and aqueous layer in the diagram below.



Upper layer: ……………………….

Bottom layer: ………………………..

Explain your answer.

……………………………………………………………………………………………

……………………………………………………………………………………………

[1]

(ii) Give a reason for the addition of sodium bicarbonate in Step 9.

……………………………………………………………………………………………

[1]

(iii) During solvent extraction, both propanone and 2-methylhexan-2-ol are found in the ether layer. Comment on the solubility of 2-methylhexan-2-ol in diethyl ether.

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[1]

(iv) Suggest different chemical tests to positively identify propanone and 2-methylhexan-2-ol in the ether layer.

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[2]

(v) Suggest how crude 2-methylhexan-2-ol can be purified from the ether layer.

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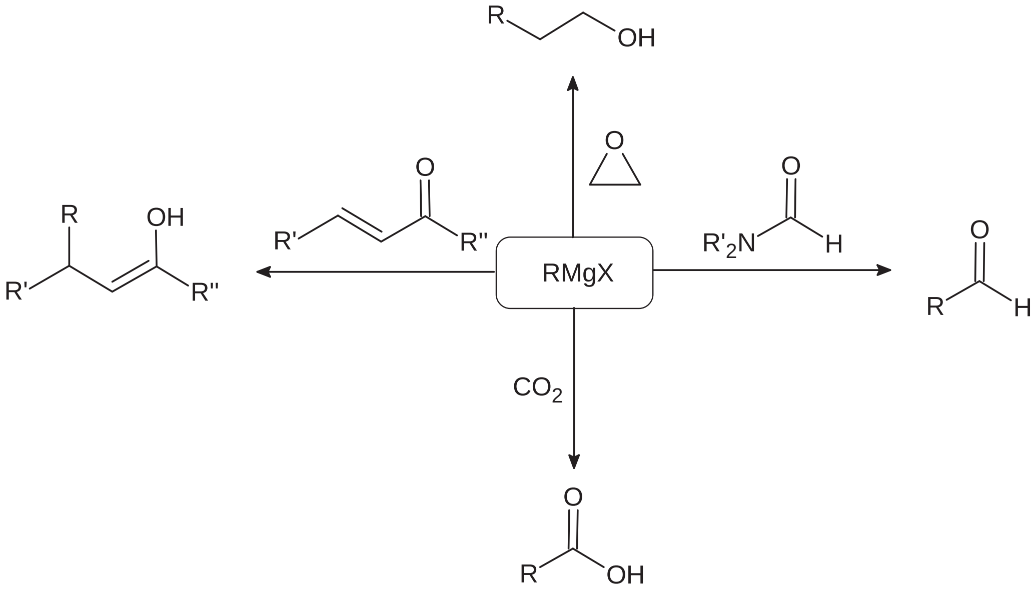
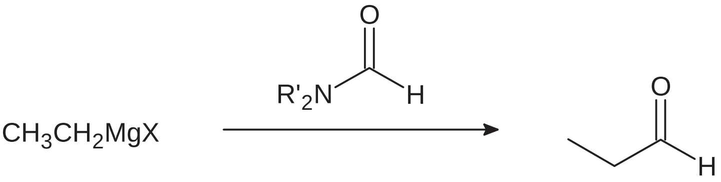
[1]

(e) Grignard reagent is used widely in organic synthesis due to its ability to increase carbon chain length. Four unique reactions involving the use of Grignard reagent are shown in the reaction map below.



(i) The following Grignard reaction to form propanal achieved a very low yield as the aldehyde formed can react with the Grignard reagent again.



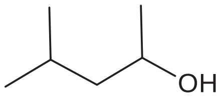
Describe the mechanism between propanal and the Grignard reagent, CH_3CH_2MgX to form the corresponding alcohol.

[2]

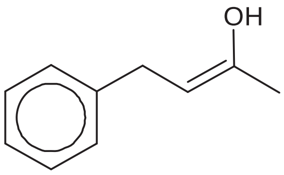
(ii) Starting with a suitable Grignard reagent, propose an alternative 3-step synthesis pathway to synthesise propanal.

[3]

(iii) Using different reaction types from the reaction map on page 15, suggest appropriate pairs of reagents in the synthesis of compounds **H** and **I**.



H



I

Reagent pair for H:	**Reagent pair for I**:

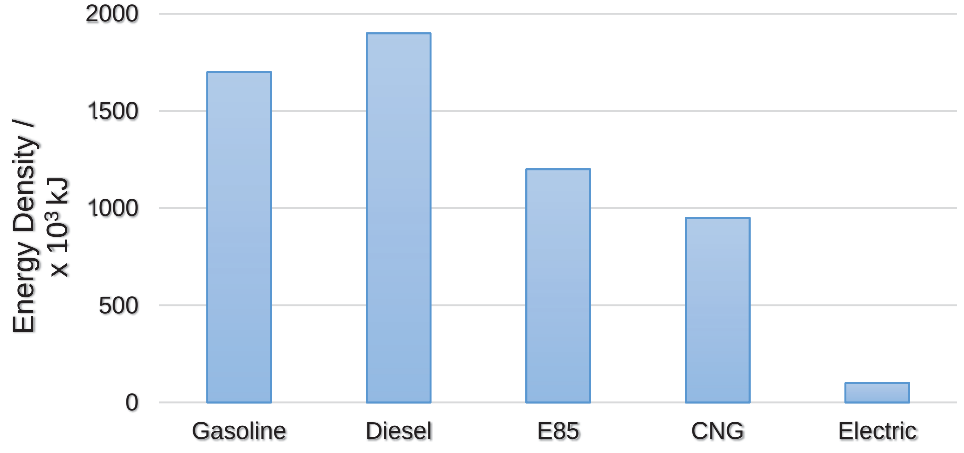
[2]
[Total: 25]

4 The use of electric vehicles has been increasing popular in the U.S. For example, hydrogen fuel cell vehicles produces zero carbon emission.

Despite the advantages of electric cars, petrol-engined cars are still widely used today. One problem with electric vehicles is their poor performance, inconvenience of finding a charging station and it takes a long time to recharge the batteries. Petrol-engined cars are better as their energy supply can be replaced over 6 million times faster than electric cars.

The infogram below shows how energy density varies widely with different fuels. Energy density is the energy produced per unit dimension of a fuel and this determines the practicality of a fuel.

Infogram 4.1: Energy Density Varies Widely



*Based on vehicles available in the U.S. market today

However, using petrol (which contains a mixture of alkanes) has its own problems. One such problem is that it’s a finite resource, and another is pollution. Hence, there is a need to improve the performance of petrol in car engines so that it burns as cleanly and efficiently as possible and to find alternative sources of fuel to replace petrol.

Some data for five fuels are given in **Table 4.2**.

Fuel	**Formula**	**Standard enthalpy change of combustion, $\Delta H_c^\ominus$ / kJ mol^{-1}**	**Relative molecular mass**	**Energy density (energy transferred on burning 1 kg of fuel) / kJ kg^{-1}**
octane	C_8H_{18} (*l*)	– 5470	114.0	
1,2-xylene	C_8H_{10} (*l*)	− 4540	106.0	
carbon	C(s)	– 393	12.0	
methanol	CH_3OH(*l*)	– 726	32.0	
hydrogen	H_2(g)	– 286	2.0	

(a) Give an example of a pollutant that can arise from the use of petrol and state a detrimental effect of the pollutant.

……

……

[1]

(b) Complete Table 4.2 by calculating the energy density for all fuels. [1]

(c) **(i)** On the basis of energy density, which is the best fuel in Table 4.2.

……………………………………………………………………………………………

[1]

(ii) Suggest a practical difficulty in using hydrogen rather than methanol as a fuel.

……………………………………………………………………………………………

……………………………………………………………………………………………

[1]

(d) Using the given data above, comment on the feasibility of using electric cars in the near future.

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[1]

Octane is commonly used as a fuel or a precursor in the production of other chemicals. The term “octane rating” is often used in the petroleum industry for rating the ability of octane’s various branched isomers in reducing engine knock in vehicles.

One important factor in making petrol is getting the right octane rating to reduce the problem of ‘knocking’. Knocking occurs when the combustion of fuel is not smooth. Knocking reduces engine power, leading to wear and tear in the engine and results in wastage of petrol. Hence, highly branched alkanes are desirable in petrols as they have higher octane ratings and reduce knocking.

Another factor for getting the right properties of petrol is the blending of petrol. In cold weather, it is difficult to vaporise petrol, which makes ignition difficult. On the other hand, in hot weather, petrol vaporises easily. Hence, petrol companies make different blends of petrol for different seasons and climates.

You are to use the information provided above to answer parts **(e)** and **(f)**.

(e) Apart from using alkanes with high octane ratings, another way to deal with the problem of knocking is through the addition of an antiknock agent, tetra-ethyl lead (**TEL**). **TEL** is a highly volatile colourless liquid which aids in the formation of free radicals. However, this method is not commonly used nowadays.

Explain, with the aid of a suitable equation, how **TEL** helps to overcome the problem of knocking and give a reason why its usage is limited nowadays.

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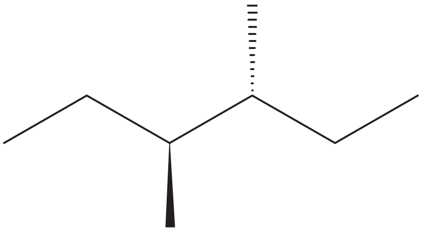
[3]

(f) Compounds **J**, **K** and **L** are isomers of the hydrocarbon octane, C_8H_{18}.

The table below shows the boiling points and data relating to the optical activity of the compounds.

Structure	**Boiling Point / °C**	**Number of chiral centres**	**Optical Activity**
Isomer **J**	120	1	Yes
 Isomer **K**	118	2	No
Isomer **L**	107	0	No

(i) Suggest why isomer **K** does not exhibit enantiomerism.

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

[1]

(ii) Propose the structures of compounds **J** and **L**.

Isomer J :	**Isomer L :**

[2]

(iii) In terms of structure and bonding, identify which of your proposed compounds (**J** or **L**) would be a more suitable fuel for use in summer and winter respectively.

Your answer should show clear and detailed comparison in your choice of fuel.

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[2]

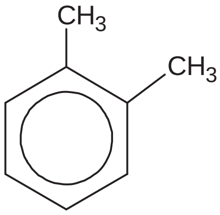
(iv) Controlled chlorination of isomer **K** in the presence of UV light produces different mono-chlorinated products with a molecular formula of $C_8H_{17}Cl$.

Draw the structural formula of any **two** possible isomers and state the ratio in which they are formed.

[2]

(g) The performance of hydrocarbons as fuels is largely improved by catalytic reforming. Reforming takes straight chain hydrocarbons in the C_6 to C_8 range from the gasoline or naphtha fractions and rearranges them into compounds containing benzene rings. They are used to make fuels with high octane number. Hydrogen is produced as a by-product of the reactions. A catalytic mixture of Pt and Al_2O_3 at a temperature of 500 ^oC and pressure of 20 atm is used.

An example of a product is 1,2-xylene.



(i) Write a balanced equation when octane undergoes the ‘reforming’ process to form 1,2-xylene.

……………………………………………………………………………..………………

[1]

(ii) What *type of reaction* has the octane undergone?

……………………………………………………………………………..………………

[1]

(iii) 1,4–xylene can be produced by a similar process. Suggest the structural formula of a C_8 alkane which might produce 1,4-xylene.

[1]

(iv) By means of an energy cycle, show and calculate the standard enthalpy change of reaction that produces 1,2-xylene from octane.

[2]

(v) Using data from the Data Booklet, calculate the enthalpy change of the reaction which reforms octane into 1,2-xylene.

[2]

(vi) By considering your answers in **(g)(iv)** and **(v)**, suggest if they are accurate descriptions of the reformation process.

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[1]

(vii) Briefly explain whether you would expect the above reaction to have its ΔG value to be more negative than its corresponding $\Delta H_{r.}$

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[1]
[Total : 24]

SERANGOON JUNIOR COLLEGE
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME

CLASS

CHEMISTRY 9729/03

JC2 Preliminary Examination 20 Sept 2017
Paper 3 Free Response 2 hours

Candidates answer on separate paper.

Additional materials : Answer Paper
Data Booklet
2 Cover Pages

READ THESE INSTRUCTIONS FIRST

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

Section A
Answer **all** questions.

Section B
Answer **one** question.

The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

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

This document consists of **11** printed pages and **1** blank page.

Section A

Answer **all** the questions in this section.

1 **(a)** Oxides of nitrogen, NO_x are a mixture of gases that are composed of nitrogen and oxygen. They are formed during combustion processes in power plants.

Thermal NO_x refers to NO_x formed through high temperature oxidation of the diatomic nitrogen found in combustion air.

The formation rate is a function of temperature and the residence time of nitrogen at that temperature. At high flame temperatures, molecular nitrogen and oxygen dissociate into their atomic states and participate in a series of reactions.

The two principal reactions producing thermal nitric oxide, NO are as follows.

Step 1 O atoms react reversibly with N_2 to form NO.

Step 2 N atoms liberated react with O_2 to produce more NO.

Nitrogen dioxide typically arises via the oxidation of nitric oxide by oxygen in the atmosphere.

$$2\ NO + O_2 \rightarrow 2\ NO_2$$

(i) Write the two principal reactions involved in the formation of thermal nitric oxide in combustion. [1]

(ii) Hence, determine the rate determining step. [1]

(iii) Suggest a method to reduce the formation of thermal NO_x. [1]

(b) Catalytic converters are used to reduce the output of NO_x into the environment. One example is the removal of nitric oxide by reaction with hydrogen gas using platinum catalyst.

		ΔH
$NO + NO \rightleftharpoons N_2O_2$	fast	positive
$N_2O_2 + H_2 \rightarrow H_2O + N_2O$	slow	negative
$N_2O + H_2 \rightarrow N_2 + H_2O$	fast	negative

(i) Write the rate equation for the above reaction, showing clearly how you derive it. [2]

(ii) Draw the probable energy profile diagram for this overall exothermic reaction. [2]

(iii) Using an appropriate sketch of the Maxwell–Boltzmann distribution curve, explain how the addition of platinum affects the rate of chemical reaction. [3]

(c) The NO_2 reacts with O_2 in the atmosphere to form colourless nitrogen pentoxide, N_2O_5 in equilibrium.

$$4\ NO_2\ (g)\ +\ O_2\ (g) \rightleftharpoons 2\ N_2O_5(g)$$

Dinitrogen pentoxide is a rare example of a compound that adopts two structures depending on the conditions. As a gas in the atmosphere, dinitrogen pentoxide exists as a molecule. However, it exists as an ionic salt in the solid state.

(i) Gaseous N_2O_5 is a symmetrical molecule with the two nitrogen atoms bonded to one central oxygen atom.

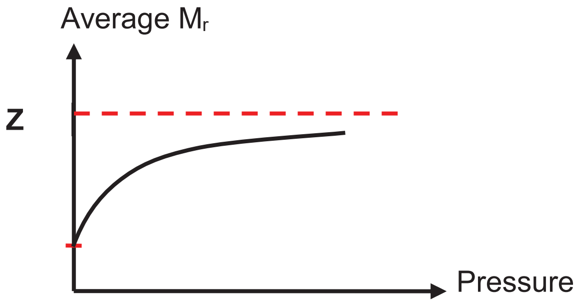
Draw a dot-and-cross diagram to show the bonding in N_2O_5 molecule. Use your diagram to:

- State the shape and the bond angle with respect to nitrogen
- Suggest with reasoning, the polarity of the molecule. [3]

(ii) A ratio of 4 to 1 mole of gaseous NO_2 and O_2 with a total initial pressure of 2.25 atm was placed in a 1000 cm^3 vessel. The total pressure at equilibrium was 1.5 atm. Calculate K_p for this equilibrium. [3]

(iii) Calculate the average M_r of the gases at equilibrium. [1]

(iv) The variation of M_r is as shown in the sketch.



Predict a value for **Z** and account for the shape of the graph. [2]

(d) Solid N_2O_5 dissolved in chloroform may be used to replace concentrated nitric acid and sulfuric acid in the nitration of benzene.

(i) Suggest why solid N_2O_5 can be used in for nitration of benzene. [1]

(ii) 0.60 mol of solid N_2O_5 was dissolved in chloroform. Some N_2O_5 decompose back into oxygen and nitrogen dioxide with a rate constant of $1.0 \times 10^{-5}\ s^{-1}$ at 45 °C.

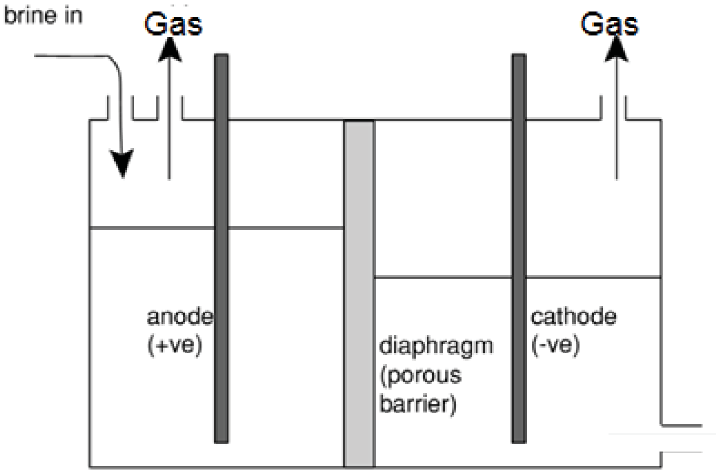
The gases produced are collected in a 10 dm^3 container over a period of 40 hours. Calculate the resultant pressure.
[Assume that the products do not dissolve in chloroform.] [3]

[Total : 23]

2 Chlorine is a yellow-green gas that was first synthesised around 1630. Chlorine forms a variety of oxides such as chlorate(VII), ClO_4^- and chlorate(V), ClO_3^-.

(a) Chlorine gas can be produced from the electrolysis of brine (concentrated sodium chloride solution) using a diaphragm cell with inert electrodes.

A diaphragm is used to keep the products of electrolysis from mixing and hence, prevent the formation of undesirable by-products.



(i) Write the ion-electron half-equations, with state symbols, for the reactions taking place at the electrodes. [2]

(ii) Calculate the mass of chlorine gas produced if a current of 5 A was passed for 7 hours through the electrolytic cell. [2]

(b) In some industrial electrolytic cells, the products of electrolysis of brine are allowed to react further when the diaphragm is removed. Two chlorine-containing products are formed, depending on the operating conditions used. At low temperatures, one of the products is a chloro-oxoanion with an oxidation state of +1.

(i) State the type of reaction taking place. [1]

(ii) Give an overall balanced equation for the reaction described above. [1]

(c) With reference from the Data Booklet, explain why dilute aqueous sodium chloride cannot be used as the electrolyte for the manufacture of chlorine in this electrolysis. [1]

(d) The standard electrode potentials, $E^\ominus$, and standard Gibbs free energy changes, $\Delta G^\ominus$, of different chlorine-containing species are tabulated below.

	Half-equation	**$E^\ominus$ / V**	**$\Delta G^\ominus$ / kJ mol^{-1}**
1	$ClO_4^- + 2H^+ + 2e^- \rightleftharpoons ClO_3^- + H_2O$	+1.19	–230
2	$2ClO_3^- + 12H^+ + 10e^- \rightleftharpoons Cl_2 + 6H_2O$	+1.47	**?**
3	$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36	–262

These electrode potentials can be summarised using the Latimer diagram shown below. In a Latimer diagram, the most highly oxidised form of the element is on the left, with successively lower oxidation states to the right. The electrode potentials are shown on the arrows.

$$\begin{tikzcd} ClO_4^- \arrow[r, "+1.19\text{ V}"] & ClO_3^- \arrow[r, "+1.47\text{ V}"] \arrow[rr, bend right, "+1.45\text{ V}"'] & Cl_2 \arrow[r, "+1.36\text{ V}"] & Cl^- \end{tikzcd}$$

(i) Calculate $\Delta G^\ominus$ for half-equation 2. [1]

(ii) The standard electrode potential of converting ClO_3^- to Cl^- is found to be +1.45 V, instead of +2.83 V. The number of electrons transferred in each step must be taken into account.

I: Write a half-equation for the conversion of ClO_3^- to Cl^-

II: Using your knowledge of Hess' Law for $\Delta G^\ominus$ and your answer to **(d)(i)**, show with the aid of an energy cycle that the $E^\ominus$ for the conversion of ClO_3^- to Cl^- is +1.45 V.

[4]

(iii) With the help of the Latimer diagram provided, calculate $E^\ominus_{cell}$ of the reaction below. Hence, determine its $\Delta G^\ominus_{cell}$.

$$4ClO_3^-(aq) \longrightarrow 3ClO_4^-(aq) + Cl^-(aq)$$

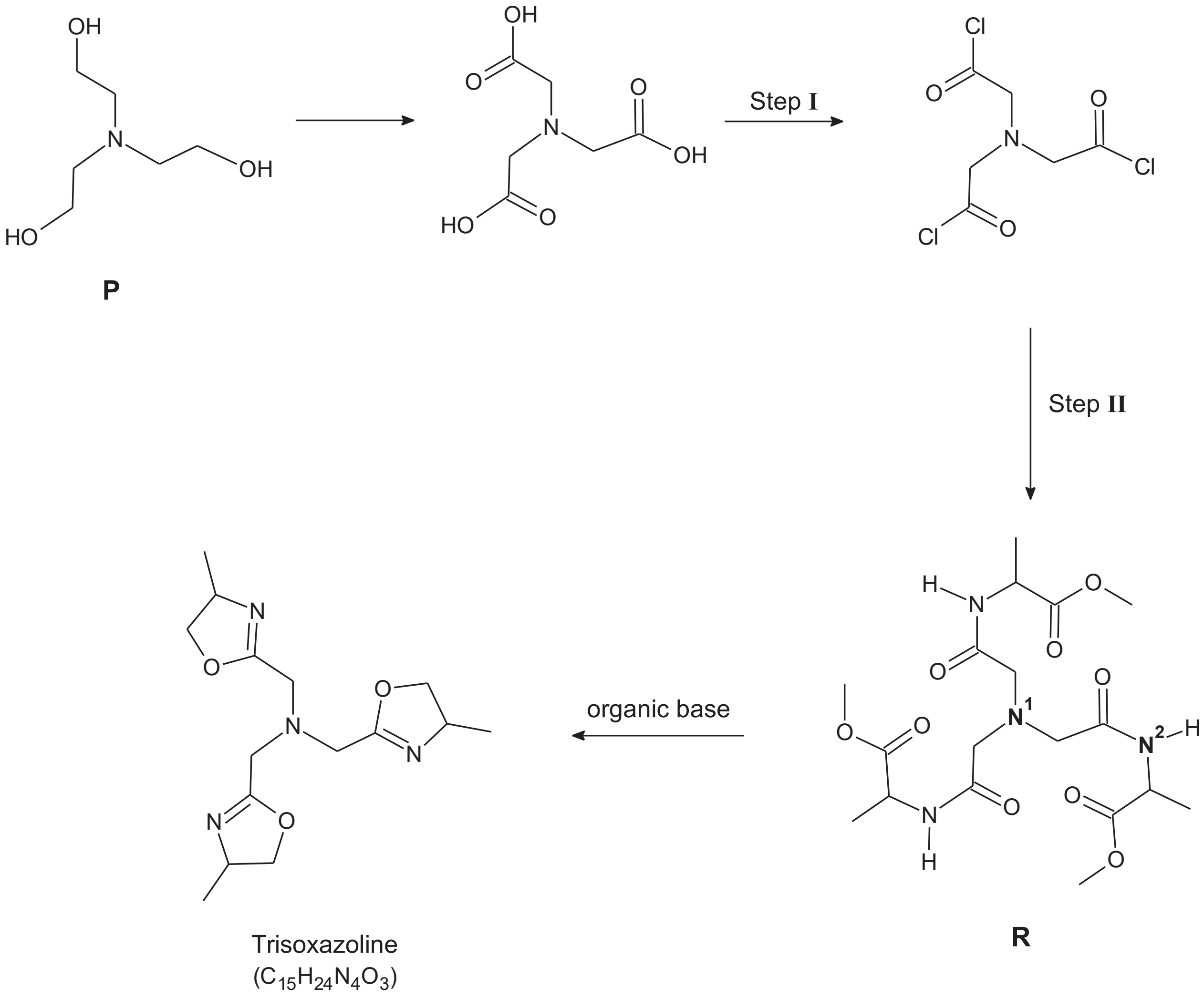
[2]

(iv) With reference to the *Data Booklet*, predict what will happen when an excess of acidified hydrogen peroxide solution is added to a solution of Cl^-(aq). [3]

[Total: 17]

3 Trisoxazoline are organic molecules that can function as ligands. Despite their huge molecular structure, they are able to form stable complexes with metals. Metal complexes with trisoxazoline are commonly used as catalyst in organic synthesis.

(a) The reaction scheme below illustrates the synthesis of trisoxazoline.



(i) Suggest the reagents and conditions required for step **I** and step **II**. [2]

(ii) Explain the difference in basicity for N^1 and N^2 present in **R**. [2]

(iii) Propose a 2-step reaction scheme to synthesise compound **P** from ethene. [2]

Trisoxazolines are usually applied to transition metals, such as copper, to form complexes. These complexes are useful in advanced organic synthesis to make specific isomers.

Table 1 shows some properties of the copper complexes, where K_{stab} refers to the stability constant of the complex, e.g.

$$Cu^{2+} + L \rightleftharpoons [CuL]^{2+} \qquad K_{stab} = \frac{[CuL]^{2+}}{[Cu^{2+}][L]}$$

Table 1

Complex	**log(K_{stab})**	**Colour**	**Shape of complex**
copper(II)-trisoxazoline	12.9	green	distorted tetrahedral
copper(II)-EDTA	18.8	blue	octahedral
copper(II)-en	18.7	violet	octahedral

(b) Describe the feature of the trisoxazoline molecule that enable it to act as polydentate ligand. Hence, state the type of bond formed between the ligand and the central Cu(II) ion and give the coordination number of the complex. [2]

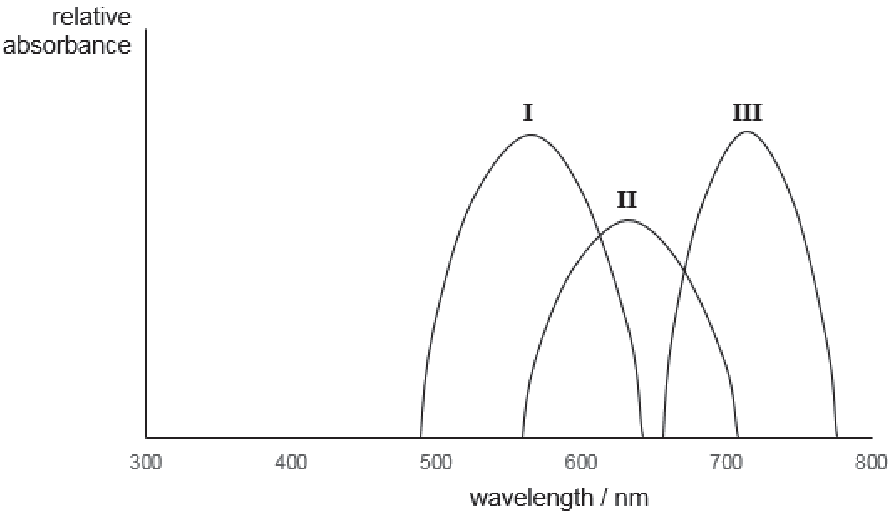
(c) **(i)** Using copper(II)-EDTA as an example, explain why the five d-orbitals are split into two different energy levels. [2]

(ii) Draw the shapes of the d-orbitals at the higher energy level. [1]

(iii) Explain why the copper(II) complexes are coloured. [3]

(iv) The visible absorption spectrum of the three complexes is shown below where each peak represents one complex.

[A visible absorption spectrum is a graph depicting the absorption of radiation by a material over a range of visible light wavelengths.]



Identify the copper(II) complex responsible for each absorption peak. Hence, arrange the three complexes in order of increasing magnitude of their energy gap.

[2]

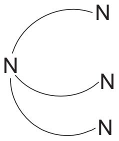
(d) Using Table 1, comment on the spontaneity of forming the respective copper(II) complexes. [2]

(e) Other than copper(II) ions, it was found that copper(I) ions are also able to form complexes with trisoxazoline.

(i) Predict and explain the colour of solid copper(I)-trisoxazoline complex. [1]

(ii) Analysis was done on copper(I)-trisoxazoline complex. The relative molecular mass of the complex was apparently 743.0. Further analysis showed that each copper(I) ion is bonded to three nitrogen atoms.

Propose the structure of copper(I)-trisoxazoline complex.

[You may use  to represent trisoxazoline.]

[1]

[Total: 20]

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Section B is on the next page

Section B

Answer **one** question in this section.

4 **(a)** At r.t.p, 1.2 dm^3 of chlorine gas is reacted with 6.7 g of compound **A**, $C_9H_{10}O$, to give compound **B**. On addition of PCl_5, **A** gives white fumes. Treatment of **A** with NaBr and concentrated H_2SO_4 under reflux gives a mixture of compounds **C** and **D**. **C** and **D** have the same molecular formula $C_9H_{10}Br_2$ and each contains only *one* chiral centre.

(i) When NaBr is mixed with concentrated H_2SO_4, the following observations are made.

- White fumes produced
- Reddish brown liquid formed
- Pungent gas decolourised purple $KMnO_4$

It is suggested that a displacement reaction occurred first, producing white fumes. Some of the white fumes further react with H_2SO_4 via a redox reaction. Using the above information, write the two corresponding chemical equations for this reaction. [2]

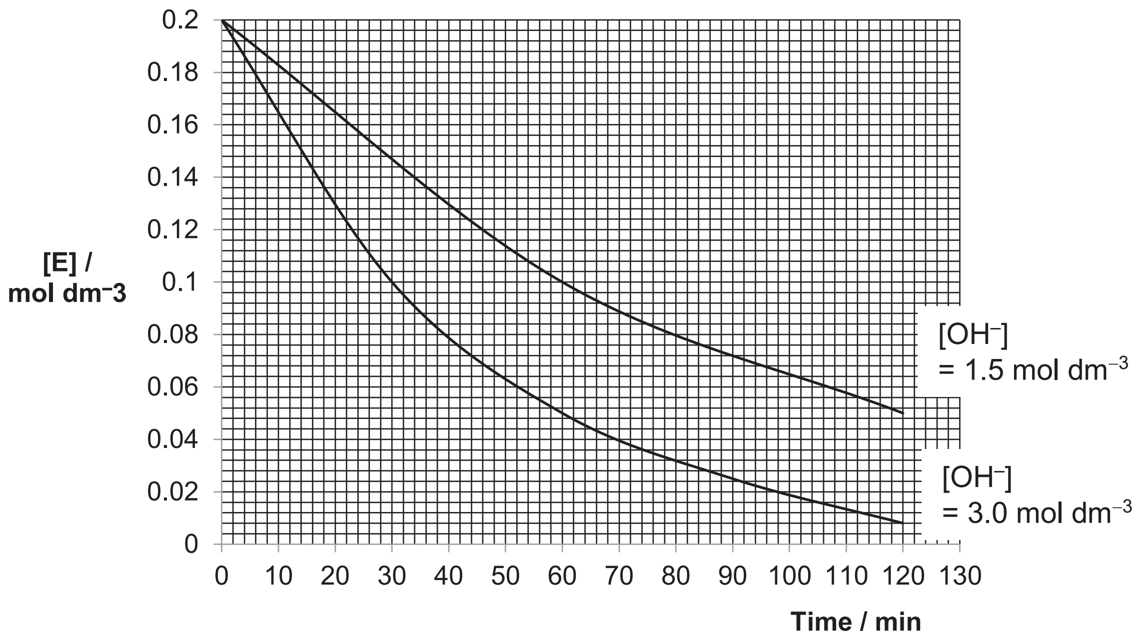
(ii) Using your answer in **(a)(i),** deduce the identities of **A** to **D**. [5]

(iii) Account for the relative quantity of compound **C** and **D** formed. [1]

(b) **E** is another constitutional isomer of **C** and **D**. A series of chemical experiments were conducted on **E**.

Experiment 1:

The reaction kinetics of **E** with aqueous sodium hydroxide was determined by monitoring the change in concentration of **E** with time.



Experiment 2:

0.2 mol of **D** and **E** were treated separately with boiling aqueous sodium hydroxide. The products from each compound were then acidified with nitric acid and then treated with silver nitrate solution.

The results obtained are shown below:

	Observation upon adding $AgNO_3$	**Mass of ppt / g**
D	formation of cream-coloured precipitate	75.12
E	formation of cream-coloured precipitate	37.56

(i) Using experiment 1, deduce the rate equation. [3]

(ii) Using Experiment 2 and **(b)(i)**, propose a possible structure of **E** and draw the mechanism for the reaction of **E** with NaOH(aq). [3]

(c) Depending on the mechanism, the solvent affects the stability of nucleophile and/or reaction intermediates in the nucleophilic substitution of halogenoalkanes. The table below shows the rate of reaction when different halogenoalkanes and solvents are used.

Solvent	**Type**	**Dielectric constant, ε**	**Relative rates for reaction with OH^-**	
			1° RX in S_N2	**3° RX in S_N1**
CH_3OH	Protic	33	1	4
H_2O	Protic	78	7	150 000
CH_3COOH	Protic	6	1	1
CH_3COCH_3	Aprotic	21	5000	-

Dielectric constant, ε, is a measure of the solvent polarity and ability to insulate charge.

(i) Suggest, using **only** structure and bonding, the difference between *protic* and *aprotic* solvents. [1]

(ii) Explain the effect of solvent on the relative rate of S_N2 reactions. [2]

(iii) Explain, with an aid of a diagram, how water increases the rate of S_N1 reaction. [2]

(iv) Name a solvent, other than those given in the table, that will result in a slower rate for S_N1 than ethanoic acid. [1]

[Total: 20]

5 **(a)** Using only the elements C, H and O, draw the structural formulae of **three** organic compounds, each containing a single carbon atom with an oxidation state of zero, +2 and +4 respectively. [3]

(b) Hot, concentrated potassium manganate (VII) oxidises several classes of organic compounds to ketones, carboxylic acids or carbon dioxide. By this means, the structures of compounds can be determined. Some compounds are easily oxidised, while others require longer heating.

The following describes some reactions of compounds **F** and **K**, and of their oxidation products.

F, $C_8H_{12}O$ reacts with excess potassium manganate (VII) to produce single organic products, **G,** $C_4H_6O_5$ while **K,** $C_{12}H_{12}$**,** reacts with the same reagent to produce **H,** $C_{10}H_{10}O_3$. Carbon dioxide is produced in both reactions in a mole ratio of 2 : 1 respectively. During oxidation of **F**, four moles of carbon dioxide were liberated.

Although **F** reacts with potassium manganate (VII), it gives no reaction with potassium dichromate (VI). When 0.10 mol of **F** is reacted with an excess of sodium metal, 1.2 dm^3 of hydrogen is formed, measured at room temperature and pressure.

G reacts with excess concentrated sulfuric acid to give **I**, $C_4H_4O_4$. Upon further oxidation, **I** is found to give **J,** $C_3H_2O_5$, and an inorganic by-product.

H gives a positive iodoform test and dissolves in aqueous sodium hydroxide. Upon further oxidation of **H**, **L,** $C_9H_6O_6$, and a similar inorganic by-product formed from **I** is also produced.

(i) Deduce the structure of compounds **F** to **L**, explaining the chemistry of the reactions described. [11]

(ii) State the type(s) of stereoisomerism shown by compound **F** and give one further piece of relevant information about it. [2]

(iii) Hence, predict the total number of isomers shown by **F**. [1]

(iv) When compound **K** undergoes prolonged heating with $KMnO_4$ to give **L**, **K** exhibits **two** types of constitutional isomerism.

Name the specific types of isomerism shown by compound **K** and hence, draw the **displayed formulae** of the isomers. [3]

[Total : 20]

SERANGOON JUNIOR COLLEGE
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME	
CLASS	

CHEMISTRY 9729/04

JC2 Preliminary Examination **25 Aug 2017**
Paper 4 Practical **2 hr 30 min**

Candidates answer on the Question Paper

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Give details of the practical shift and laboratory in the boxes provided.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough work.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 22 and 23.

Shift
Laboratory

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

For Examiner's Use	
1	/14
2	/19
3	/12
4	/10
TOTAL	**/ 55**

This document consists of 22 printed pages and 2 blank pages.

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

1 You are to determine the concentration of aqueous copper(II) sulfate by titration. The concentration of Cu^{2+} ions in a solution can be found by reaction with an excess of aqueous iodide ions to produce iodine. The amount of iodine formed can be found by titration with thiosulfate ions, $S_2O_3^{2-}$.

FB 1 is aqueous copper(II) sulfate, $CuSO_4$.
FB 2 is 0.100 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$.
FB 3 is aqueous potassium iodide, KI.
starch indicator

(a) **Method**

(i)
1. Fill the burette with **FB 2**.
2. Using a pipette, transfer 25.0 cm^3 of **FB 1** into a conical flask.
3. Use an appropriate measuring cylinder, transfer 10 cm^3 of **FB 3** to the same conical flask.
4. Titrate this mixture with **FB 2** until the colour of the mixture changes from brown to yellow-brown. An off-white precipitate will also be present in the flask throughout the titration.
5. Add 5 drops of starch indicator.
6. Continue the titration until the blue-black colour of the starch-iodine complex just disappears leaving the off-white precipitate.
7. Record your titration results in the space provided below. Make certain that your recorded results show the precision of your working.
8. Repeat points **1** to **7** as necessary until consistent results are obtained.

Results

I	
II	
III	
IV	
V	

[5]

(ii) From your titrations, obtain a suitable volume of **FB 2** to be used in your calculations. Show clearly how you obtained this volume.

volume of **FB 2** = ……………………………………[1]

(b) **(i)** The equations for the formation of iodine and its reaction with thiosulfate ions are given below.

$$2Cu^{2+} + 4I^{-} \rightarrow 2CuI + I_2$$
$$I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^{-}$$

Calculate the amount of thiosulfate ions, $S_2O_3^{2-}$, present in the volume of **FB 2** in **(a)(ii)**.

amount of $S_2O_3^{2-}$ = ……………………………………[1]

(ii) Using the equations above, calculate the amount of Cu^{2+} ions present in 25.0 cm^3 of **FB 1**.

amount of Cu^{2+} = ……………………………………[1]

(iii) Calculate the concentration, in mol dm^{-3}, of copper(II) sulfate in **FB 1**.

concentration of $CuSO_4$ = ……………………………………[1]

(c) Two students repeated the experiment but each obtained different values for the concentration of $CuSO_4$.

The students each suggested possible improvements.

Student 1 suggested that a larger volume of potassium iodide, **FB 3**, should be added.
Student 2 suggested that the contents of the conical flask should be filtered before titration.

Comment on the effectiveness of **each** of these possible improvements.
Explain your answers.

Student 1

…………………………………………………………………………………………………….......

…………………………………………………………………………………………………….......

Student 2

…………………………………………………………………………………………………….......

…………………………………………………………………………………………………….......

[2]

(d) The maximum error in each burette reading is ± 0.05 cm^3.
The maximum error in each titration is therefore ± 0.10 cm^3.
The 25.0 cm^3 pipette, used in this titration, is labelled with an error of ± 0.06 cm^3.

Explain why the maximum error when 25.0 cm^3 of solution is run from a pipette is only ± 0.06 cm^3 and not ± 0.12 cm^3.

…………………………………………………………………………………………………….......

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

(e) Considering the maximum errors from the pipette and burette used, calculate the total percentage error in one titration.

[2]
[Total: 14]

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2 You are to determine the enthalpy change of reaction, ΔH, for the reaction shown below.

$$Cu(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + H_2(g)$$

Since copper is an unreactive metal it does not react directly with dilute acids. You will therefore need to find the enthalpy change of reaction for two reactions that do occur. The equations for these two reactions are below.

$Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$ **Reaction 1**

$Mg(s) + CuSO_4(aq) \rightarrow MgSO_4(aq) + Cu(s)$ **Reaction 2**

You will carry out experiments to find the enthalpy changes for each of **Reaction 1** and **Reaction 2** and use these values to calculate the enthalpy change for the reaction of copper with sulfuric acid.

TURN OVER FOR EXPERIMENTAL METHOD

Determining the enthalpy change for Reaction 1

For Examiner's use

$Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$ **Reaction 1**

(a) Method

FB 4 is 1.00 mol dm^{-3} sulfuric acid, H_2SO_4.
FB 5 is magnesium powder, Mg.

Read through the method before you start any practical work and prepare suitable tables for your results.

1. Weigh the stoppered weighing bottle containing **FB 5**. Record the mass.
2. Support the styrofoam cup in the 250cm^3 beaker.
3. Use the measuring cylinder to transfer 25cm^3 of **FB 4** into the styrofoam cup.
4. Measure the temperature of **FB 4** in the styrofoam cup and start the stop watch. Record this temperature as being the temperature at time = 0.
5. Measure, and record, the temperature of this **FB 4** every half minute for 2 minutes.
6. At time = 2.5 minutes, add **FB 5** to the acid and stir carefully to reduce acid spray.
   ****Caution: Inhalation of the fumes may cause choking.***
7. Measure the temperature of the mixture in the cup at time = 3 minutes and then every half minute up to time = 7 minutes.
8. Continue stirring occasionally throughout this time.
9. Weigh the weighing bottle that had contained **FB 5**. Record the mass.
10. Calculate and record the mass of **FB 5** added to the sulfuric acid.
11. Discard the used styrofoam cup.

Results

I	
II	
III	
IV	
V	

[5]

(b) **(i)** On the grid below plot a graph of temperature (*y*-axis) against time (*x*-axis).

[2]

(ii) Complete the graph by inserting **two**, **straight** lines of best fit:

- one to show the temperature up to time = 2.5 minutes,
- one to show the temperature after time = 2.5 minutes.

[1]

(iii) From your graph, use the two straight lines of best fit to calculate the change in temperature at time = 2.5 minutes.

temperature change = ……………………………………[1]

(c) Calculations

(i) In the reaction in **(a)**, the sulfuric acid was in excess. Without carrying out any additional tests, what observation could you have made during your experiment to confirm this?

……………………………………………………………………………………………………

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

(ii) Calculate the energy change that occurred during the reaction in **(a)**.

[Assume that 4.2 J is needed to raise the temperature of 1.0 cm^3 of solution by 1.0°C.]

energy change = ……………………………………[1]

(iii) Use your answer to **(ii)** to calculate the enthalpy change, in kJ mol^{-1}, for the reaction between sulfuric acid and magnesium.

[A_r : Mg, 24.3]

$Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$ **Reaction 1**

enthalpy change for **Reaction 1** = ……………………………………[1]

Determining the enthalpy change for Reaction 2

$Mg(s) + CuSO_4(aq) \rightarrow MgSO_4(aq) + Cu(s)$ **Reaction 2**

(d) Method

FB 6 is 1.00 mol dm^{-3} copper(II) sulfate, $CuSO_4$.
FB 7 is magnesium powder, Mg.

Read through the method before you start any practical work and prepare suitable tables for your results.

1. Weigh the weighing bottle containing **FB 7**. Record the mass.
2. Support the styrofoam cup in the 250cm^3 beaker.
3. Use the measuring cylinder to transfer 25cm^3 of **FB 6** into the styrofoam cup.
4. Measure the temperature of **FB 6** in the styrofoam cup and record the temperature.
5. Add the **FB 7** to the **FB 6** in the cup and stir the mixture constantly.
6. Measure and record the maximum temperature reached during the reaction.
7. Calculate and record the maximum temperature change that occurred during the reaction.
8. Weigh the weighing bottle that had contained **FB 7**. Record the mass.
9. Calculate and record the mass of **FB 7** added to the copper(II) sulfate.
10. Empty the contents of the styrofoam cup into the bottle labelled **waste**.
11. Discard the used styrofoam cup.

Results

I	
II	

[2]

For Examiner's use

(e) Calculations

(i) Show, using suitable calculations, that the copper(II) sulfate was in excess in the reaction.
[*A*r : Mg, 24.3]

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[1]

(ii) Hence, calculate the enthalpy change, in kJ mol^{-1}, for the reaction between magnesium and copper(II) sulfate.

[Assume that 4.2 J is needed to raise the temperature of 1.0cm^3 of solution by 1.0°C.]

$Mg(s) + CuSO_4(aq) \rightarrow MgSO_4(aq) + Cu(s)$ **Reaction 2**

enthalpy change for **Reaction 2** = ……………………………………[1]

Enthalpy change for Reaction 3

Reaction 3 is shown below.

$Cu(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + H_2(g)$ **Reaction 3**

(f) Use your values for the enthalpy changes for **Reactions 1** and **2** to calculate the enthalpy change for **Reaction 3**.

$Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$ **Reaction 1**

$Mg(s) + CuSO_4(aq) \rightarrow MgSO_4(aq) + Cu(s)$ **Reaction 2**

Show clearly how you obtained your answer.

(If you were unable to calculate the enthalpy changes for **Reactions 1** and **2**, you should assume that the value for **Reaction 1** is – 444 kJ mol^{-1} and that the value for **Reaction 2** is – 504 kJ mol^{-1}. Note: these are not the correct values.)

enthalpy change for **Reaction 3** = ……………………………………[1]

(g) **(i)** The method you used to determine the enthalpy change for **Reaction 1** was more accurate than the method you used to determine the enthalpy change for **Reaction 2**. Suggest why the method used for **Reaction 2** was less accurate. Explain your answer.

…………………………………………………………………………………………………

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

(ii) A student suggested that the accuracy of the method used for **Reaction 2** could be improved by using a larger volume of copper(II) sulfate. Is this a correct suggestion? Give a reason for your answer.

…………………………………………………………………………………………………

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

[Total : 19]

3 Qualitative Analysis

At each stage of any test, you are to record details of the following.

- Colour changes seen
- The formation of any precipitate
- The solubility of such precipitates in an excess of the reagent added

Where gases are released, they should be identified by a test, described in the appropriate place in your observations.

You should indicate clearly at what stage in a test a change occurs.
No additional tests for ions present should be attempted.

FB 8 is a solution containing 2 cations and 1 anion.

(a)

Test	Procedure	Observation
1	To 1 cm depth of **FB 8** in a test tube, add aqueous ammonia until it is in excess.	
2	To 1 cm depth of **FB 8** in a **boiling tube**, add aqueous sodium hydroxide until it is in excess. Then heat the boiling tube gently with care. Keep the mixture for **Test 3**.	
3	To the mixture from **Test 2**, add 1 cm depth of aqueous hydrogen peroxide. Shake the boiling tube gently.	
4	To 1 cm depth of **FB 8** in a test tube, add aqueous barium chloride, followed by dilute hydrochloric acid.	

[4]

(b) Using your observations above, identify the ions in **FB 8**. Give evidence to support your conclusion.

……………………………………………………………………………………………………….....

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[3]

(c) What type of reaction has taken place in **Test 3**? Explain your answer.

……………………………………………………………………………………………………….....

……………………………………………………………………………………………………….....

……………………………………………………………………………………………………….....

[1]

(d) **FB 9** is an aqueous solution, containing one cation and one anion.
Carry out the following tests in test-tubes.
Complete the table by recording your observations.

Test	Procedure	Observations
5	To 1 cm depth of **FB 9**, add aqueous sodium hydroxide until it is in excess.	
6	To 1 cm depth of **FB 9**, add a piece of magnesium ribbon.	
7	To 1 cm depth of **FB 9**, add 2 drops of aqueous silver nitrate, followed by aqueous ammonia until in excess.	

[2]

(e) Using your observations above, identify the ions in **FB 9**. Give evidence to support your conclusion.

…….....

…….....

…….....

[2]

[Total: 12]

4 Many transition metal complex ions are coloured. It is possible to use this property to determine the concentration of a solution of a coloured ion. A few cm^3 of the solution is placed inside a *spectrometer*.

A *spectrometer* measures the amount of light that is absorbed when a specific wavelength of visible light is shone through a coloured solution. It does this by comparing the amount of light passing through the sample with the amount of light passing through the pure solvent. The amount of light absorbed is expressed as an absorbance value. The more concentrated the solution, the higher the absorbance value.

Beer-Lambert's Law states that the absorbance values, A, is directly proportional to the concentration of absorbing species, c, as shown below. The general Beer-Lambert's Law is usually written as,

$$A = \varepsilon c l$$

Where ε is the molar extinction coefficient and l is the path length, which is usually 1.0cm.

This equation can be used to calculate the absorbance value when the concentration of copper(II) ions is known.

You may assume that you are provided with the following in the subsequent parts of the question.

- **FB 1** from Question 1
- solid hydrated copper(II) sulfate, $CuSO_4.5H_2O$ (M_r = 249.6);
- access to a spectrometer and instructions for its use;
- graph paper;
- the apparatus and chemicals normally found in a school or college laboratory.

(a) The spectrometer is set to use the wavelength of light that is absorbed most strongly by the copper(II) ions.

Suggest a colour in the visible spectrum from which a suitable wavelength of light might be chosen. Explain your answer.

………

………

[1]

(b) Spectrometry can be used to determine the concentration of a solution of aqueous copper(II) sulfate, **FB 1**. A series of known, but different, concentrations of copper(II) sulfate is prepared. A spectrometer is used to measure the absorbance of each solution.

According to Beer-Lambert's Law, a graph of absorbance against concentration is then plotted. This graph is known as *calibration* line.

The experiment is then repeated using a solution of unknown concentration. By comparing the absorbance of this solution with the calibration line, the concentration of copper(II) ions in the unknown solution can be determined.

Propose a simple plan on how you would prepare

- a 100.0 cm^3 of 1.00 mol dm^{-3} standard aqueous copper(II) sulfate;
- a suitable range of diluted solutions of accurate concentrations

You are to show detailed calculations and suitable tables (where appropriate) in your answer.

(i) a 100.0 cm^3 of 1.00 mol dm^{-3} standard aqueous copper(II) sulfate;

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[2]

(ii) a suitable range of diluted solutions of accurate concentrations, keeping the total volume of each solution constant at 20.00 cm^3.

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[3]

(c) Using the solutions prepared in **(b)**, the absorbance value of each copper(II) sulfate solution can be determined and hence a calibration line can be obtained via the spectrometer.

Describe a plan to determine the concentration of **FB 1**.

Your plan should include details of:

- calculation of the absorbance value for each copper(II) sulfate solution prepared in **(b)**, given ε of $CuSO_4$ is **2.81** $\text{mol}^{-1}\,\text{dm}^{3}\,\text{cm}^{-1}$.
- a sketch of the calibration line you would expect to obtain;
- a brief outline of how the results would be obtained.
- how the calibration line would be used to determine the concentration of copper(II) ions in **FB 1**.

[3]

(d) Given that the absorbance for **FB 1** is 0.286, calculate the concentration of **FB 1**.

For Examiner's use

concentration of **FB 1** = ……………………………………[1]

[Total : 10]

Qualitative Analysis Notes
[ppt. = precipitate]
(a) Reactions of aqueous cations

cation	***reaction with***	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq),	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt., turning brown on contact with air insoluble in excess	green ppt., turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt., rapidly turning brown on contact with air insoluble in excess	off-white ppt., rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

ion	***reaction***
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, Cl^-(aq)	gives white ppt. with Ag^+(aq) (soluble in NH_3(aq))
bromide, Br^-(aq)	gives pale cream ppt. with Ag^+(aq) (partially soluble in NH_3(aq))
iodide, I^-(aq)	gives yellow ppt. with Ag^+(aq) (insoluble in NH_3(aq))
nitrate, NO_3^-(aq)	NH_3 liberated on heating with OH^-(aq) and A*l* foil
nitrite, NO_2^-(aq)	NH_3 liberated on heating with OH^-(aq) and A*l* foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, SO_4^{2-}(aq)	gives white ppt. with Ba^{2+}(aq) (insoluble in excess dilute strong acids)
sulfite, SO_3^{2-}(aq)	SO2 liberated with dilute acids; gives white ppt. with Ba^{2+}(aq) (soluble in dilute strong acids)

(c) Tests for gases

gas	***test and test result***
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	“pops” with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	***colour of element***	***colour in aqueous solution***	***colour in hexane***
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

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2017 SRJC H2 Chemistry 9729

Preliminary Examination Paper 1 Solution

1 An acidified solution of the salt $KClO_x$ will oxidise Fe^{2+}(aq) to Fe^{3+}(aq) quantitatively, the chlorine being reduced to Cl^-(aq).

When 0.302 g of the salt $KClO_x$ was reacted with 0.540 mol dm^{-3} Fe^{2+}(aq) in the presence of H^+(aq), 21.0 cm^3 of Fe^{2+}(aq) was needed for complete reaction.

Which of the following is the value of x?

A 1
B 2
C 3
D 4

Answer: **B**

$ClO_x^- + 2xe^- \rightarrow Cl^-$
$Fe^{2+} \rightarrow Fe^{3+} + e^-$
$\therefore\ 2xFe^{2+} \equiv ClO_x^-$
OR mole ratio of ClO_x^- : Fe^{2+} is
1 : $2x$

Amount of Fe^{2+} used = $\frac{21.0}{1000} \times 0.540$ = 0.01134 mol

Amount of ClO_x^- = $\frac{0.01134}{2\boldsymbol{x}}$ mol

Amount of $KClO_x$ = $\frac{0.302}{39.1+35.5+\boldsymbol{x}(16)}$

Amount of ClO_x^- = $\frac{0.302}{39.1+35.5+\boldsymbol{x}(16)} = \frac{0.01134}{2\boldsymbol{x}}$

$$\frac{2(0.302)\boldsymbol{x}}{0.01134} = 74.6 + \boldsymbol{x}(16)$$

$$53.263\boldsymbol{x} - 16\boldsymbol{x} = 74.6$$

$$\boldsymbol{x} = 1.99 \approx \mathbf{2}$$

2 A student made up a 0.10 mol dm^{-3} solution of $Ba(OH)_2.8H_2O$ which she found in the laboratory cupboard and left the solution in an open beaker. A week later, she returned to the laboratory, used the solution for titration with 0.10 mol dm^{-3} HC*l* and was surprised to discover her titres were lower than expected.

Which of the following explains why the values were so low?

A Some of the barium hydroxide has reacted with carbon dioxide in the air to form solid barium carbonate.
B Some water had evaporated from the barium hydroxide solution.
C The concentration of HC*l* was less than the stated 0.10 mol dm^{-3}.
D The crystals had less water of crystallisation than stated.
Answer : A

A: will lower the concentration of $Ba(OH)_2$ and thus a lower than expected titre value.

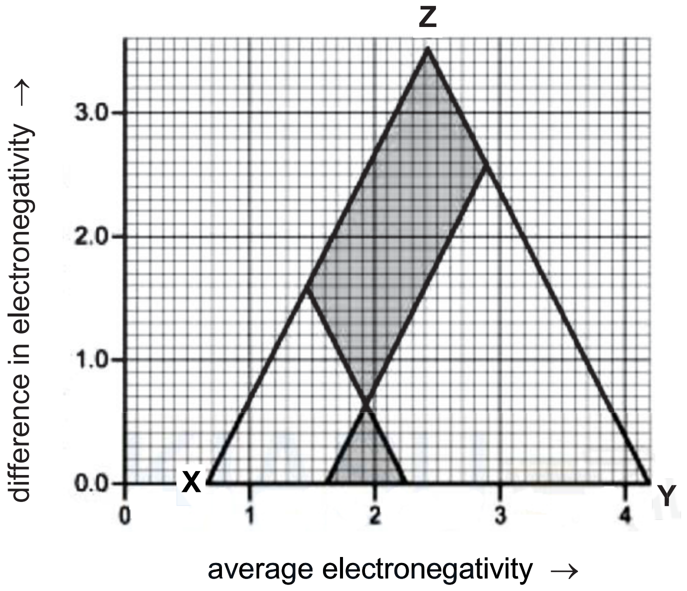
B: will increase the concentration of $Ba(OH)_2$ and cause the titre value to be higher than expected.

C: will cause the titre value to be higher than expected.

D: will increase the concentration of $Ba(OH)_2$ and thus a higher than expected titre value.

3 The type of bonding between two elements can be rationalised and even predicted using a van Arkel triangle. The triangle is based on electronegativity values. Difference in electronegativity is plotted along the y–axis and average electronegativity is plotted along the x–axis.

What is the type of bonding present at each of these bonding extremes, labelled **X**, **Y** and **Z** on the triangle?



	X	Y	Z
A	metallic	covalent	ionic
B	covalent	metallic	ionic
C	covalent	ionic	metallic
D	ionic	covalent	metallic

Answer: **A**

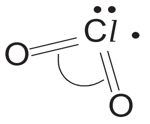
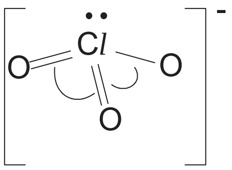
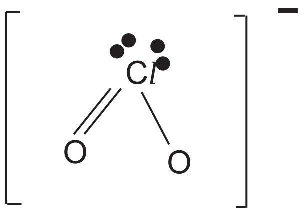
Difference in electronegativity is zero for **X** & **Y**
⇒ metallic bonding or covalent bonding.
Since metals have low electronegativity
⇒ **X** is metallic bonding.

4 Equimolar amou ct according to the equation below.

$$2ClO_2\ (aq) + 2OH^-\ (aq) \rightarrow ClO_3^-\ (aq) + ClO_2^-\ (aq) + H_2O\ (l)$$

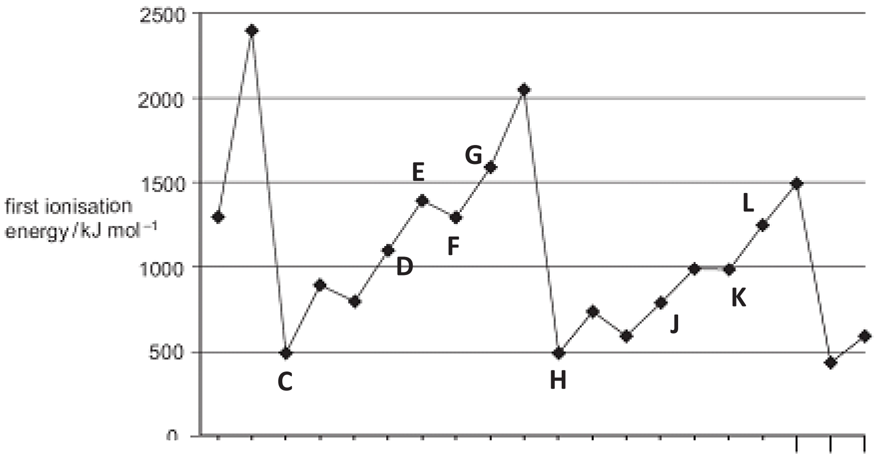
Which statement is correct?

A The shape changes from linear in ClO_2 to bent in ClO_2^-.
B The shape changes from bent in ClO_2 to trigonal planar in ClO_3^-.
C The bond angle changes from about 120° in ClO_2 to 107° in ClO_3^-.
D The bond angle changes from about 105° in ClO_2 to 107° in ClO_3^-.
Answer: D

ClO_2	ClO_3^-	ClO_2^-
 Bond angle ≈ 105° Shape: bent	 Bond angle ≈107° Shape: trigonal pyramidal	 Bond angle ≈105° Shape: bent

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

The first ionisation energies of successive elements in the Periodic Table are represented in the graph.



Which of the following statements about elements **C** to **L** are correct?

1 **E** and **J**$^-$ have half–filled p–orbitals.
2 Chlorides of **D** and **J** undergo hydrolysis.
3 **F** and **K** reacts to form acidic compounds.
4 **D** and **F** forms compounds with formula **DF** and **DF**$_2$.
5 **G** and **L** forms compounds with variable oxidation states from –1 to +7.

A 1 and 4 only
B 2 and 5 only
C 1, 3 and 4 only
D 2, 3 and 5 only

Answer : C (Statements 1, 3, 4 only)

Elements **C** and **H** are from group 1 as they have the lowest first I.E.
They are lithium and sodium respectively.

1 is correct.
E is from Group 15 and J is from Group 14.
Element **E** is nitrogen and has half-filled 2p orbitals.
Element **J** is silicon, and Si^- has half-filled 3p orbitals.

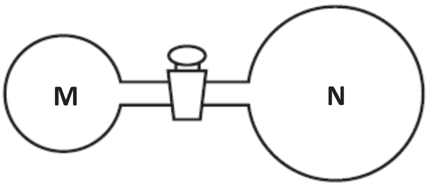
2 is wrong.
D and J are from Group 14.
D is a Period 2 element and is carbon. It cannot undergo hydrolysis as they do not have low lying d-orbitals to accommodate the lone pair of electrons from water, hence no hydrolysis can occur.

3 is correct.
Element **F** is oxygen and element **K** is sulfur. SO_2 and SO_3 are acidic in nature.

4 is correct.
Element **D** is carbon and **F** is oxygen. Hence **DF** and **DF_2** is possible (ie, CO and CO_2).

5 is wrong.
Elements **G** is fluorine and **L** is chlorine. Chlorine can have variable oxidation states from –1 to +7, but fluorine only exists in states of –1 and 0.

6 Two glass vessels **M** and **N** are connected by a closed valve.



M contains helium at 25 °C at a pressure of 1×10^5 Pa. **N** has been evacuated, and has three times the volume of **M**. In an experiment, the valve is opened and the whole set-up placed in boiling water.

What is the final pressure in the system?

A 3.13×10^4 Pa
B 3.76×10^4 Pa
C 1.00×10^5 Pa
D 1.33×10^5 Pa
Answer: A

Let the volume of M be v, hence volume of N is 3v. Total volume = 4v

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\frac{10^5 \times v}{298} = \frac{P_2 \times 4v}{373}$$

$P_2 = 3.13 \times 10^4$ Pa

7 Consider the following equilibrium system:

$$Fe_3O_4(s) + CO(g) \rightleftharpoons CO_2(g) + 3FeO(s) \qquad \Delta H = +ve$$

Given that $K_p = K_c\,(RT)^{\Delta n}$, where Δn is the sum of gaseous products – sum of gaseous reactants.

Which of the following statements are correct?

1 $K_c = K_p$ for this system.
2 The equilibrium constant, K_c, for this reaction has no units.
3 Adding FeO causes the position of equilibrium to shift to the left.
4 Increasing the temperature causes the position of equilibrium to shift to the right.

A 1 and 2
B 1 and 3
C 2, 3 and 4
D 1, 2 and 4
Answer : **D**

1 is correct: $\Delta n = 0$, $K_c = K_p$ for this system
2 is correct: $K_c = \frac{[CO_2]}{[CO]}$ no units
3 is incorrect: FeO is a solid. Position of equilibrium is not affected by it.
4 is correct: Increasing temperature would favour the forward endothermic reaction. Position of equilibrium would shift to the right.

8 In an experiment to measure the enthalpy change of neutralisation, 20 cm^3 of aqueous sulfuric acid containing 0.02 mol of H_2SO_4 is placed in a plastic cup of negligible heat capacity.

A 20 cm^3 sample of aqueous sodium hydroxide containing 0.04 mol of NaOH, at the same initial temperature, is added and the temperature rises by 15 K.

If the heat capacity per unit volume of the final solution is 4.2 J K^{-1} cm^{-3}, what is the enthalpy change of neutralisation?

A $-\left(\frac{20 \times 4.2 \times 15}{0.04 \times 1000}\right)$ kJ mol^{-1}

B $-\left(\frac{40 \times 4.2 \times 15}{0.04 \times 1000}\right)$ kJ mol^{-1}

C $-\left(\frac{20 \times 4.2 \times 15}{0.02 \times 1000}\right)$ kJ mol^{-1}

D $-\left(\frac{40 \times 4.2 \times 15}{0.02 \times 1000}\right)$ kJ mol^{-1}

Answer : **B**

$$\begin{array}{lllll} H_2SO_4 & + & 2\,NaOH & \rightarrow Na_2SO_4 & + 2H_2O \\ 0.02 & & 0.04 & & \end{array}$$

$$Q = -\frac{mc\Delta T}{nH_2O x1000} = -\frac{40 \times 4.2 \times 15}{0.04 \times 1000} = -63 kJmol^{-1}$$

9 The conversion of graphite into diamond is a non–spontaneous reaction at 298 K. The entropy change of this reaction is negative at 298 K.

$$\text{C(graphite)} \rightarrow \text{C(diamond)} \qquad \Delta G = +3.08 \text{ kJ mol}^{-1}, \ \Delta S = -3.3 \text{ J mol}^{-1} \text{ K}^{-1}$$

With reference to the enthalpy change, ΔH, of the reaction above, which statements are correct?

1 Enthalpy change of atomisation of diamond is more endothermic than that of graphite.

2 Enthalpy change of combustion of diamond is more exothermic than that of graphite.

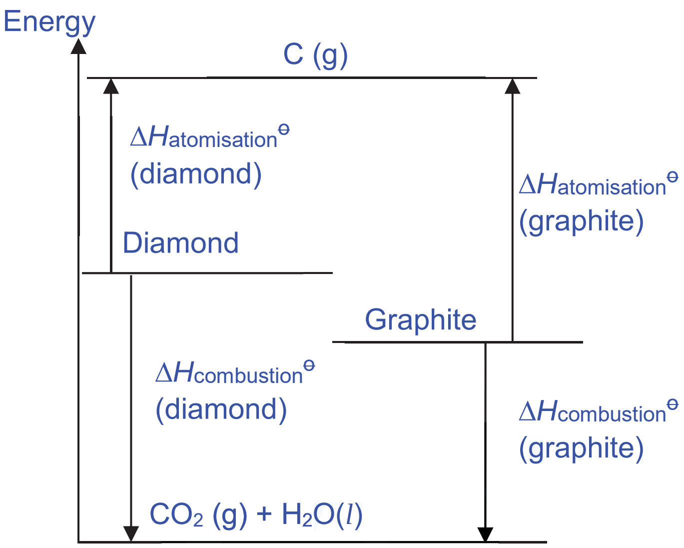
3 Bond energy of carbon–carbon bonds in graphite is greater than that in diamond.

4 The activation energy to convert graphite to diamond is lower than the activation energy for the reverse reaction.

A 1 and 4
B 2 and 3
C 1, 2 and 3
D 2, 3 and 4

Answer : **B (2 & 3 are correct)**

$$\Delta G = \Delta H - T\Delta S$$
$$3.08 = \Delta H - (298)(-3.3/1000)$$
$$\Delta H = +2.10 \text{ kJ mol}^{-1}$$



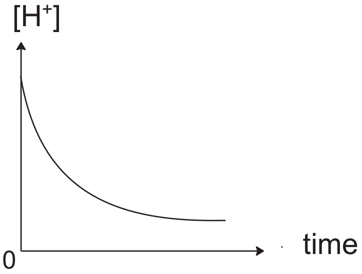
The carbon in graphite is sp^2 hybridised and carbon in diamond is sp^3 hybridised. Since the s character is higher in C-C bond in graphite, it will be a stronger bond than C-C bond in diamond.

10 The reaction between acidified KI and aqueous H_2O_2 involves the following steps:

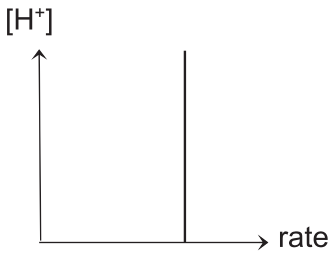
$H_2O_2 + I^- \rightarrow H_2O + OI^-$ slow
$OI^- + H^+ \rightarrow HOI$ fast
$HOI + H^+ + I^- \rightarrow I_2 + H_2O$ fast

Which graph would be obtained?

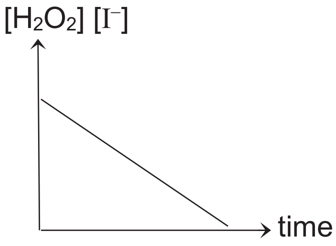
A



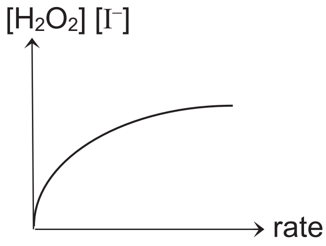
B



C

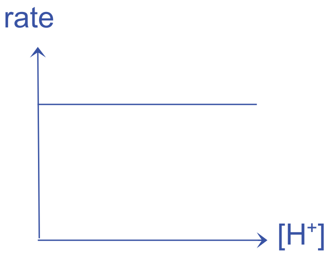


D



Answer: **B**

Base on the slow step, rate = k $[H_2O_2][I^-]$
The rate is independent of $[H^+]$.



11 Compounds of beryllium are amphoteric, like compounds of aluminium.

In which equations is the beryllium-containing reactant acting as a Brønsted-Lowry acid?

A $BeO(s) + 2OH^-(aq) + H_2O(l) \rightarrow [Be(OH)_4]^{2-}(aq)$
B $BeCl_2 + 4H_2O \rightarrow Be(H_2O)_4^{2+} + 2Cl^-$
C $2Be + O_2 \rightarrow 2BeO$
D $Be(H_2O)_2(OH)_2 + 2OH^- \rightarrow Be(OH)_4^{2-} + 2H_2O$

Answer: **D**

A Brønsted-Lowry acid is a proton donor.

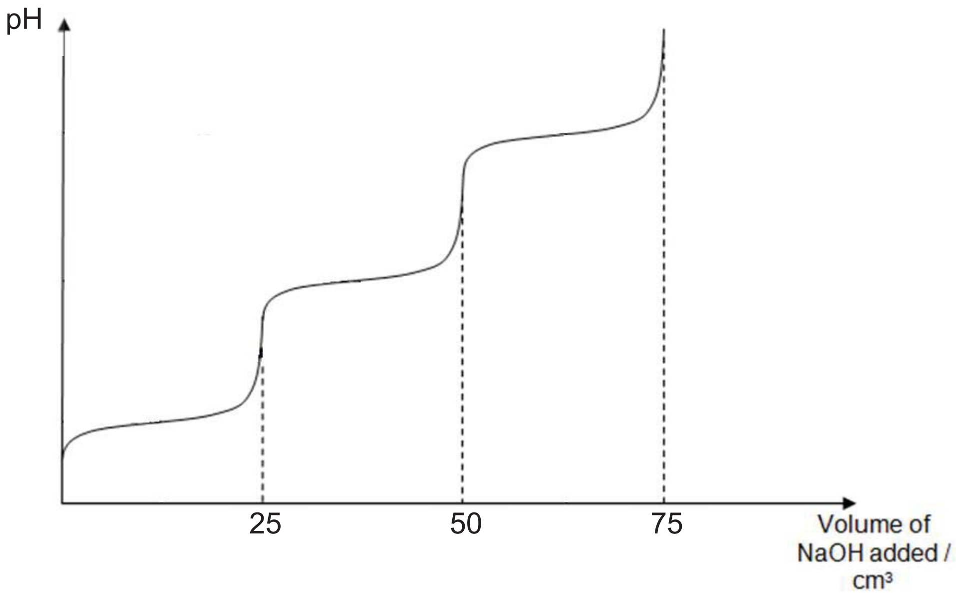
A: This is neutralisation reaction but BeO is not a Brønsted-Lowry acid as it does not donate a H^+ ion.

B: This is simply a dissociation reaction and $BeCl_2$ is not a Brønsted-Lowry acid as it does not donate a H^+ ion.

C: This is a combustion reaction.

D: $Be(H_2O)_2(OH)_2$ is acting as a Brønsted-Lowry acid as 2 H_2O molecules are deprotonated to form 2 additional OH^- ions and result in a negatively charged $Be(OH)_4^{2-}$ ion.

12 25 cm^3 of 1 mol dm^{-3} of the fully protonated form of compound **O** was titrated against a standard sodium hydroxide solution of a similar concentration and the following titration curve was obtained.



Which of the following compounds is a possible identity of compound **O**?

A $NH_2CH(CH_2CH_2CONH_2)COOH$
B $NH_2CH(CH_2CH_2CH_2OH)COOH$
C $NH_2CH(CH_2CH_2CH_2NH_2)COOH$
D $NH_2CH(CH_2CH_2CHO)COOH$

Answer: C
All amine groups are protonated and can act as a bronsted-lowry acid.

A : only two acidic groups as the amide on the R group is neutral

B : only two acidic groups as the OH on the R group is not able to be neutralised by NaOH

C : three acidic groups

D : only two acidic groups as the aldehyde on the R group is also neutral

13 A sparingly soluble calcium salt dissociates in solution according to the equation:

$$Ca_3\mathbf{Q}_2\text{ (s)} \rightleftharpoons 3Ca^{2+}\text{ (aq)} + 2\mathbf{Q}^{3-}\text{ (aq)}$$

If the solubility product of $Ca_3\mathbf{Q}_2$ is p, what is the concentration of $\mathbf{Q}^{3-}$ at equilibrium in a saturated solution of $Ca_3\mathbf{Q}_2$ (aq)?

A $2p^{\frac{1}{5}}$

B $2(\frac{p}{36})^{\frac{1}{5}}$

C $2(\frac{p}{72})^{\frac{1}{5}}$

D $2(\frac{p}{108})^{\frac{1}{5}}$

Answer: D

$Ca_3\mathbf{Q}_2\text{ (s)} \rightleftharpoons 3Ca^{2+}\text{ (aq)} + 2\mathbf{Q}^{3-}\text{ (aq)}$
Let solubility be x mol dm^{-3}

$K_{sp} = [Ca^{2+}]^3 [Q^{3-}]^2$

$p = (3x)^3(2x)^2$

$p = (27x^3)(4x^2)$

$p = 108x^5$

$x = (\frac{p}{108})^{\frac{1}{5}}$

$2x = 2(\frac{p}{108})^{\frac{1}{5}}$

14 A transition metal cation can exist in a ‘high spin’ or ‘low spin’ state while exposed to different ligands in an octahedral complex.

A ‘high-spin’ state has the electrons occupying all the d-orbitals singly first, before pairing in the lower energy d-orbitals.

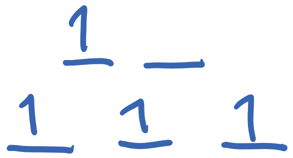
A ‘low-spin’ state has the lower energy d-orbitals filled first, pairing up if necessary, before the higher energy d-orbitals are filled.

Which cation would have the largest number of unpaired electrons?

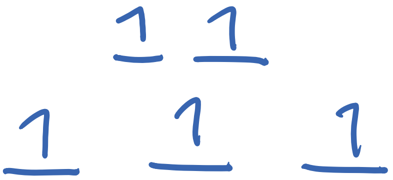
A ‘High-spin’ Mn^{3+}
B ‘High-spin’ Fe^{3+}
C ‘Low-spin’ Co^{2+}
D ‘Low-spin’ Ni^{4+}

Answer: B

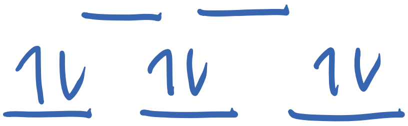
A: ‘High-spin’ Mn^{3+} → 4 unpaired electrons



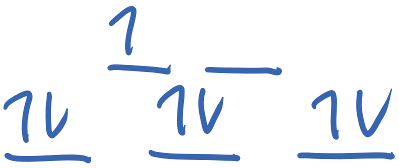
B: ‘High-spin’ Fe^{3+} → 5 unpaired electrons



D: ‘Low-spin’ Ni^{4+} → no unpaired electrons



C: ‘Low-spin’ Co^{2+} → 1 unpaired electron



15 Which of the following is **not** a result of the small energy gap between 3d and 4s orbitals?

A Transition metals have higher electrical conductivity than aluminium.
B Transition metals can exhibit variable oxidation states.
C Transition metals have higher melting point than calcium.
D Transition metals ions are usually coloured.
Answer : **D**

The smaller energy gap allow for valence electrons to be removed from both 3d and 4s orbitals. This leads to transition metals having higher conductivity, having variable oxidations states and higher melting point.

The energy gap is due to absorption in the visible light region due to d-d orbital splitting and transition.

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

Two catalysed reactions and their respective catalysts are shown below.

Reaction	**Equation**	**Catalyst**
I	$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$	Fe^{3+}
II	$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$	Mn^{2+}

Which statements about the reactions and the catalysts are correct?

1 Mn^{2+} is an auto-catalyst in reaction **II**.
2 Fe^{2+} could replace Fe^{3+} as a heterogeneous catalyst in reaction **I**.
3 Mn^{2+} could replace Fe^{3+} as a homogeneous catalyst in reaction **I**.
4 Both catalysts increase the energetic feasibility of their respective reactions.

A 1 and 3
B 2 and 3
C 1, 2 and 4 only
D 2, 3 and 4 only
Answer: A (1 and 3 only)

1 is correct: Mn^{2+} is a catalyst as well as a product of reaction **II**. Thus, Mn^{2+} is an auto-catalyst.

2 is incorrect: Fe^{2+} can replace Fe^{3+} as homogeneous catalyst, not heterogeneous catalyst.

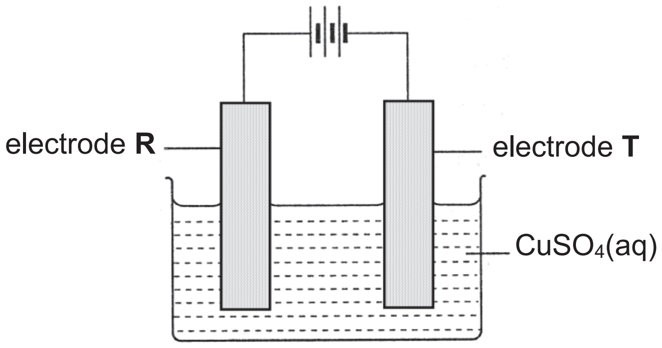
3 is correct:
From Data Booklet: $E^\ominus(S_2O_8^{2-}/SO_4^{2-}) = +2.01$ V
$E^\ominus(I_2/I^-) = +0.54$ V
$E^\ominus(Mn^{3+}/Mn^{2+}) = +1.54$ V

$2Mn^{2+} + S_2O_8^{2-} \rightarrow 2Mn^{3+} + 2SO_4^{2-}$
$E^\ominus_{cell} = 2.01 - 1.54 = +0.47 \text{ V} > 0$
$2Mn^{3+} + 2I^- \rightarrow 2Mn^{2+} + I_2$
$E^\ominus_{cell} = 1.54 - 0.54 = +1.00 \text{ V} > 0$
Thus, Mn^{2+} could replace Fe^{3+} as a homogeneous catalyst in reaction I.

4 is incorrect: ΔH remains the same for a catalysed or uncatalysed reaction. Reaction will remain just as energetically feasible.

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

Impure copper obtained from copper ores can be purified by electrolysis as shown below. The cell potential is adjusted such that copper of the impure copper electrode dissolves and impurities such as silver, iron and zinc can be removed through this process.



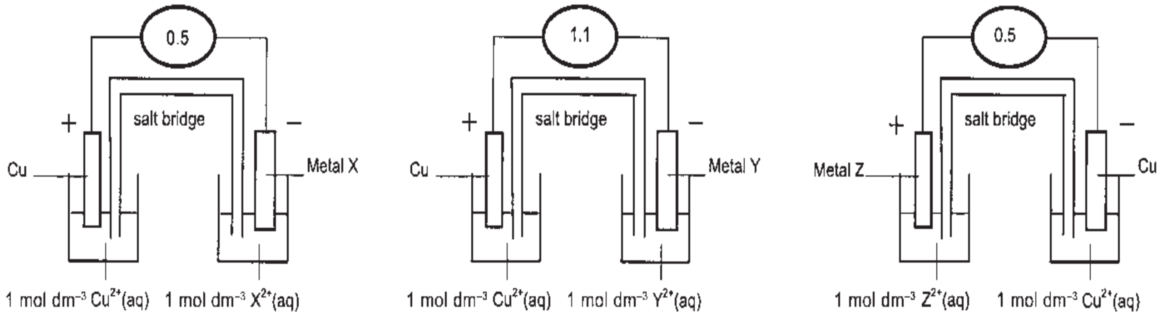
Which statement is **not** correct regarding the above electrolytic process?

A Reduction occurs at electrode **T**.
B Electrode **R** contains impure copper.
C Zinc impurity goes into the solution as Zn^{2+} ions.
D Iron and silver impurities fall to the bottom as sludge.
Answer: D

Option A is correct: Electrode T is the cathode where reduction occurs.
Option B is correct. Electrode R is the anode which contains impure copper.
Option C is correct. $E^{\ominus}(Zn^{2+}/Zn)$ is more negative than $E^{\ominus}(Cu^{2+}/Cu)$, hence Zn will be oxidised to form Zn^{2+} ions.
Option D is incorrect. $E^{\ominus}(Fe^{2+}/Fe)$ is more negative than $E^{\ominus}(Cu^{2+}/Cu)$, hence Fe will be oxidised to form Fe^{2+} ions, instead of falling to the bottom as sludge.

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

Three electrochemical cells are set up as shown below. The *e.m.f* in volts is shown on each voltmeter.



These *e.m.f* indicate the order of reactivity of the metals. The order of the weakest to the strongest reducing agent is

A **X**, **Y**, Cu, **Z**
B Cu, **Z**, **X**, **Y**
C **Z**, Cu, **X**, **Y**
D **Y**, **X**, **Z**, Cu
Answer: C

$E^{\ominus}(Cu^{2+}/Cu) = +0.34$ V

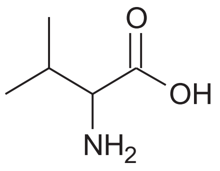
For electrochemical cell on the left, Cu^{2+}/Cu half-cell is the cathode. Hence, $E^{\ominus}(X^{2+}/X) = 0.34 - 0.5 = -0.16$ V

For electrochemical cell in the centre, Cu^{2+}/Cu half-cell is the cathode. Hence, $E^{\ominus}(Y^{2+}/Y) = 0.34 - 1.1 = -0.76$ V

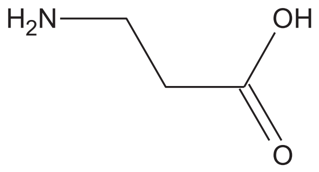
For electrochemical cell on the right, Cu^{2+}/Cu half-cell is the anode. Hence, $E^{\circ}(Z^{2+}/Z) = 0.5 + 0.34 = +0.84$ V

Order of weakest reducing regent (least easily oxidised, least negative $E^{\ominus}$ value) to strongest reducing agent (most easily oxidised, most negative $E^{\ominus}$ value): Z, Cu, X, Y

19 Valine is a naturally occurring amino acid.



Valine



3-aminopropanoic acid

Which statements about valine and 3-aminopropanoic acid are correct?

A Both compounds are able to form zwitterions.
B Both compounds are able to react with ethanoic acid to give amide.
C Both compounds are able to react with $NaBH_4$ in methanol to give alcohol.
D Both compounds are soluble in water due to the formation of intermolecular hydrogen bonding.

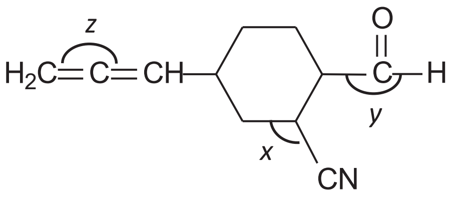
Answer: A

Option B is incorrect: Both compounds are not able to react with ethanoic acid to give amide. Acid-base neutralization would occur, producing a salt.

Option C is incorrect: Both compounds are not able to react with $NaBH_4$ in methanol to give alcohol. They must react with $LiAlH_4$ in dry ether.

Option D is incorrect: Both valine and 3-aminopropanoic acid are soluble in water due to formation of ion-dipole interactions, not hydrogen bonding.

20 Which of the following statements are correct about compound **U**?



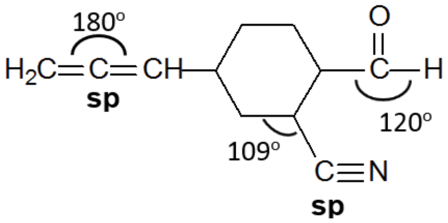
compound **U**

1 The bond angles in compound **U** increase in the order $x < y < z$.
2 There is only one sp hybridised carbon atom in compound **U**.
3 There are 26 σ and 5 π bonds.
4 Compound **U** is planar.

A 1 and 2
B 1 and 3
C 1, 2 and 4 only
D 2, 3 and 4 only

Answer : **B** (1 and 3 are correct)

26 σ and 5 π bonds.



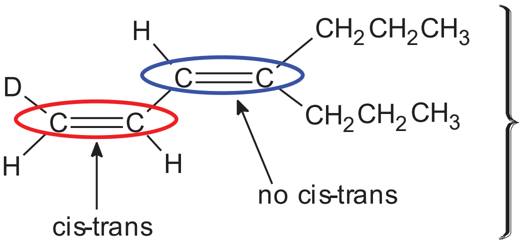
21 Deuterium (D or ^{2}H) is a heavy isotope of hydrogen. A deutero-hydrocarbon has the part structural formula shown below.

$$CDH{=}CH{-}CH{=}C(C_3H_7)_2$$

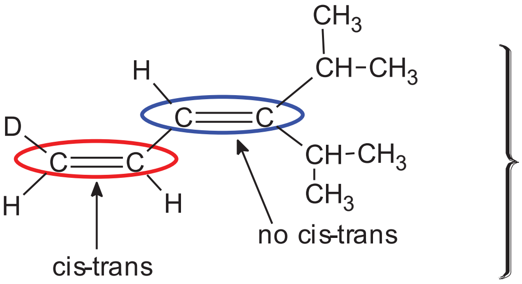
What is the total number of isomers with the above part-structural formula?

A 2
B 4
C 8
D 10

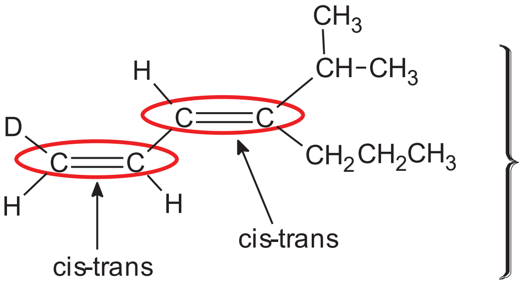
Answer: C



no. of isomer = 2



no. of isomer = 2



no. of isomer = 2^2 = 4

Total no. of isomers = 8

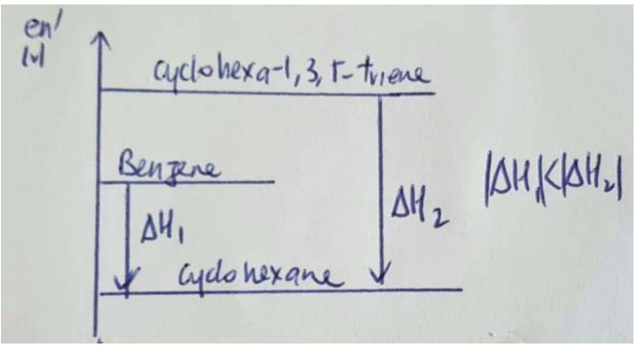
22 The molecule of benzene, C_6H_6 is a regular hexagon in which the π electrons are described as delocalised.

Which of the following statements support this structure?

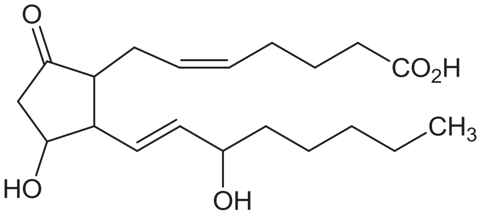
1 Benzene is a good conductor of electricity.
2 Addition reactions of benzene take place more easily than substitution.
3 All C–C bonds lengths in benzene are intermediate between C–C bond in an alkane and C=C bond in an alkene.
4 The enthalpy change of hydrogenation of benzene is less exothermic than that predicted for cyclohexatriene.

A 1 and 3
B 3 and 4
C 1, 2 and 3 only
D 1, 2 and 4 only

Answer : B (3 and 4 are correct)

1	Benzene is a simple molecular structure and does not conduct electricity.
2	Benzene will undergo substitution reactions easily as a result of its resonance stability.
3	The bond order of all C−C bonds in benzene are 1.5 due to resonance which arises from the continuous overlap of unhybridised p-orbitals.
4	Benzene is more stable than cyclohexa-1,3,5-triene due to resonance. Thus, it exists at a lower energy level (see below). Hydrogenation of benzene gives cyclohexane. 

23 PGE$_2$ is a prostaglandin that has pharmacological activity.



PGE$_2$

Which of the following is incorrect?

	Reducing agent	Number of hydrogen atoms incorporated per molecule of PGE$_2$
A	H_2 / Ni	6
B	Na in ethanol	8
C	$NaBH_4$ in methanol	6
D	$LiAlH_4$ in dry ether	4

Answer : **C**

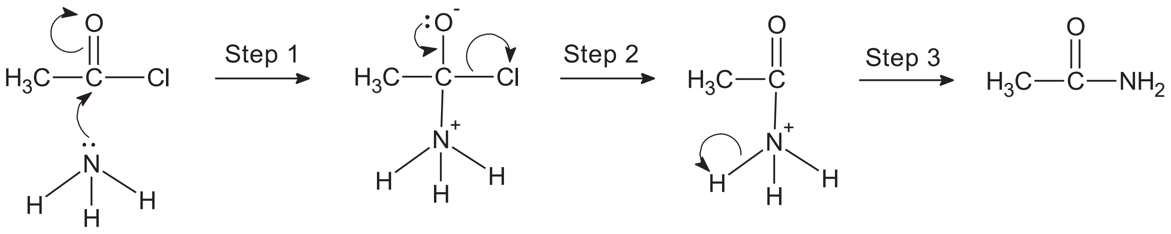
A H_2 / Ni will reduce the ketone and the two C=C. H_2 / Ni cannot reduce the carboxylic acid. Hence **6 hydrogen atoms** will be incorporated in the product.

B Na in ethanol will reduce all the functional groups – ketone, the two C=C. H_2 / Ni and the carboxylic acid. Hence **8 hydrogen atoms** will be incorporated in the product.

C $NaBH_4$ in methanol will only reduce the ketone. Carboxylic acid and C=C cannot be reduced. Hence **only 2 hydrogen atoms** will be incorporated in the product.

D $LiAlH_4$ in dry ether will reduce the ketone and carboxylic acid. C=C cannot be reduced. Hence **4 hydrogen atoms** will be incorporated in the product.

24 A mechanism for the reaction between ammonia and ethanoyl chloride is given below.



Which of the following statements are correct?

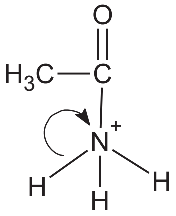
1 The ammonia behaves as a nucleophile.
2 The loss of proton in **step 3** is shown incorrectly.
3 The ammonia attacks an electron-deficient carbon atom.
4 The rate of reaction will increase if ethanoyl bromide is used.

A 1, 2, 3 and 4.
B 1, 3 and 4 only
C 1 and 3 only.
D 2 and 4 only.

Answer : A (1,2,3 and 4)

1: Correct. NH_3 has a lone pair of electrons and uses it to attack the electron deficient carbon.

2: Correct. The arrow in step 3 is shown incorrectly. The correct arrow movement should be



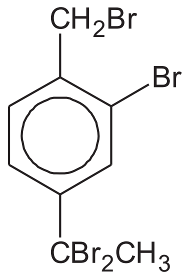
3: Correct. The carbon has two electron withdrawing groups (oxygen and chlorine) bonded to it, resulting in an very electron-deficient carbon.

4: Step 2 involves the breakage of C-Cl bond. Comparing the bond energy of C-Cl (340 kJ) and C-Br (280 kJ), less energy required to break the C-Br bond, activation energy for the reaction involving ethanoyl bromide will be lower, hence the rate of reaction will be faster.

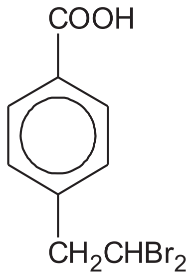
25 Diols formed on the same carbon atom are generally unstable and will undergo the following reaction.

$$RCR'(OH)_2 \rightarrow RCOR' + H_2O$$

Compounds **V** and **W** are both reacted with hot aqueous NaOH followed by dilute HC*l* at room temperature.



Compound **V**



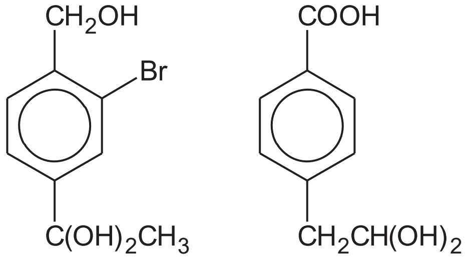
Compound **W**

Which reagents could be used to distinguish the final products of **V** and **W**?

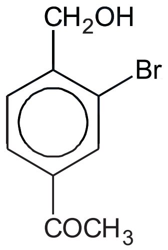
1 2,4 DNPH
2 Fehling's solution
3 Sodium carbonate
4 Hot acidified $K_2Cr_2O_7$
5 Iodine in aqueous NaOH

A 1 and 2 only
B 3 and 4 only
C 1, 4 and 5 only
D 2, 3 and 5 only
Answer : D (2, 3 and 5 only)

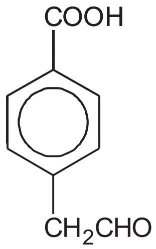
The halogenoalkanes will undergo **nucleophilic substitution** to give alcohols.



Diols on the same C atom are unstable, hence they **decompose (with the loss of water)** to give the respective **carbonyl compounds**.



V1



W1

1	+ve for V1	+ve for W1
2	-ve for V1	+ve for W1
3	-ve for V1	+ve for W1
4	+ve for V1	+ve for W1
5	+ve for V1	-ve for W1

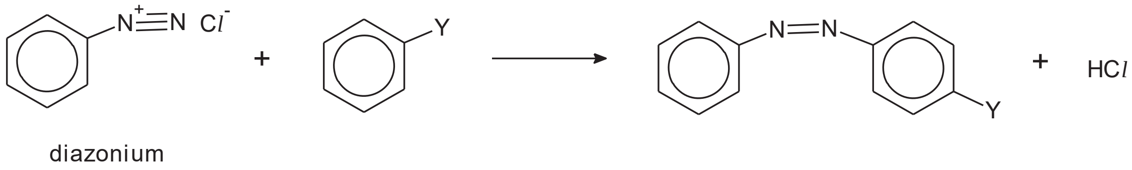
26 The ozone depletion potential (ODP) of a chemical compound is the relative amount of degradation to the ozone layer it can cause, with trichlorofluoromethane being fixed at an ODP of 1.0.

Which of the following compounds has an ODP of greater than 1.0?

A methane
B dichlorodifluoromethane
C chlorotrifluoromethane
D bromotrifluoromethane
Answer: D

C-Br is weaker than C-Cl bond. Less energy is required to homolytically break C-Br bond, hence the bromide radical will be easier to generate. Bromide radical would then break down ozone.

27 Azo coupling is an organic reaction between a diazonium compound and another aromatic compound that produces an azo compound.



Which of the following correctly represents the type of reaction and the role of diazonium compound?

	Type of reaction	Role of diazonium
A	nucleophilic substitution	nucleophile
B	electrophilic substitution	electrophile
C	nucleophilic substitution	electrophile
D	electrophilic substitution	nucleophile

Answer: B

Diazonium has a positive charge, hence it is an electrophile. Electrophilic substitution occurs on the benzene ring.

28 What is the order of increasing pH of 1 mol dm^{-3} of each organic compound?

A CH_3CO_2Na, CH_3CO_2H, CF_3CO_2H, $HOCH_2CHO$
B CH_3CO_2Na, $HOCH_2CHO$, CH_3CO_2H, CF_3CO_2H
C CF_3CO_2H, CH_3CO_2H, $HOCH_2CHO$, CH_3CO_2Na
D CF_3CO_2H, CH_3CO_2H, CH_3CO_2Na, $HOCH_2CHO$
Answer: C

CF_3CO_2H and CH_3CO_2H are both acids, both pH < 7, CF_3CO_2H has 3 electron-withdrawing fluorine which stabilises the conjugate to greater extent, CF_3CO_2H is the strongest acid, hence lowest pH.

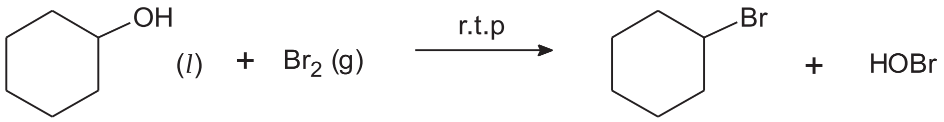
$HOCH_2CHO$ has alcohol and aldehyde hence it is neutral, pH = 7.

CH_3CO_2Na is the conjugate base of CH_3CO_2H, hence it has a pH > 7.

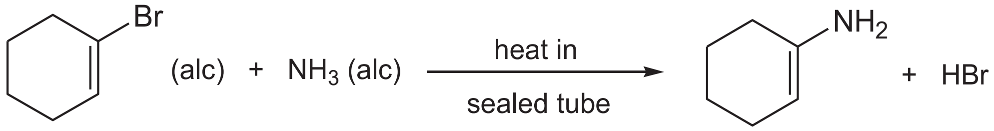
29 Which reaction gives the best yield of products?

[(*alc*) indicates an alcoholic solution.]

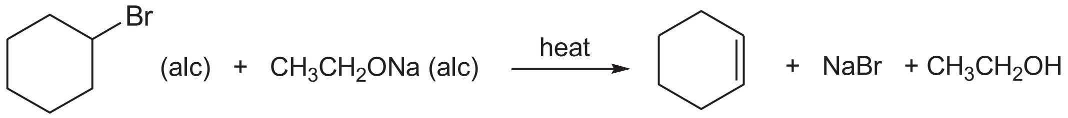
A



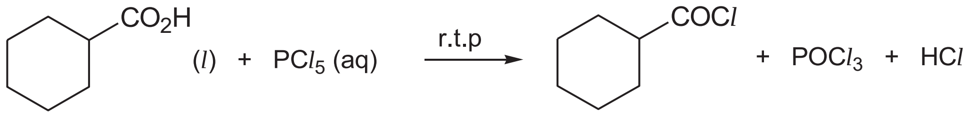
B



C



D



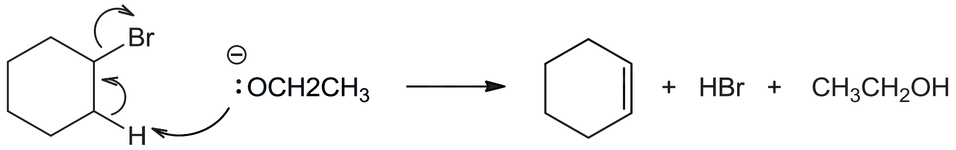
Answer: C

A Substitution of OH with Br requires HBr or PBr_3, as the C-O is strong and difficult to break.

B Br attached to C=C is unreactive towards nucleophilic substitution as the p orbital on Br overlaps with the π orbital of C=C, resulting in partial double bond character for the carbon-bromine bond which requires more energy to break.

C Elimination of HBr can take place in presence of a strong base in alcoholic medium.

$CH_3CH_2O^-$ is a stronger base than OH^- since the ethyl group is electron donating which intensify the negative charge on oxygen. Thus it is able to abstract the H atom on the carbon next to carbon attached to Br.

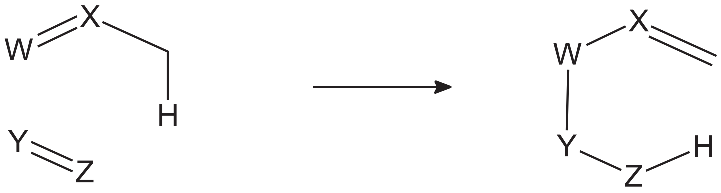


Na^+ is a spectator ion.

D PCl_5 will hydrolyse in aqueous medium and hence anhydrous PCl_5 should be used instead.

$PCl_5 + H_2O \rightarrow 5HCl + H_3PO_4$

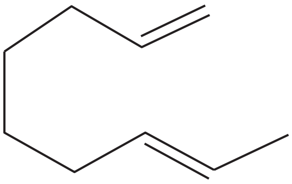
30 The Alder-ene reaction is a reaction between two alkenes and is capable of forming new carbon-carbon bonds. An example of the Alder-ene reaction is given below:



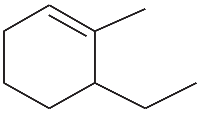
Note: W, X, Y & Z are carbon atoms and other hydrogens are not sho

The Alder-ene reaction typically produces many products as the roles of the two alkenes can be exchanged.

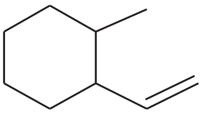
Which compound will **not** be formed when the following compound undergoes Alder-ene reaction?



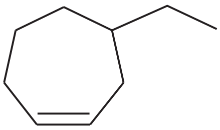
A



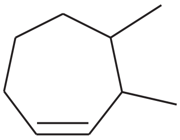
B



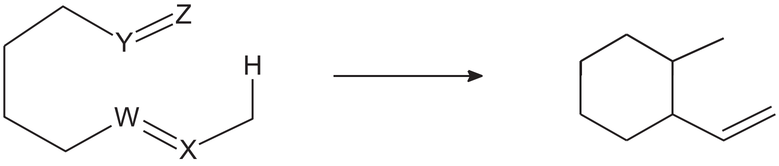
C



D

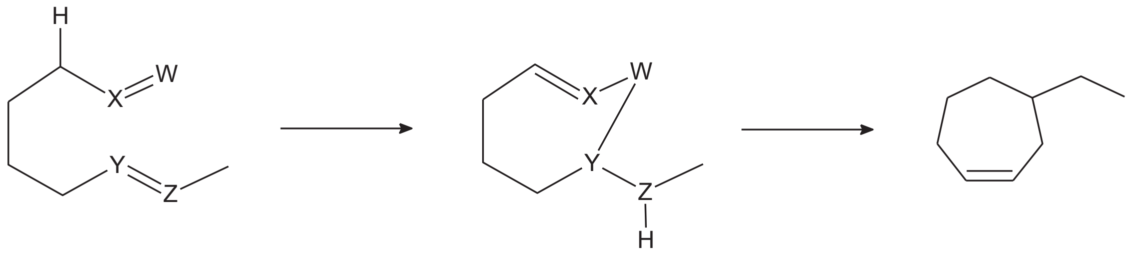


Answer: **A**

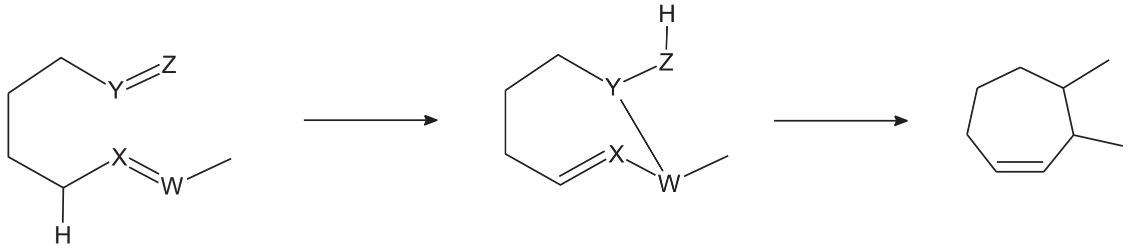


B:

C:



D:



2017 SRJC H2 Chemistry 9729
Preliminary Examination Paper 2 Solution

1 The size of an atom can be measured using the distance between the nuclei of two atoms.

For example, the 'metallic radius' of the Na atom is half the distance between two Na atoms in the crystal lattice of the metal. The 'covalent radius' of the C*l* atom is taken to be half the distance between the nuclei in a Cl_2 molecule. Finally, the 'van der Waals' radius' of the A_r atom is assumed to be half the distance between two atoms in the solid state.

These three types of radius are commonly known as 'atomic radii' and the corresponding values for Period 3 elements can be found in the Data Booklet.

(a) **(i)** Explain the general trend in atomic radius across Period 3.

Across Period 3, **nuclear charge increases as no. of protons increases. Shielding effect remains relatively constant** due to the **same no. of electron shells. Effective nuclear charge increases. Stronger electrostatic forces of attraction between nucleus and valence electrons lead to decrease in atomic radius.**

[2]

(ii) Suggest a reason for the anomaly in the measurement of atomic radius for argon.

The instantaneous dipole-induced dipole interactions between the two Ar atoms are **much weaker** than the strong metallic bonds for metals and strong covalent bonds for molecules. Thus, the two atoms for Ar will be **further apart** leading to a much higher measurement.

[1]

(b) **(i)** State the general relationship between atomic radius and first ionisation energy across Period 3.

The first ionisation energy is **inversely proportional** to atomic radius.

[1]

(ii) Explain why the relationship does not hold from P to S.

It is easier to remove an electron from S due to the **inter-electronic repulsion between the paired electrons** in the **same 3p orbital of S.** Thus 1st IE decreases from P to S.

[1]

(c) Across period 3, the elements changes from metallic to non-metallic nature. Correspondingly, the difference in electronegativity between the elements and the oxide decreases, giving rise to different types of oxides.

A, **B** and **C** are Period 3 elements, from Na to S, inclusive.

- **A** has the highest melting point among Period 3 elements.
- **B** has the highest electrical conductivity in Period 3.
- **C** burns in air with a coloured flame.
- **B** and **C** can show the same oxidation state in their compounds.

Identify **A**, **B** and **C** and hence, write equations, including state symbols, to show the acid-base properties of their oxides.

[Give the chemical formulae for only the highest oxide formed.]

A – Si

$SiO_2(s) + 2NaOH(conc.) \rightarrow Na_2SiO_3(aq) + H_2O(l)$

B – A*l*

$Al_2O_3(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2O(l)$

$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2NaAl(OH)_4(aq)$

C – P_4 or P

$P_4O_{10}(s) + 12NaOH(aq) \rightarrow 4Na_3PO_4(aq) + 6H_2O(l)$

[3]
[Total : 8]

2 Benzoic acid occurs naturally in many plants and it has many uses. It is an important precursor for the industrial synthesis of many organic substances.

(a) The benzoic acid and sodium benzoate buffer is commonly used as food preservatives in many acidic foods such as salad dressings and carbonated drinks.

(i) With the aid of relevant chemical equations, explain how the system can control pH when a small amount of base is added.

When small amount of OH^- is added,

$C_6H_5COOH + OH^- \longrightarrow C_6H_5COO^- + H_2O$

The **added OH^- is removed as $C_6H_5COO^-$, pH remains fairly constant**.

[1]

(ii) Given that the acid dissociation constant for benzoic acid is 6.3×10^{-5} mol dm^{-3}, calculate the mass of solid sodium benzoate required to be added to 250 cm^3 of 0.50 mol dm^{-3} of benzoic acid to form a buffer solution with an initial pH 4.

$pK_a = -\lg(6.3 \times 10^{-5}) = 4.20$

$$pH = pK_a + \lg\frac{[\text{benzoate}]}{[\text{benzoic acid}]}$$

$$4 = 4.20 + \lg\frac{[\text{benzoate}]}{[0.50]}$$

[benzoate] = **0.3155 mol dm^{-3}**

$$\text{Amt of benzoate} = 0.3155 \times \frac{250}{1000} = 0.07887 \text{ mol}$$

Mass of sodium benzoate required = 0.07887 x (144.0) = **11.4 g**

[2]

(iii) To achieve the optimal buffering capacity of a 25 cm^3 sample of the buffer prepared in **(ii),** a standard solution of 1.5 mol dm^{-3} sodium hydroxide was added. Calculate the volume of sodium hydroxide needed.

$$\text{Amt of benzoic acid in sample} = \frac{25}{1000} \times 0.5 = 0.0125 \text{ mol}$$

$$\text{Amt of benzoate in sample} = \frac{25}{1000} \times 0.3155 = 0.007888 \text{ mol}$$

At maximum buffering capacity: [benzoic acid] = [benzoate]

$$\text{Amt of benzoic acid} = \text{amt of benzoate} = \frac{0.0125 + 0.007888}{2} = 0.01019 \text{ mol}$$

Amt of NaOH to add = 0.0125 – 0.01019 = 0.00231 mol

$$\text{Vol of NaOH required} = \frac{0.00231}{1.5} = \mathbf{1.54\ cm^3}$$

[3]

(b) The presence of benzoic acid in plant extracts can be confirmed using neutral iron(III) chloride according to the following equation.

$$Fe^{3+}(aq) + 3C_6H_5COOH(aq) \longrightarrow Fe(C_6H_5CO_2)_3(s) + 3H^+(aq)$$

When 50 cm^3 iron(III) chloride is added to an equal volume of the plant extract, 0.0532 g of iron(III) benzoate, $Fe(C_6H_5CO_2)_3$ precipitate is formed.

The resultant mixture has a pH value of 2.33.

(i) Calculate the amount of benzoic acid that has reacted with neutral iron(III) chloride solution and H^+ in the mixture.

$$\text{Amt of } Fe(C_6H_5CO_2)_3 = \frac{0.0532}{418.8} = 0.000127 \text{ mol}$$

Amt of benzoic acid reacted = 3 x 0.000127 = **<u>0.000381 mol</u>**

$$[H^+] = 10^{-2.33} = 0.004677 \text{ mol dm}^{-3}$$

$$\text{Amt of } H^+ \text{ in mixture} = 0.004677 \times \frac{100}{1000} = \underline{\mathbf{0.000468 \text{ mol}}}$$

[1]

(ii) Assuming that the H^+ ions in solution are formed from the dissociation of benzoic acid and the reaction of benzoic acid with iron(III) chloride, calculate the concentration of benzoate ions in the equilibrium mixture.

Total amt of H^+ in solution = 0.0004677 mol

Amount of H^+ produced from acid and Fe^{3+} reaction = 0.0003811 mol

Amount of H^+ produced from benzoic acid dissociation
= 0.0004677 – 0.0003811 = 0.000086611 mol

$C_6H_5CO_2^- \equiv H^+$

$$[C_6H_5CO_2^-] = 0.0000866 \div \frac{100}{1000} = \underline{\mathbf{0.000866 \text{ mol dm}^{-3}}}$$

[2]

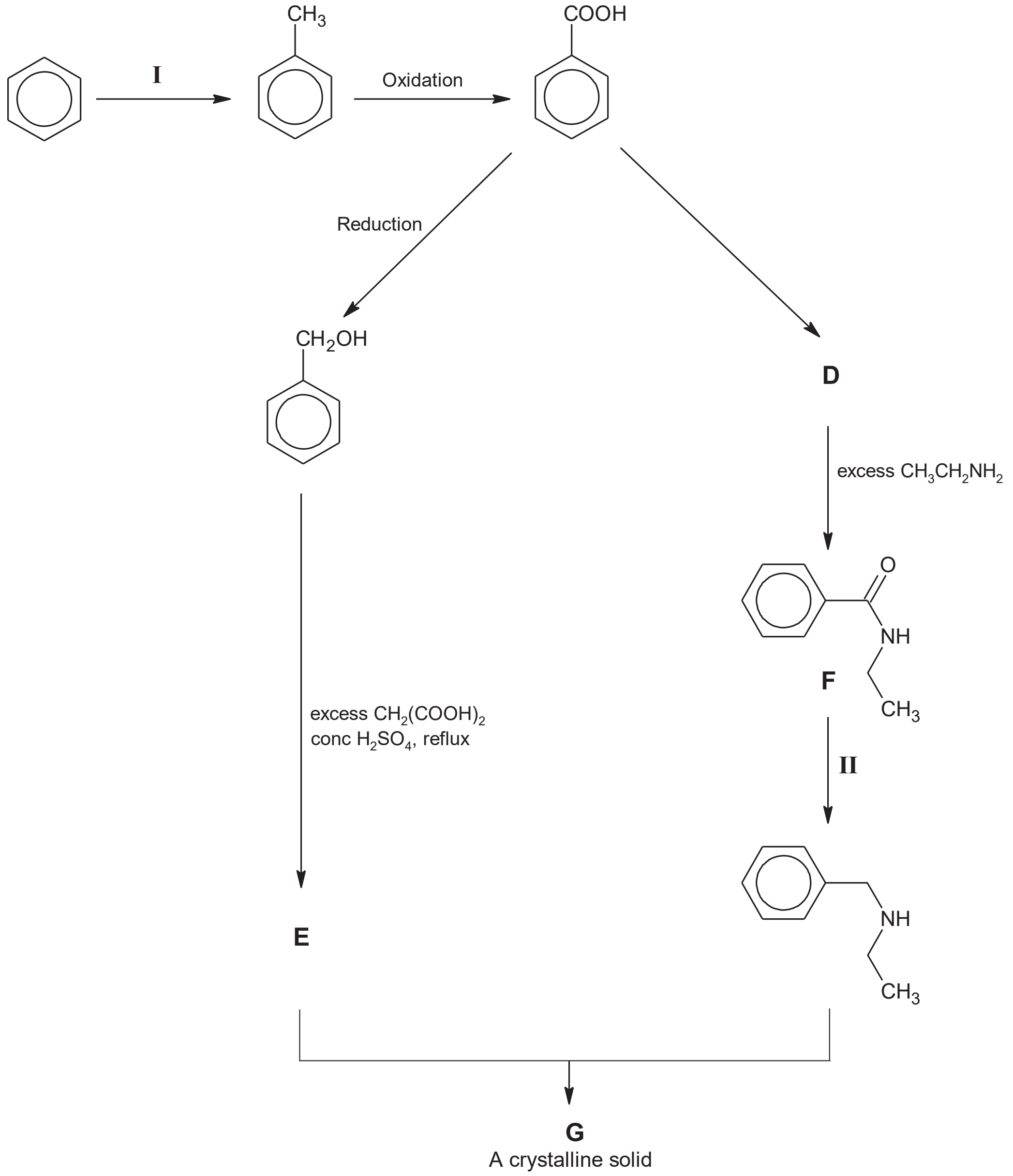
(iii) Calculate the K_{sp} of iron(III) benzoate, given that the concentration of iron(III) ions in the mixture is 1.83×10^{-3} mol dm^{-3} at equilibrium.

$K_{sp} = [Fe^{3+}][C_6H_5CO_2^-]^3$

$K_{sp} = (1.83 \times 10^{-3})(0.0008611)^3 = \mathbf{1.19 \times 10^{-12} \text{ mol}^4 \text{ dm}^{-12}}$

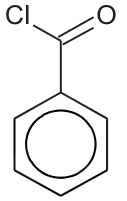
[1]

(c) Benzoic acid is involved in the reaction scheme below:

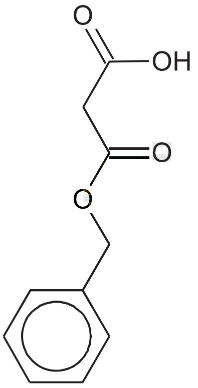


(i) Draw the structures for **D**, **E** and **G** in the boxes below.

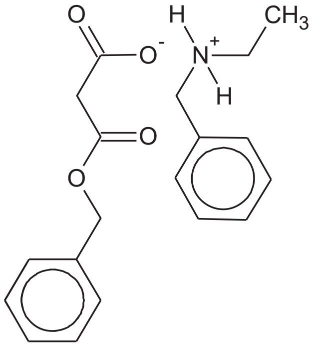
D



E



G



[3]

(ii) Suggest the reagents and conditions for reactions **I** and **II**.

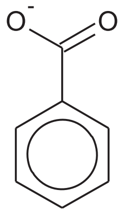
Reactions **I**: **CH_3Br, anhydrous $FeBr_3$ (s)**
Reactions **II**: **$LiAlH_4$ in dry ether, rtp**

[2]

(iii) Compound **F** was heated with aqueous sodium hydroxide and excess carbon dioxide was bubbled through the solution.

Given the acid dissociation constants below, suggest the products that would be formed after the introduction of carbon dioxide.

acid	**formula**	**K_a / mol dm^{-3}**
carbonic acid	H_2CO_3	4.5×10^{-7}
benzoic acid	C_6H_5COOH	6.3×10^{-5}
ethylamine salt	$CH_3CH_2NH_3^+$	1.6×10^{-11}

Products formed: 

and **$CH_3CH_2NH_3^+$**

Benzoate salt will not be neutralised by carbon dioxide.
Benzoic acid is a stronger acid than carbonic acid as shown by the K_a values, thus suggesting that the benzoate ion is more stable than carbonate.

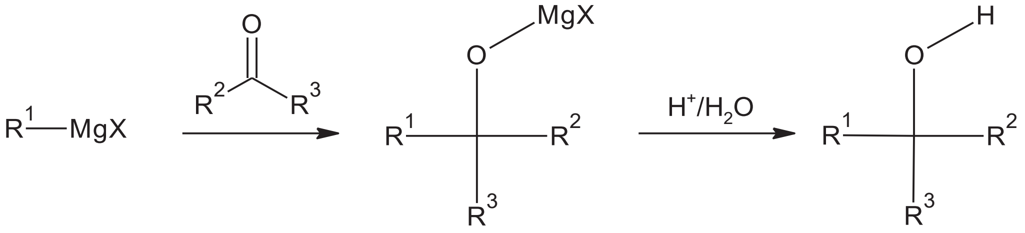
[3]
[Total : 18]

3 Grignard reagents are organomagnesium halides, RMgX commonly used in organic synthesis. The R in RMgX behaves like an anion, R^- and is a strong Lewis base. It can be made by the reaction between halogenoalkane and magnesium under anhydrous conditions, using ether as a solvent.

$$R^1\text{—}X \quad + \quad Mg \longrightarrow R^1\text{—}MgX$$

where R= alkyl group, X= C*l*, Br, I

In a Grignard reaction, the Grignard reagent behaves as a nucleophile and may be added to a carbonyl compound for the formation of an alcohol. This reaction is useful for the formation of carbon–carbon bonds.



(a) **(i)** Suggest, with an equation, why the synthesis of Grignard reagent has to be done under anhydrous conditions.

The **R in RMgX reacts with water** to form an alkane, destroying the nucleophile for the Grignard reaction.

$RMgX + H_2O \rightarrow RH + (OH)MgX$

or

$R^- + H_2O \rightarrow RH + OH^-$

[2]

(ii) Besides organomagnesium compounds, organolithium compounds can be formed between lithium and relevant organic substances. Account for the similarity in the reactions involving lithium and magnesium.

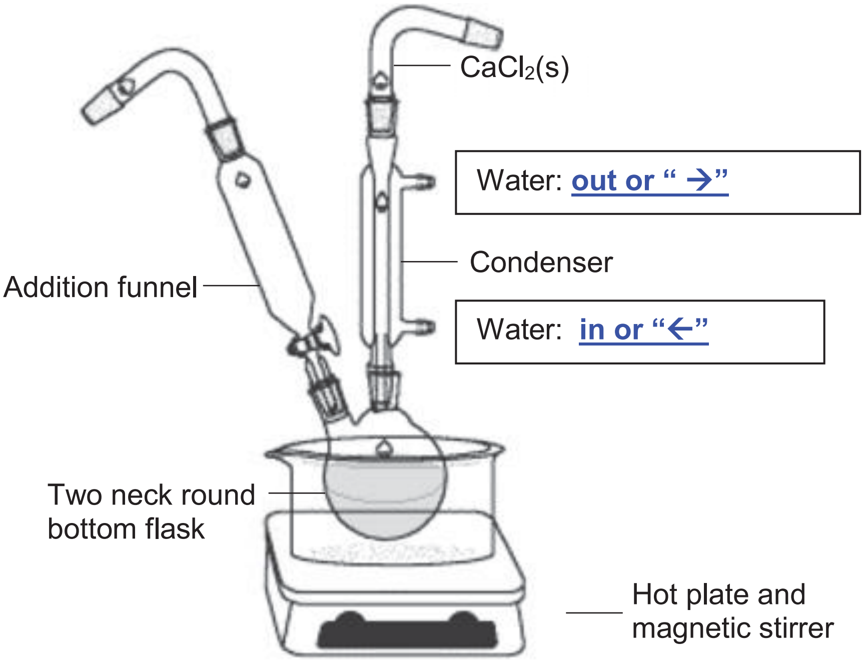
q+: $Mg^{2+} > Li^+$
r+: $Mg^{2+} > Li^+$
Li^+ and Mg^{2+} have **similar charge density**

[2]

The preparation and set up of Grignard synthesis of 2-methylhexan-2-ol is described below:

Table 3.1

Compound	Melting pt / °C	Boiling pt / °C	Molar mass / g mol^{-1}	Density / g cm^{-3}	Solubility in water
1-bromobutane	−11.2	101.4	136.9	1.27	Insoluble
Magnesium	651	1100	24.3	1.74	Insoluble
Diethyl ether	−116.3	34.6	74.0	0.713	Insoluble
Propanone	−94.7	56.1	58.0	0.785	Soluble
Sulfuric acid	10.3	337	98.1	1.84	Soluble
2-methylhexan-2-ol	−	143	116.0	0.82	Soluble



Preparation of Grignard reagent, RMgX

1. Add 15 g of 1-bromobutane and 3 g of magnesium into the 250 cm^3 two-neck round bottom flask.

2. Add 50 cm^3 of anhydrous diethyl ether using the addition funnel. Gently stir the mixture under reflux for 30 minutes. The reaction is exothermic and will boil without external heat.

3. When the reaction is complete, cool the reaction mixture using an ice bath.

(b) **(i)** With reference to Table 3.1, suggest why a reflux set up is necessary in this organic synthesis.

The reflux set up is to **minimise the loss of volatile organic compounds** such **as diethyl ether**.

[1]

(ii) On the diagram above, label and account for the direction of water flow.

Water 'IN' should be connected at the bottom of the reflux condenser to ensure all hot volatile organic vapour is condensed **immediately** into the flask or ensure **efficient cooling**.

[1]

(iii) Some heating may be required at the beginning as the initial rate of formation of RMgX is slow. Magnesium metal has to be scrapped or sliced into smaller pieces to increase the reaction rate.

Write an equation to suggest why magnesium may not be as reactive as expected.

Mg is not as reactive as the surface of Mg is covered by inert/unreactive MgO.

$\mathbf{Mg + ½\,O_2 \rightarrow MgO}$

[1]

(iv) Excess diethyl ether is added to keep the Grignard reagent at a low concentration. This will prevent the Grignard reagent from reacting with unreacted 1-bromobutane. Draw the structure of the organic by-product.

 octane

[1]

Synthesis of alcohol

4. Using the addition funnel, add 6.5 g (dissolved in 15 cm^3 of diethyl ether) of propanone to the Grignard reagent.

5. To a separate 250 cm^3 beaker, add 100 cm^3 of ice water and 4 cm^3 of concentrated sulfuric acid and mix well.

6. When the reaction with propanone is completed, add the reaction mixture into a 250 cm^3 beaker, sitting in an ice bath. Carefully transfer sulfuric acid solution from step 5 into reaction mixture. Stir gently to mix well.

(c) **(i)** Using Table 3.1, calculate the theoretical mass of 2-methylhexan-2-ol.

Amt of 1-bromobutane = $\frac{15}{136.9}$ = 0.1096 mol
Amt of Mg = $\frac{3}{24.3}$ = 0.1235 mol (in excess)
Amt of propanone = $\frac{6.5}{58.0}$ = 0.112 mol (in excess)

Mole ratio: 1 bromobutane: 2-methylhexan-2-ol
Mass of 2-methylhexan-2-ol = 0.1096 x 116.0 = **12.7 g**

[2]

(ii) The actual yield for 2-methylhexan-2-ol is 4 g. Calculate the percentage yield for this reaction.

Actual % yield = $\frac{4}{12.7}$ x 100 = **31.5 %**

[1]

(iii) Suggest why the addition of sulfuric acid has to be carried out in an ice bath in step 6.

[1]

The reaction of sulfuric acid with unreacted Mg is **highly exothermic**.

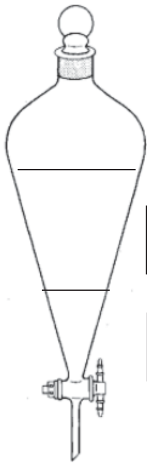
Solvent extraction

7. Add the mixture from step 6 into a 500 cm^3 separation funnel and add 10 cm^3 of diethyl ether. Shake the separation funnel, releasing any gas formed. Allow the layers to separate and collect both layers separately.

8. Repeat step 7 with the aqueous layer and a fresh sample of 10 cm^3 diethyl ether. Collect and combine each ether layer.

9. The combined ether layer is poured back to the separation funnel and mixed with several 20 cm^3 portions of 5 % sodium bicarbonate solution until no more carbon dioxide is generated.

(d) **(i)** After step 7, there are two layers in the separation funnel. Identify the ether and aqueous layer in the diagram below.



Upper layer: Ether/organic layer

Bottom layer: Aqueous layer **[1] for both**

Explain your answer.

Diethyl ether is **less dense than water**. [1]

(ii) Give a reason for the addition of sodium bicarbonate in Step 9.

To remove unreacted traces of **sulfuric acid** in the **ether layer**

[1]

(iii) During solvent extraction, both propanone and 2-methylhexan-2-ol are found in the ether layer. Comment on the solubility of 2-methylhexan-2-ol in diethyl ether.

The presence of **hydrophobic / non polar alkyl group** in 2-methylhexan-2-ol allow more **favourable instantaneous dipole – induced dipole interactions** with diethyl ether.

[1]

(iv) Suggest different chemical tests to positively identify propanone and 2-methylhexan-2-ol in the ether layer.

Add **2-4 DNPH, r.t.p**: formation of **orange ppt** suggest presence of propanone
Or **I_2(aq), NaOH(aq) and heat**: **yellow ppt** and **decolourisation of brown iodine** solution.

Add **PCl_5(s), r.t.p**: **White fumes** in the presence of 2-methylhexan-2-ol
Or
use **Na(s) r.t.p**: hydrogen gas which **extinguish lighted splint with "pop" sound**

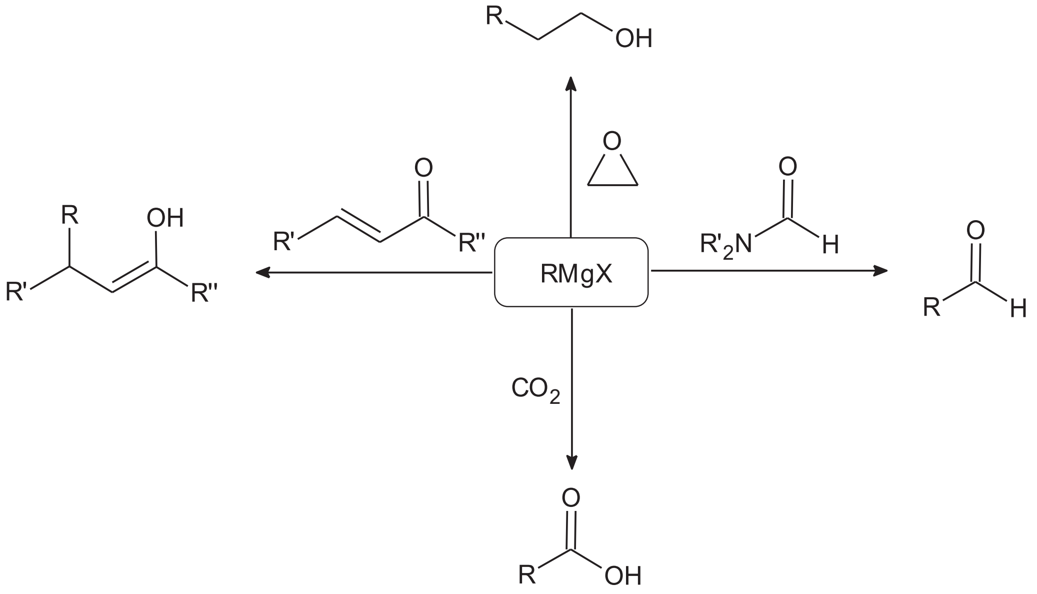
[2]

(v) Suggest how crude 2-methylhexan-2-ol can be purified from the ether layer.

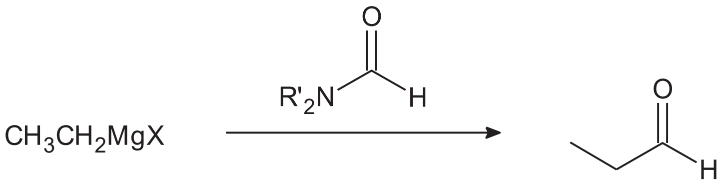
Via **distillation.** Since propanone and diethyl ether has lower boiling point, propanone and diethylether will be collected as the first distillate.

[1]

(e) Grignard reagent is used widely in organic synthesis due to its ability to increase carbon chain length. Four unique reactions involving the use of Grignard reagent are shown in the reaction map below.

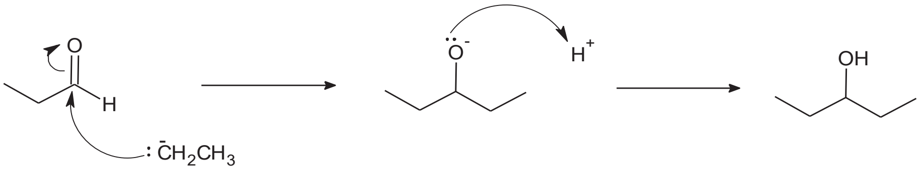


(i) The following Grignard reaction to form propanal achieved a very low yield as the aldehyde formed can react with the Grignard reagent again.

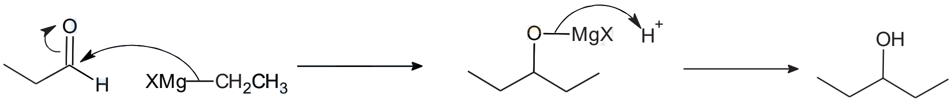


Describe the mechanism between propanal and the Grignard reagent, CH_3CH_2MgX to form the corresponding alcohol.

Nucleophilic addition.

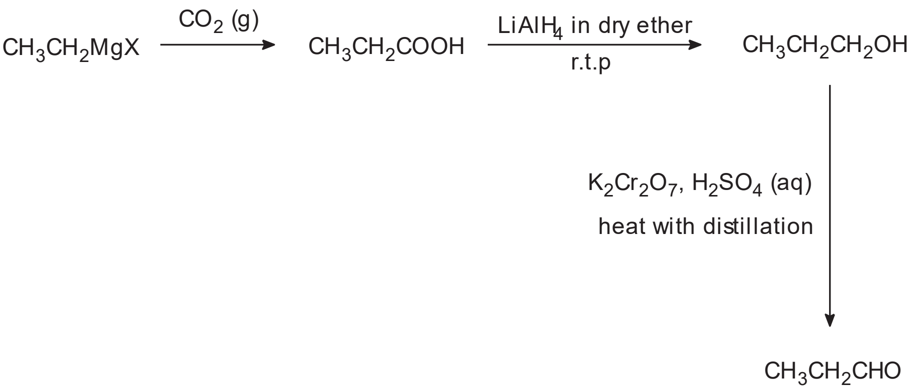


Or



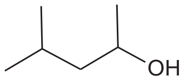
[2]

(ii) Starting with a suitable Grignard reagent, propose an alternative 3-step synthesis pathway to synthesise propanal.

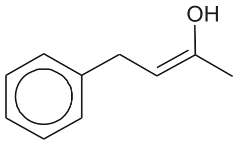


[3]

(iii) Using different reaction types from the reaction map above, suggest appropriate pairs of reagents in the synthesis of compounds **H** and **I**.

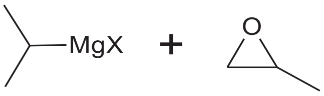


H

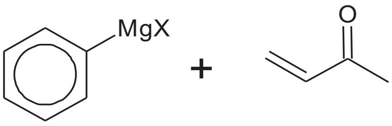


I

H:



I:

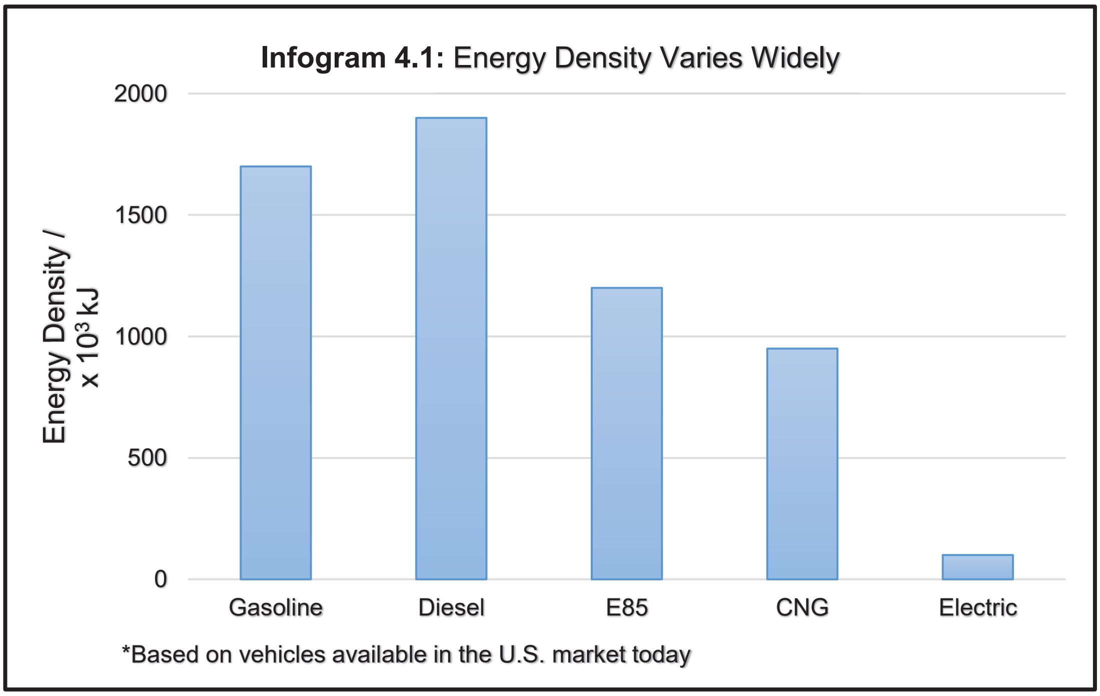


[2]
[Total: 25]

4 The use of electric vehicles has been increasing popular in the U.S. For example, hydrogen fuel cell vehicles produces zero carbon emission.

Despite the advantages of electric cars, petrol-engined cars are still widely used today. One problem with electric vehicles is their poor performance, inconvenience of finding a charging station and it takes a long time to recharge the batteries. Petrol-engined cars are better as their energy supply can be replaced over 6 million times faster than electric cars.

The infogram below shows how energy density varies widely with different fuels. Energy density is the energy produced per unit dimension of a fuel and this determines the practicality of a fuel.



However, using petrol (which contains a mixture of alkanes) has its own problems. One such problem is that it's a finite resource, and another is pollution. Hence, there is a need to improve the performance of petrol in car engines so that it burns as cleanly and efficiently as possible and to find alternative sources of fuel to replace petrol.

Some data for five fuels are given in **Table 4.2**.

Fuel	**Formula**	**Standard enthalpy change of combustion, ΔH_c^o / kJ mol^{-1}**	**Relative molecular mass**	**Energy density (energy transferred on burning 1 kg of fuel) / kJ kg^{-1}**
octane	C_8H_{18} (*l*)	– 5470	114.0	
1,2-xylene	C_8H_{10} (*l*)	– 4540	106.0	
carbon	C(s)	– 393	12.0	
methanol	CH_3OH(*l*)	– 726	32.0	
hydrogen	H_2(g)	– 286	2.0	

(a) Give an example of a pollutant that can arise from the use of petrol and state a detrimental effect of the pollutant.

- Carbon monoxide / CO – causes **carbon monoxide poisoning**
- Unburnt hydrocarbons – becomes **photochemical smog** in strong sunlight
- Lead bromide vapour – causes **brain damage**
- Sulphur dioxide / SO_2 – causes **acid rain**

[1]

(b) Complete Table 4.2 by calculating the energy density for all fuels. [1]

Fuel	**Formula**	**Standard enthalpy change of combustion, $\Delta H_c^{\ominus}$ / kJ mol^{-1}**	**Relative molecular mass**	**Energy density (energy transferred on burning 1 kg of fuel) / kJ kg^{-1}**
octane	C_8H_{18} (*l*)	– 5470	114.0	48000
1,2-xylene	C_8H_{10} (*l*)	– 4540	106.0	42800
carbon	C(s)	– 393	12.0	32800
methanol	CH_3OH(*l*)	– 726	32.0	22700
hydrogen	H_2(g)	– 286	2.0	143000

(c) **(i)** On the basis of energy density, which is the best fuel in table 4.2.

Hydrogen as it has the highest energy density.

[1]

(ii) Suggest a practical difficulty in using hydrogen rather than methanol as a fuel.

1. It is a light gas and **occupies too much volume**
   ⇒ storage difficult
2. It is also **flammable/ explosive** ⇒ cause **safely concerns**.

[1]

(d) Using the given data above, comment on the feasibility of using electric cars in the near future.

[1]

Despite the high energy density of hydrogen, gasoline/petrol is still the preferred choice as it is efficient in producing energy for consumer's use.

Octane is commonly used as a fuel or a precursor in the production of other chemicals. The term "octane rating" is often used in the petroleum industry for rating the ability of octane's various branched isomers in reducing engine knock in vehicles.

One important factor in making petrol is getting the right octane rating to reduce the problem of 'knocking'. Knocking occurs when the combustion of fuel is not smooth. Knocking reduces engine power, leading to wear and tear in the engine and results in wastage of petrol. Hence, highly branched alkanes are desirable in petrols as they have higher octane ratings and reduce knocking.

Another factor for getting the right properties of petrol is the blending of petrol. In cold weather, it is difficult to vaporise petrol, which makes ignition difficult. On the other hand, in hot weather, petrol vaporises easily. Hence, petrol companies make different blends of petrol for different seasons and climates.

You are to use the information provided above to answer parts **(e)** and **(f)**.

(e) Apart from using alkanes with high octane ratings, another way to deal with the problem of knocking is through the addition of an antiknock agent, tetra-ethyl lead (**TEL**). **TEL** is a highly volatile colourless liquid which aids in the formation of free radicals. However, this method is not commonly used nowadays.

Explain, with the aid of a suitable equation, how **TEL** helps to overcome the problem of knocking and give a reason why its usage is limited nowadays.

The **weak lead-carbon bonds** in tetra-ethyl lead are easily broken, giving **$CH_3CH_2\bullet$ which initiates smooth burning**.

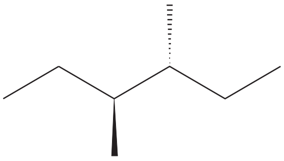
$$Pb(CH_2CH_3)_4 \rightarrow Pb + 4\ CH_3CH_2\bullet$$

PbO will be formed, which coats car cylinders and reduces their effectiveness over time
Or **Release of toxic lead compounds into the atmosphere**

[3]

(f) Compounds **J**, **K** and **L** are isomers of the hydrocarbon octane, C_8H_{18}.

The table below shows the boiling points and data relating to the optical activity of the compounds.

Structure	**Boiling Point / °C**	**Number of chiral centres**	**Optical Activity**
Isomer J	120	1	Yes
 **Isomer K**	118	2	No
Isomer L	107	0	No

(i) Suggest why isomer **K** does not exhibit enantiomerism.

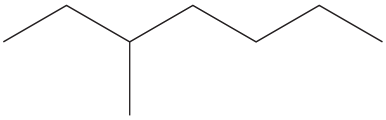
There is a **plane of symmetry in the molecule** or both chiral centres contain the same groups attached to it, forming a meso compound.

Or
The two chiral centres **rotate the plane of polarised light** to the same extent but in the opposite direction hence cancelling out the optical activity.

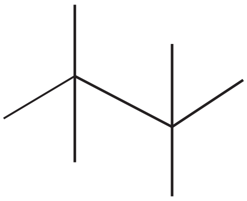
[1]

(ii) Propose the structures of compounds **J** and **L**.

Isomer J :



Isomer L :



[2]

(iii) In terms of structure and bonding, identify which of your proposed compounds (**J** or **L**) would be a more suitable fuel for use in summer and winter respectively.

Your answer should show clear and detailed comparison in your choice of fuel.

[2]

M_r: J = L

Molecular shape : J (elongated) vs L (spherical)

Surface area of contact : J > L

Extent of weak instantaneous dipole-induced dipole: J > L

Energy requirement: J > L

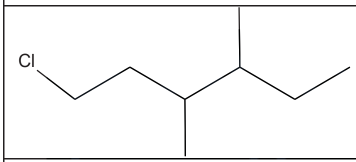
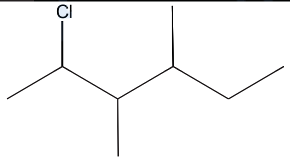
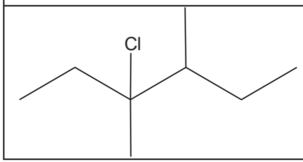
Boiling point: J > L

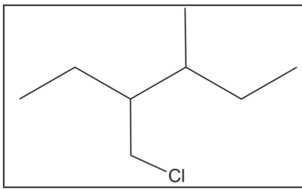
Volatility : J < L

Hence, with more volatile alkanes (with a lower boiling point) like **L in winter petrol**, it will be **easier for the petrol to vaporise** and with less volatile alkanes like **J** (with a higher boiling point) in **summer petrol**, it will be **harder for the petrol to vaporise**.

(iv) Controlled chlorination of isomer **K** in the presence of UV light produces different mono-chlorinated products with a molecular formula of $C_8H_{17}Cl$.

Draw the structural formula of any **two** possible isomers and state the ratio in which they are formed.

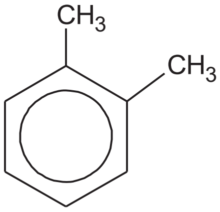
Structural formula	**mole ratio**	
	**6**	**3**
	**4**	**2**
	**2**	**1**

	**6**	**3**

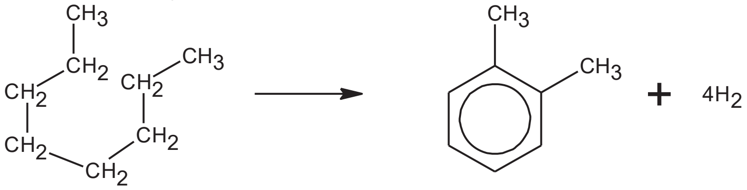
[2]

(g) The performance of hydrocarbons as fuels is largely improved by catalytic reforming. Reforming takes straight chain hydrocarbons in the C_6 to C_8 range from the gasoline or naphtha fractions and rearranges them into compounds containing benzene rings. They are used to make fuels with high octane number. Hydrogen is produced as a by-product of the reactions. A catalytic mixture of Pt and Al_2O_3 at a temperature of 500 °C and pressure of 20 atm is used.

An example of a product is 1,2-xylene.



(i) Write a balanced equation when octane undergoes the ‘reforming’ process to form 1,2-xylene.



1,2-xylene

Or

$C_8H_{18} \rightarrow C_8H_{10} + 4H_2$

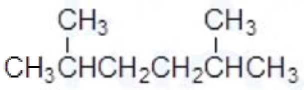
[1]

(ii) What *type of reaction* has the octane undergone?

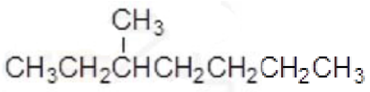
Oxidation / aromatisation / cyclisation

[1]

(iii) 1,4–xylene can be produced by a similar process. Suggest the structural formula of a C_8 alkane which might produce 1,4-xylene.


$CH_3\overset{\overset{CH_3}{|}}{C}HCH_2CH_2\overset{\overset{CH_3}{|}}{C}HCH_3$

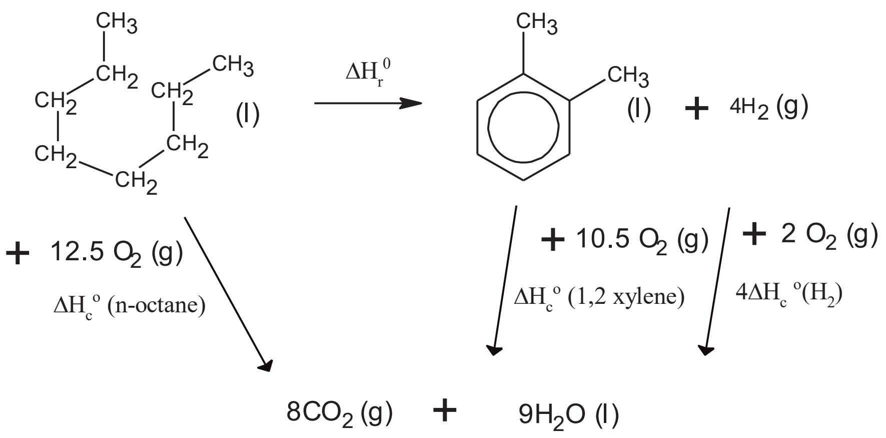
or


$CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCH_2CH_2CH_2CH_3$

[1]

(iv) By means of an energy cycle, show and calculate the standard enthalpy change of reaction that produces 1,2-xylene from octane.

[2]



ΔH_r^o = -5470 – [(-4540) + 4(-286)] = **+214** kJ mol^{-1}

(v) Using data from the Data Booklet, calculate the enthalpy change of the reaction which reforms octane into 1,2-xylene.

Bond broken	**Bonds formed**
7 C - C	**2 C – C**
18 C – H	6 C$\overset{\cdots}{-}$C
	10 C – H
	4 H – H

ΔH_r = 7(+350) + 18(+410) – [2(+350) + 6(+520) + 10(+410) + 4(+436)]
= (+9830) – (+9664) = **+166 kJ mol^{-1}**

[2]

(vi) By considering your answers in **(g)(iv)** and **(v)**, suggest if they are accurate descriptions of the reformation process.

(g)(iv) involve the use of **enthalpy values at standard conditions**.

(g)(v) **did not include the enthalpy change of vaporisation** as octane and xylene are liquids in standard states.

Hence, both are inaccurate descriptions as **reforming take place at 500 °C and pressure of 20 atm which are non-standard conditions.** *(Underline portion is necessary to get this mark. Must make reference to the passage.)*

[1]

(vii) Briefly explain whether you would expect the above reaction to have its ΔG value to be more negative than its corresponding ΔH_r.

Since, ΔG = ΔH - TΔS,
ΔS > 0 because there is a production of **4 moles of H_2**, which results in **n(gas) to increase after the reaction**. Hence, ΔG value will be **more negative**.

[1]
[Total : 24]

2017 SRJC H2 Chemistry 9729
Preliminary Examination Paper 3 Solution
Section A

1 **(a)** Oxides of nitrogen, NO_x are a mixture of gases that are composed of nitrogen and oxygen. They are formed during combustion processes in power plants.

Thermal NO_x refers to NO_x formed through high temperature oxidation of the diatomic nitrogen found in combustion air.

The formation rate is a function of temperature and the residence time of nitrogen at that temperature. At high flame temperatures, molecular nitrogen and oxygen dissociate into their atomic states and participate in a series of reactions.

The two principal reactions producing thermal nitric oxide, NO are as follows.

Step 1 O atoms react reversibly with N_2 to form NO.

Step 2 N atoms liberated react with O_2 to produce more NO.

Nitrogen dioxide typically arises via the oxidation of nitric oxide by oxygen in the atmosphere.

$$2\,NO + O_2 \rightarrow 2\,NO_2$$

(i) Write the two principal reactions involved in the formation of thermal nitric oxide in combustion. [1]

Step 1 : $\mathbf{N_2 + O \rightleftharpoons NO + N}$
Step 2 : $\mathbf{N + O_2 \rightarrow NO + O}$

(ii) Hence, determine the rate determining step. [1]

Step 1. Step **1** involves the breaking of very strong **N≡N (triple) bond** which requires a large amount of energy to overcome.

(iii) Suggest a method to reduce the formation of thermal NO_x. [1]

Reduce peak flame **temperature**/**Reduce time** of gas spent in flame.

(b) Catalytic converters are used to reduce the output of NO_x into the environment. One example is the removal of nitric oxide by reaction with hydrogen gas using platinum catalyst.

		ΔH
$NO + NO \rightleftharpoons N_2O_2$	fast	positive
$N_2O_2 + H_2 \rightarrow H_2O + N_2O$	slow	negative
$N_2O + H_2 \rightarrow N_2 + H_2O$	fast	negative

(i) Write the rate equation for the above reaction, showing clearly how you derive it. [2]

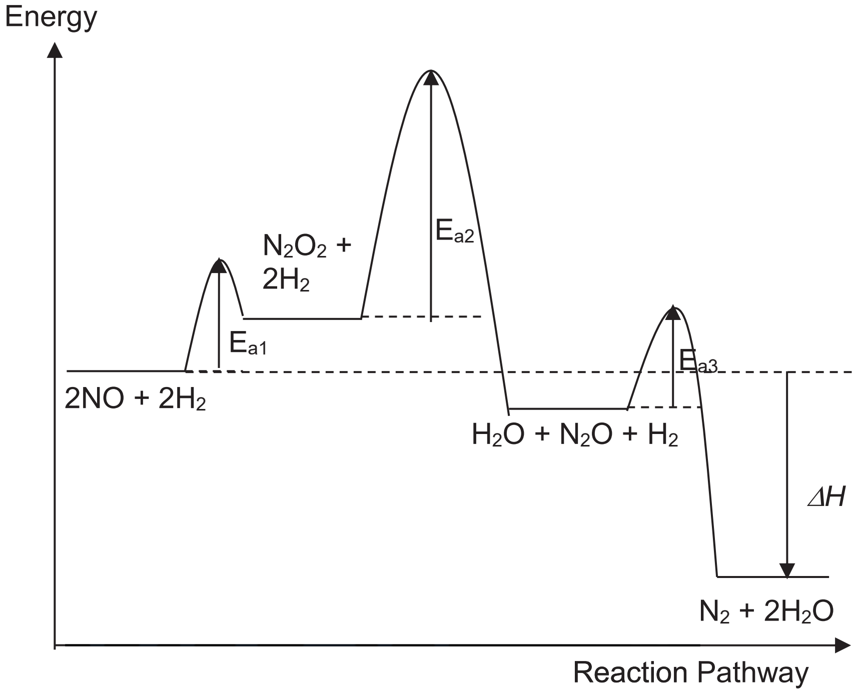
rate = k $[N_2O_2][H_2]$
N_2O_2 is an intermediate and should not be included in the rate equation.

Let the equilibrium constant of step 1 be **K**.

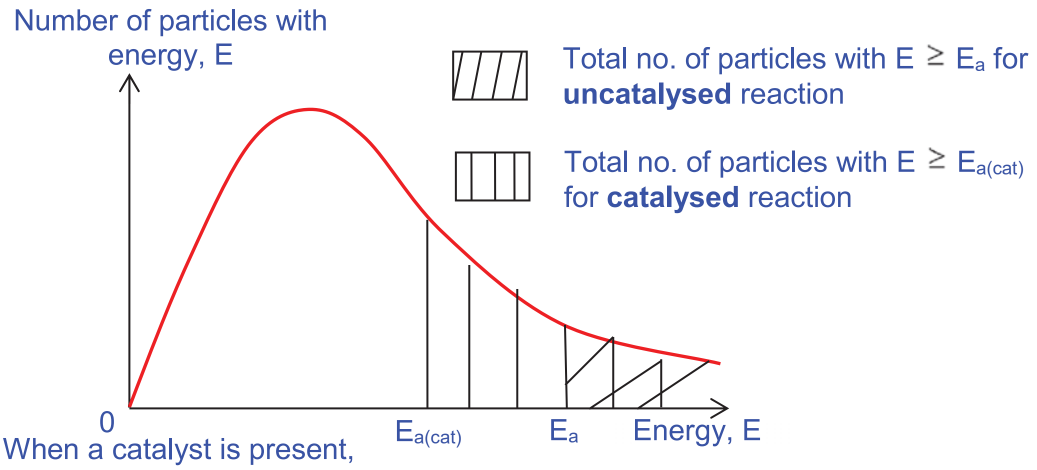
$$\mathbf{K}=\frac{[N_2O_2]}{[NO]^2}$$

$[N_2O_2] = \mathbf{K}\,[NO]^2$
rate = $k\mathbf{K}\,[NO]^2[H_2] = k'\,[NO]^2[H_2]$
where $k' = k\mathbf{K}$

(ii) Draw the probable energy profile diagram for this overall exothermic reaction. [2]



(iii) Using an appropriate sketch of the Maxwell–Boltzmann distribution curve, explain how the addition of platinum affects the rate of chemical reaction. [3]



When a catalyst is present,
-activation energy is lowered
-more reactant particles with energy ≥ $E_{a(cat)}$
-more effective collisions
-rate of reaction is proportional to the frequency of effective collisions
rate of reaction increases

(c) The NO_2 reacts with O_2 in the atmosphere to form colourless nitrogen pentoxide, N_2O_5 in equilibrium.

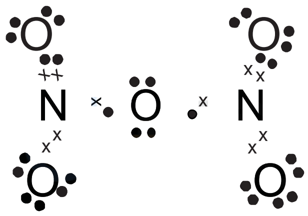
$$4\ NO_2\ (g) + O_2\ (g) \rightleftharpoons 2\ N_2O_5(g)$$

Dinitrogen pentoxide is a rare example of a compound that adopts two structures depending on the conditions. As a gas in the atmosphere, dinitrogen pentoxide exists as a molecule. However, it exists as an ionic salt in the solid state.

(i) Gaseous N_2O_5 is a symmetrical molecule with the two nitrogen atoms bonded to one central oxygen atom.

Draw a dot-and-cross diagram to show the bonding in N_2O_5 molecule. Use your diagram to:

- State the shape and the bond angle with respect to nitrogen
- Suggest with reasoning, the polarity of the molecule. [3]



O–N–O bond angle is **120°**, **trigonal planar**

N_2O_5 is **polar**. The centre O atom is bent. Hence the **dipole moment does not cancel out/ there is net dipole moment.**

(ii) A ratio of 4 to 1 mole of gaseous NO_2 and O_2 with a total initial pressure of 2.25 atm was placed in a 1000 cm^3 vessel. The total pressure at equilibrium was 1.5 atm. Calculate K_p for this equilibrium. [3]

Initial pressures
P_{NO2} = 4/5 $\times$ 2.25 = **1.8 atm**
P_{O2} = 1/5 $\times$ 2.25 = **0.45 atm**

	$4\ NO_2(g)$	+	$O_2(g)$	⇌	$2\ N_2O_5(g)$
Initial P/ atm	1.8		0.45		0
Change P / atm	$-2x$		$-0.5x$		$+x$
Eqm P / atm	$1.8 - 2x$		$0.45 - 0.5x$		$+x$

$P_{total} = 1.8 - 2x + 0.45 - 0.5x + x = 1.5$ atm
$x = 0.500$ atm

$$K_p = \frac{P(N_2O_5)^2}{P(O_2)\ P(NO_2)^4}$$

$$K_p = \frac{0.50^2}{0.2 \times 0.8^4}$$

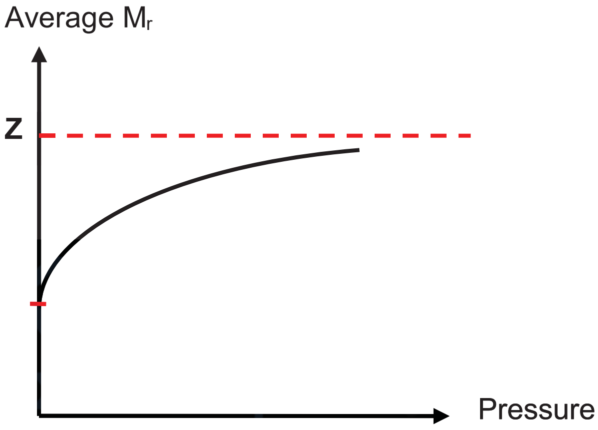
K_p = **3.05 atm^{-3}**

(iii) Calculate the average M_r of the gases at equilibrium. [1]

Average M_r = Sum of mole fraction x M_r

$$= \frac{0.5}{1.5} \times 108.0 + \frac{0.2}{1.5} \times 32.0 + \frac{0.8}{1.5} \times 46.0 = \underline{\mathbf{64.8}}$$

(iv) The variation of M_r is as shown in the sketch.



Predict a value for **Z** and account for the shape of the graph. [2]

Z = 108.0

By LCP, as pressure increases, the **position of equilibrium would shift right** to **decrease the amount of gas**. Hence, more N_2O_5 will be produced as **average M_r increases**.

A curve with decreasing rate and not straight line is obtained as the rate of N_2O_5 formation decreases with decreasing NO_2 and O_2. Also, the repulsion increases as NO_2 and O_2 molecules are forced closer together with increasing pressure, resulting in a gentler gradient.

The **maximum M_r approaches 108.0** but does not reach 108 as the **equilibrium mixture must always contain all three gases**.

(d) Solid N_2O_5 dissolved in chloroform may be used to replace concentrated nitric acid and sulfuric acid in the nitration of benzene.

(i) Suggest why solid N_2O_5 can be used in for nitration of benzene. [1]

$[NO_2^+][NO_3^-]$

N_2O_5 contains nitronium ion, **NO_2^+** which is an **electrophile** in the electrophilic substitution of benzene.

(ii) 0.60 mol of solid N_2O_5 was dissolved in chloroform. Some N_2O_5 decompose back into oxygen and nitrogen dioxide with a rate constant of $1.0 \times 10^{-5}\ s^{-1}$ at 45 °C.

The gases produced are collected in a 10 dm^3 container over a period of 40 hours. Calculate the resultant pressure.

[Assume that the products do not dissolve in chloroform.] [3]

Since decomposition follows a first order w.r.t. N_2O_5 (based on units of k)

$$t_{1/2} = \frac{\ln 2}{k} = \frac{\ln 2}{1.0 \times 10^{-5}} = 6.931 \times 10^4\ s$$

$$\text{Number of } t_{1/2} = \frac{40 \times 60 \times 60}{6.931 \times 10^4} = \underline{\mathbf{2.08}}$$

$N_2O_5 \rightarrow 2\ NO_2 + ½\ O_2$

After 40 hours, 0.60 x 0.75 = **0.45 mol** of N_2O_5 has decomposed.

$n_{(\text{gaseous products})} = 2(0.45) + ½\,(0.45) = 1.125$ mol

$pV = nRT$

$$p = \frac{1.125 \times 8.31 \times 318}{10 \times 10^{-3}} = \mathbf{2.97 \times 10^5\ Pa} = 2.97\ bar$$

Alternative answer

$$n_{N2O5} = 0.60\,(^1/_2)^{2.08} = 0.1419$$

After 40 hours, 0.60 – 0.1419 = 0.4581 mol of N_2O_5 has decomposed.

$n_{(\text{gaseous products})} = 2(0.4581) + ½\,(0.4581) = 1.145$ mol

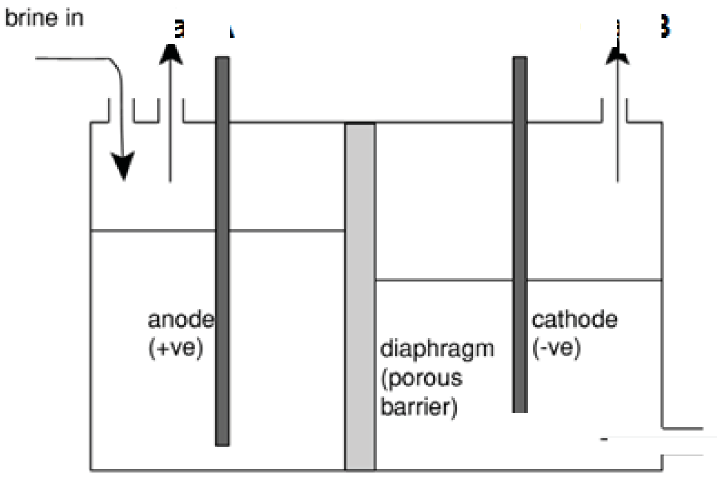
$$p = \frac{1.145 \times 8.31 \times 318}{10 \times 10^{-3}} = \mathbf{3.03 \times 10^5\ Pa} = 3.03\ bar$$

[Total : 23]

2 Chlorine is a yellow-green gas that was first synthesised around 1630. Chlorine forms a variety of oxides such as chlorate(VII), ClO_4^- and chlorate(V), ClO_3^-.

(a) Chlorine gas can be produced from the electrolysis of brine (concentrated sodium chloride solution) using a diaphragm cell with inert electrodes.

A diaphragm is used to keep the products of electrolysis from mixing and hence, prevent the formation of undesirable by-products.



(i) Write the ion-electron half-equations, with state symbols, for the reactions taking place at the electrodes. [2]

Cl^- (anion) would migrate to the anode and be oxidised to Cl_2 gas.

Anode reaction: $2Cl^-(aq) \rightarrow Cl_2(g) + 2e$

Cathode reaction: $2\underline{H_2O}\,(l) + 2e \rightarrow H_2(g) + 2OH^-(aq)$

(ii) Calculate the mass of chlorine gas produced if a current of 5 A was passed for 7 hours through the electrolytic cell. [2]

$Q = I \times t = 5 \times 7 \times 60 \times 60 = 1.26 \times 10^5$ C

$Q = n_e \times F$

Amount of electrons passed = $\dfrac{1.26 \times 10^5}{96500}$ = 1.306 mol

Amount of chlorine = $\dfrac{1.306}{2}$ = 0.653 mol

Mass of chlorine produced = 0.653 x 2 x 35.5 = **<u>46.4 g</u>**

(b) In some industrial electrolytic cells, the products of electrolysis of brine are allowed to react further when the diaphragm is removed. Two chlorine-containing products are formed, depending on the operating conditions used. At low temperatures, one of the products is a chloro-oxoanion with an oxidation state of +1.

(i) State the type of reaction taking place. [1]

Disproportionation

(ii) Give an overall balanced equation for the reaction described above. [1]

$Cl_2 + 2e \rightarrow 2Cl^-$ ---(1)

$Cl_2 + 4OH^- \rightarrow 2ClO^- + 2H_2O + 2e$ ----(2)

Overall: **$Cl_2\,(g) + 2OH^-\,(aq) \rightarrow Cl^-\,(aq) + ClO^-\,(aq) + H_2O\,(l)$**

(c) With reference from the Data Booklet, explain why dilute aqueous sodium chloride cannot be used as the electrolyte for the manufacture of chlorine in this electrolysis. [1]

$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ $E^\circ = +1.36$ V -----(1)

$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ $E^\circ = +1.23$V ---(2)

When dilute sodium chloride is used, the E° (O_2/H_2O) is less positive than E° (Cl_2/Cl^-) and H_2O is preferentially oxidised at the anode to give O_2 gas, instead of chlorine gas.

(d) The standard electrode potentials, E°, and standard Gibbs free energy changes, ΔG°, of different chlorine-containing species are tabulated below.

	Half-equation	**E° / V**	**ΔG° / kJ mol^{-1}**
1	$ClO_4^- + 2H^+ + 2e^- \rightleftharpoons ClO_3^- + H_2O$	+1.19	–230
2	$2ClO_3^- + 12H^+ + 10e^- \rightleftharpoons Cl_2 + 6H_2O$	+1.47	**?**
3	$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36	–262

These electrode potentials can be summarised using the Latimer diagram shown below. In a Latimer diagram, the most highly oxidised form of the element is on the left, with successively lower oxidation states to the right. The electrode potentials are shown on the arrows.

$$\begin{tikzcd}
ClO_4^- \arrow[r, "+1.19\text{ V}"] & ClO_3^- \arrow[r, "+1.47\text{ V}"] \arrow[rr, bend right, "+1.45\text{ V}"'] & Cl_2 \arrow[r, "+1.36\text{ V}"] & Cl^-
\end{tikzcd}$$

(i) Calculate ΔG° for half-equation 2. [1]

$2ClO_3^- + 12H^+ + 10e^- \rightleftharpoons Cl_2 + 6H_2O$

$\Delta G^\circ = -nFE^\circ$

$= -(10)(1.47)(96500) = -1418.6 =$ **-1420 kJ mol^{-1}**

(ii) The standard electrode potential of converting ClO_3^- to Cl^- is found to be +1.45 V, instead of +2.83 V. The number of electrons transferred in each step must be taken into account.

I: Write a half-equation for the conversion of ClO_3^- to Cl^-

II: Using your knowledge of Hess' Law for $\Delta G^\ominus$ and your answer to **(d)(i)**, show with the aid of an energy cycle that the $E^\ominus$ for the conversion of ClO_3^- to Cl^- is +1.45 V.

[4]

I : $2ClO_3^- + 12H^+ + 12e^- \rightarrow 2Cl^- + 6H_2O$

Or

$ClO_3^- + 6H^+ + 6e^- \rightarrow Cl^- + 3H_2O$

$$\begin{tikzcd}
2ClO_3^-\,(aq) + 12H^+\,(aq) + 12e^- \arrow[rr, "\Delta G^\ominus = ?"] \arrow[dr, swap, "\begin{matrix}\textbf{Ans from (b)(i)}\\ \Delta G^\ominus = -1418.6\ \text{kJ mol}^{-1}\end{matrix}"] & & 2Cl^-\,(aq) + 6H_2O\,(l) \\
& Cl_2\,(g/aq) + 2e^- + 6H_2O\,(l) \arrow[ur, swap, "\Delta G^\ominus = -262\ \text{kJ mol}^{-1}"] &
\end{tikzcd}$$

Applying Hess Law,

$\Delta G^\ominus = -1418.6 + (-262) = \underline{\mathbf{-1680.6\ kJ\ mol^{-1}}}$

$E^\ominus = -[-1680.6 \times 10^3 / (12 \times 96500)] = \underline{\mathbf{+1.45\ V}}$ (shown)

(iii) With the help of the Latimer diagram provided, calculate $E^\ominus_{cell}$ of the reaction below. Hence, determine its $\Delta G^\ominus_{cell}$.

$$4ClO_3^-(aq) \longrightarrow 3ClO_4^-(aq) + Cl^-(aq)$$

[2]

Using Latimer diagram: $E^\ominus_{cell} = +1.45 - (+1.19) = \underline{\mathbf{+0.26\ V}}$

1 ClO_3^- ion is reduced to Cl^-, gaining 6 electrons.

3 ClO_3^- ions are oxidised to 3 ClO_4^- ions, losing 3 x 2 = 6 electrons

Amount of electrons transferred = 6 mol

$\Delta G^\ominus_{cell} = -(6)(96500)(+0.26) = \underline{\mathbf{-151\ kJ\ mol^{-1}}}$

(iv) With reference to the *Data Booklet*, predict what will happen when an excess of acidified hydrogen peroxide solution is added to a solution of Cl^-(aq). [3]

$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$ (+1.77)

$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ (+1.36)

$2ClO_3^- + 12H^+ + 10e^- \rightleftharpoons Cl_2 + 6H_2O$ (+1.47)

$ClO_4^- + 2H^+ + 2e^- \rightleftharpoons ClO_3^- + H_2O$ (+1.19)

$H_2O_2\,(aq) + 2H^+\,(aq) + 2Cl^-\,(aq) \rightarrow Cl_2\,(aq) + 2H_2O\,(l)$

$E^\ominus_{cell} = (+1.77) - (1.36) = \mathbf{+0.41\ V} > 0$ ∴ reaction is feasible.

$Cl_2\,(aq) + 5H_2O_2\,(aq) \rightarrow 2ClO_3^-\,(aq) + 4H_2O\,(l) + 2H^+\,(aq)$

$E^\ominus_{cell} = (+1.77) - (+1.47) = \underline{\mathbf{+0.30\ V}} > 0$ ∴ reaction is feasible.

$H_2O_2\,(aq) + ClO_3^-\,(aq) \rightarrow H_2O\,(l) + ClO_4^-\,(aq)$

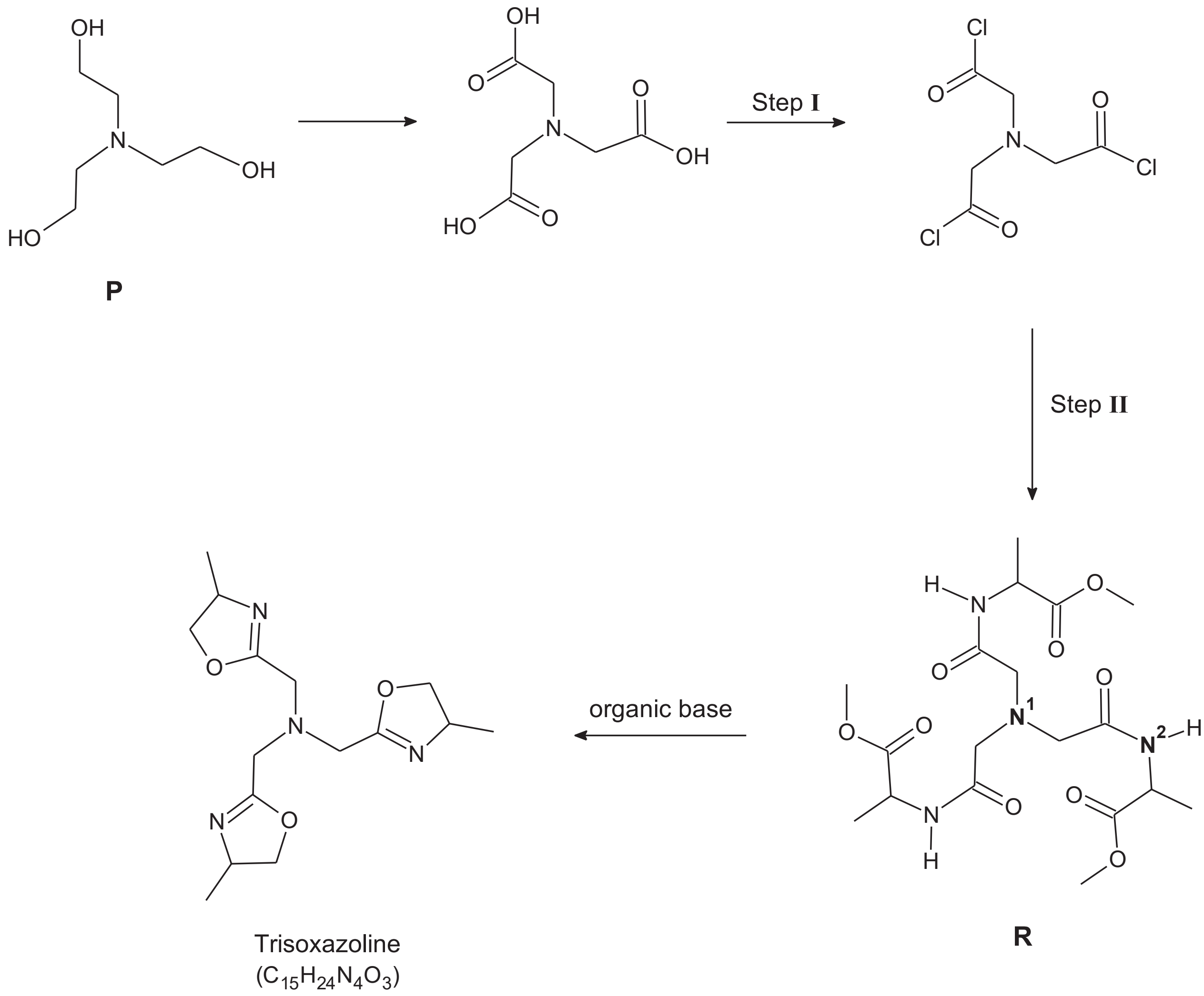
$E^\ominus_{cell} = (+1.77) - (+1.19) = \underline{\mathbf{+0.58\ V}} > 0$ ∴ reaction is feasible.

Cl^- will be oxidised to Cl_2, then to ClO_3^- and finally to ClO_4^- while H_2O_2 will be reduced to H_2O.

[Total: 17]

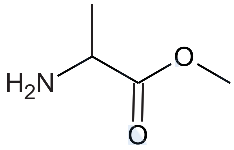
3 Trisoxazoline are organic molecules that can function as ligands. Despite their huge molecular structure, they are able to form stable complexes with metals. Metal complexes with trisoxazoline are commonly used as catalyst in organic synthesis.

(a) The reaction scheme below illustrates the synthesis of trisoxazoline.



(i) Suggest the reagents and conditions required for step **I** and step **II**. [2]

Step I: **PCl_5(s), rtp or PCl_3(s), rtp or $SOCl_2$(*l*), rtp**

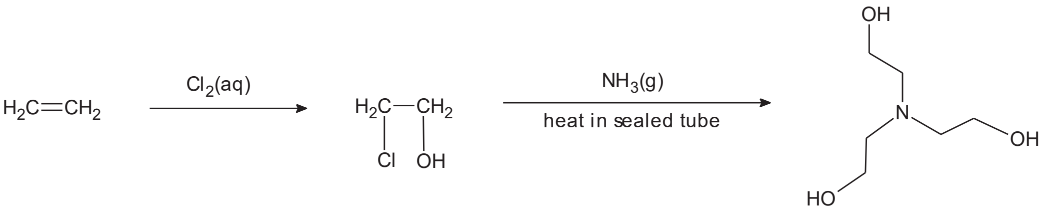
Step II:

, rtp

(ii) Explain the difference in basicity for N^1 and N^2 present in **R**. [2]

N^2 on amide is neutral as the **lone pair of electrons is delocalised with the π-electrons of C=O**. Hence lone pair of electrons not available to form dative bond with proton.

N^1 atom is basic as **the lone pair of electrons is available to form dative bond with proton**.

(iii) Propose a 2-step reaction scheme to synthesise compound **P** from ethene. [2]



P

Trisoxazolines are usually applied to transition metals, such as copper, to form complexes. These complexes are useful in advanced organic synthesis to make specific isomers.

Table 1 shows some properties of the copper complexes, where K_{stab} refers to the stability constant of the complex, e.g.

$$Cu^{2+} + L \rightleftharpoons [CuL]^{2+}$$

$$K_{stab} = \frac{[CuL]^{2+}}{[Cu^{2+}][L]}$$

Table 1

Complex	log(K_{stab})	Colour	Shape of complex
copper(II)-trisoxazoline	12.9	green	distorted tetrahedral
copper(II)-EDTA	18.8	blue	octahedral
copper(II)-en	18.7	violet	octahedral

(b) Describe the feature of the trisoxazoline molecule that enable it to act as polydentate ligand. Hence, state the type of bond formed between the ligand and the central Cu(II) ion and give the coordination number of the complex. [2]

The presence of 4 **N atoms with lone pairs available** to form **dative bonds** with metal centre. Coordination number is **4**

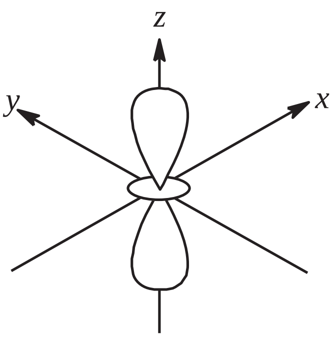
(c) **(i)** Using copper(II)-EDTA as an example, explain why the five d-orbitals are split into two different energy levels. [2]

The lone pair of electrons on EDTA approaches the Cu^{2+} along the axis of octahedral complex.

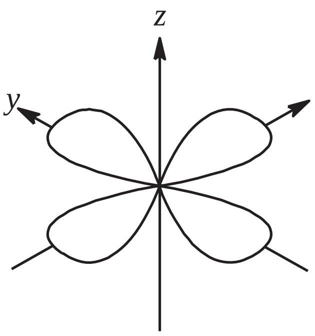
The d_{x2-y2} and d_{z2} orbitals lie along the **x, y, z axis** will experience **greater inter-electronic repulsion** as the **electrons** in these **d orbitals are pointing towards the lone pairs of electrons from EDTA**.

Hence, the five d orbitals will be split into 2 energy levels - the d_{xy}, d_{yz} and d_{xz} orbitals at a **lower energy level** and the d_{z2} and d_{x2-y2} orbitals at a higher energy level.

(ii) Draw the shapes of the d-orbitals at the higher energy level. [1]



d_{z^2}



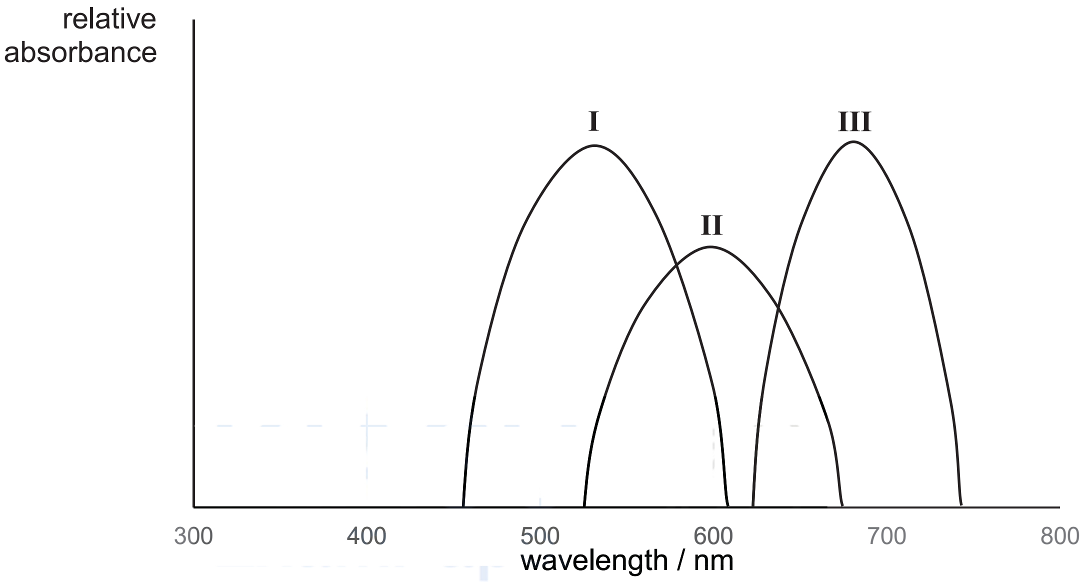
$d_{x^2-y^2}$

(iii) Explain why the copper(II) complexes are coloured. [3]

Presence of ligands **splits the d-orbitals into 2 energy levels**.
1 of the d-electrons **absorbs certain wavelength from the visible light spectrum** and undergoes **d-d transition**.

The d-electron is promoted to a higher energy level. The **remaining wavelengths are transmitted and the complementary colour of the wavelength absorbed is observed**.

(iv) The visible absorption spectrum of the three complexes is shown below where each peak represents one complex.
[A visible absorption spectrum is a graph depicting the absorption of radiation by a material over a range of visible light wavelengths.]



Identify the copper(II) complex responsible for each absorption peak. Hence, arrange the three complexes in order of increasing magnitude of their energy gap. [2]

I: copper(II)-en
II : copper(II)-EDTA
III : copper(II)-trisoxazoline
Since $\Delta E \propto \frac{1}{\lambda}$, energy gap in increasing order:
copper(II)-trisoxazoline < copper(II)-EDTA < copper(II)-en

(d) Using Table 1, comment on the spontaneity of forming the respective copper(II) complexes. [2]

$\Delta G^{\circ} = -RT \ln K$

K_{stab}: copper(II)-EDTA > copper(II)-ethylenediamine > copper(II)-trisoxazoline
Magnitude of ΔG°:
copper(II)-EDTA > copper(II)-ethylenediamine > copper(II)-trisoxazoline
spontaneity: **Cu(II)-EDTA > Cu(II)-en > Cu(II)-trisoxazoline**

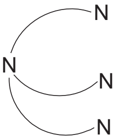
(e) Other than copper(II) ions, it was found that copper(I) ions are also able to form complexes with trisoxazoline.

(i) Predict and explain the colour of solid copper(I)-trisoxazoline complex. [1]

White. The **d-orbitals are fully filled** in copper(I), **no d-d transition**.

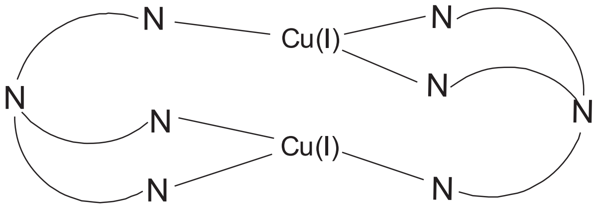
(ii) Analysis was done on copper(I)-trisoxazoline complex. The relative molecular mass of the complex was apparently 743.0. Further analysis showed that each copper(I) ion is bonded to three nitrogen atoms.

Propose the structure of copper(I)-trisoxazoline complex.

[You may use 

to represent trisoxazoline.]

[1]



[Total: 20]

Section B

4 **(a)** At r.t.p, 1.2 dm^3 of chlorine gas is reacted with 6.7 g of compound **A**, $C_9H_{10}O$, to give compound **B**. On addition of PCl_5, **A** gives white fumes. Treatment of **A** with NaBr and concentrated H_2SO_4 under reflux gives a mixture of compounds **C** and **D**. **C** and **D** have the same molecular formula $C_9H_{10}Br_2$ and each contains only *one* chiral centre.

(i) When NaBr is mixed with concentrated H_2SO_4, the following observations are made.

- White fumes produced
- Reddish brown liquid formed
- Pungent gas decolourised purple $KMnO_4$

It is suggested that a displacement reaction occurred first, producing white fumes. Some of the white fumes further react with H_2SO_4 via a redox reaction. Using the above information, write the two corresponding chemical equations for this reaction. [2]

$NaBr + H_2SO_4 \rightarrow HBr + NaHSO_4$
$2HBr + H_2SO_4 \rightarrow Br_2 + SO_2 + H_2O$

(ii) Using your answer in **(a)(i),** deduce the identities of **A** to **D**. [5]

Amt of A = 6.7/134 = 0.05 mol
Amt of Cl_2 = 1.2/24 = 0.05 mol

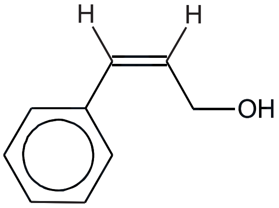
A has similar ratio of C and H atoms, and no. of C > 6
➔ **A** contains a benzene ring

A undergoes **electrophilic addition** with chlorine gas
➔ **A** contains **1 alkene** functional group (or C=C) and **B** is a **halogenoalkane/chloroalkane**

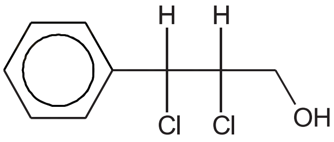
A undergoes **nucleophilic substitution** with PCl_5 to give white fumes of HCl
➔ **A** is an **alcohol**

A undergoes both **electrophilic addition and nucleophilic substitution** to give **C** and **D**.
Since **C** and **D** each only contains 1 chiral centre,

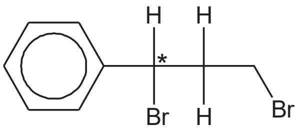
A can only be



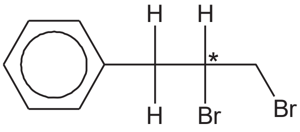
B:



C and **D**:



(major)



(minor)

(iii) Account for the relative quantity of compound **C** and **D** formed. [1]

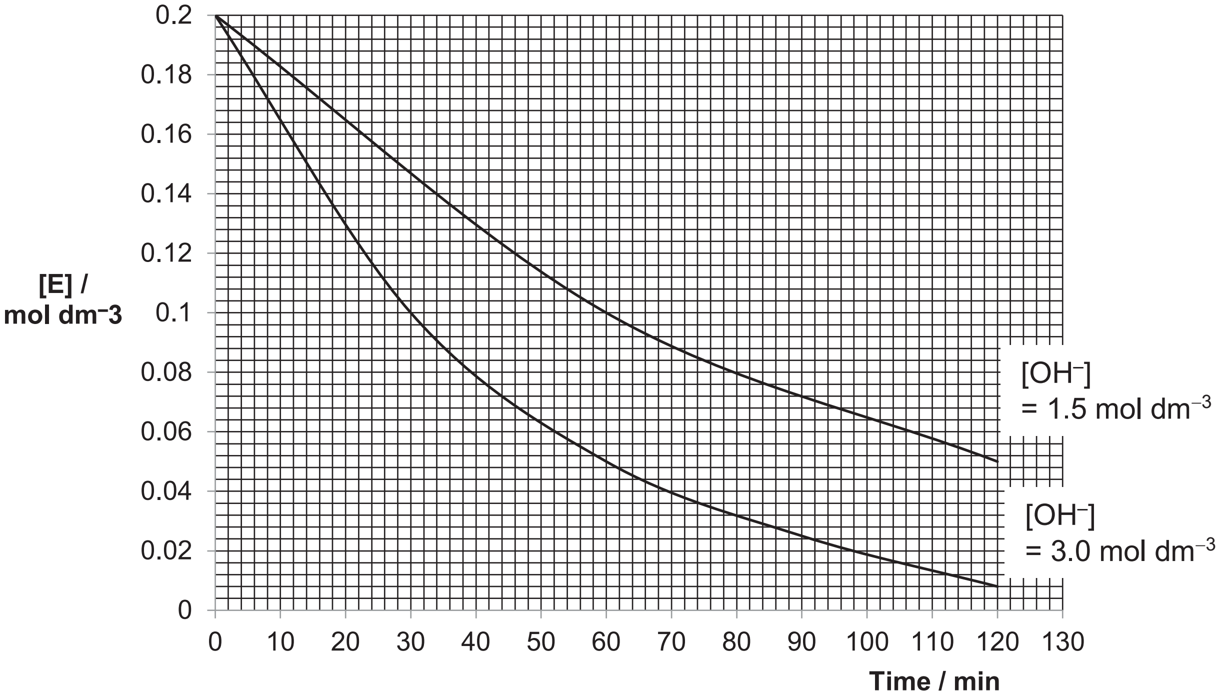
Compound **C** is the major product while **D** is the minor product.

For compound **D**, the benzylic **carbocation intermediate is more stable** due to **resonance / positive charge dispersed into the benzene ring.**

(b) **E** is another constitutional isomer of **C** and **D**.
A series of chemical experiments were conducted on **E**.

Experiment 1:

The reaction kinetics of **E** with aqueous sodium hydroxide was determined by monitoring the change in concentration of **E** with time.



Experiment 2:

0.2 mol of **D** and **E** were treated separately with boiling aqueous sodium hydroxide. The products from each compound were then acidified with nitric acid and then treated with silver nitrate solution.
The results obtained are shown below:

	Observation upon adding $AgNO_3$	**Mass of ppt / g**
D	formation of cream-coloured precipitate	75.12
E	formation of cream-coloured precipitate	37.56

(i) Using experiment 1, deduce the rate equation. [3]

using [OH⁻] = 3.0 mol dm⁻³ graph,

$t_{1/2}$ is constant at 30 min, reaction is 1st order with respect to E.

OR

using [OH⁻] = 1.5 mol dm⁻³ graph,

$t_{1/2}$ is constant at 60 min reaction is 1st order with respect to E.

Using initial rate method,

Initial rate for graph where [OH⁻] = 1.5 mol dm⁻³
= 0.2/110 = 0.001818 mol dm⁻³ min⁻¹

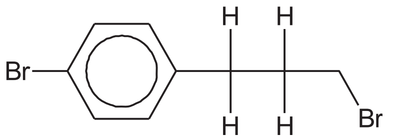
Initial rate for graph where [OH^-] = 3.0 mol dm^{-3}
= 0.2/52 = 0.003846 mol dm^{-3} min^{-1}
As [OH^-] increases 2 times, initial rate also increases 2 times
($\frac{0.004}{0.00211} = 1.90 \approx 2$)

Hence, **order of reaction with respect to OH^- is 1.**
Rate = k [E] [OH^-]

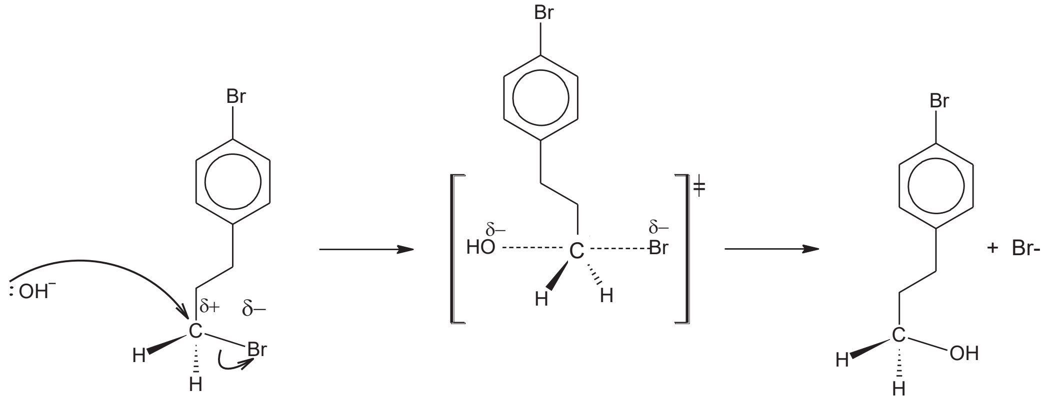
(ii) Using Experiment 2 and **(b)(i)**, propose a possible structure of **E** and draw the mechanism for the reaction of **E** with NaOH(aq). [3]

From (b)(ii), E undergoes S_N2 mechanism
→ it is a **1° halogenoalkane**

From expt 2, 0.2 mol of **E** forms 0.2 mol of AgBr
→ There is **only one** Br in the alkyl side chain

E is 

(accept any mono substituted position of Br on benzene with 1° or 2° bromoalkane)



(c) Depending on the mechanism, the solvent affects the stability of nucleophile and/or reaction intermediates in the nucleophilic substitution of halogenoalkanes. The table below shows the rate of reaction when different halogenoalkanes and solvents are used.

Solvent	**Type**	**Dielectric constant, ε**	**Relative rates for reaction with OH^-**	
			1° RX in S_N2	**3° RX in S_N1**
CH_3OH	Protic	33	1	4
H_2O	Protic	78	7	150 000
CH_3COOH	Protic	6	1	1
CH_3COCH_3	Aprotic	21	5000	-

Dielectric constant, ε, is a measure of the solvent polarity and ability to insulate charge.

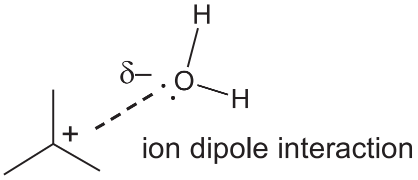
(i) Suggest, using **only** structure and bonding, the difference between *protic* and *aprotic* solvents. [1]

Protic refers to molecules with **H atoms that can be used to form hydrogen bond**. Aprotic solvents can only form **permanent dipole- permanent dipole interactions between molecules/ have no H atoms that can form hydrogen bond**

(ii) Explain the effect of solvent on the relative rate of S_N2 reactions. [2]

For S_N2, protic solvent like water can form **hydrogen bond with OH^-**. Hence **decreasing the nucleophilic ability of OH^-** and lower the rate of reaction.
While aprotic solvent like CH_3COCH_3, do not form hydrogen bond and hence the **lone pair of electron** on **OH^- is more available to attack the electron deficient C on 1° RX.**

(iii) Explain, with an aid of a diagram, how water increases the rate of S_N1 reaction. [2]



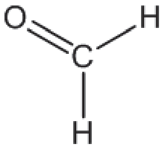
The ion dipole interaction **stabilised the carbocation/reaction intermediate**

(iv) Name a solvent, other than those given in the table, that will result in a slower rate for S_N1 than ethanoic acid. [1]

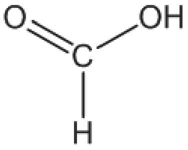
Name of any suitable hydrocarbon e.g Benzene, hexane ..etc

[Total: 20]

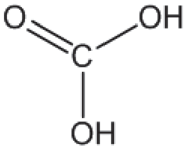
5 **(a)** Using only the elements C, H and O, draw the structural formulae of **three** organic compounds, each containing a single carbon atom with an oxidation state of zero, +2 and +4 respectively. [3]



O.S. = 0



O.S. = +2



O.S. = +4

(b) Hot, concentrated potassium manganate (VII) oxidises several classes of organic compounds to ketones, carboxylic acids or carbon dioxide. By this means, the structures of compounds can be determined. Some compounds are easily oxidised, while others require longer heating.

The following describes some reactions of compounds **F** and **K**, and of their oxidation products.

F, $C_8H_{12}O$ reacts with excess potassium manganate (VII) to produce single organic products, **G,** $C_4H_6O_5$ while **K,** $C_{12}H_{12}$, reacts with the same reagent to produce **H,** $C_{10}H_{10}O_3$. Carbon dioxide is produced in both reactions in a mole ratio of 2 : 1 respectively. During oxidation of **F**, four moles of carbon dioxide were liberated.

Although **F** reacts with potassium manganate (VII), it gives no reaction with potassium dichromate (VI). When 0.10 mol of **F** is reacted with an excess of sodium metal, 1.2 dm^3 of hydrogen is formed, measured at room temperature and pressure.

G reacts with excess concentrated sulfuric acid to give **I**, $C_4H_4O_4$. Upon further oxidation, **I** is found to give **J,** $C_3H_2O_5$, and an inorganic by-product.

H gives a positive iodoform test and dissolves in aqueous sodium hydroxide. Upon further oxidation of **H**, **L,** $C_9H_6O_6$, and a similar inorganic by-product formed from **I** is also produced.

(i) Deduce the structure of compounds **F** to **L**, explaining the chemistry of the reactions described. [11]

F and **K** undergoes **strong oxidation** with $KMnO_4$ to give **G** and **H**
➔ Since there is a decrease in no of C atoms after oxidation, both F and K must contain **alkenes**.

F liberates four mole of carbon dioxide
→ **F** contains (terminal) **alkenes**.

F undergoes **redox** with Na metal
→ 0.10mol ≡ 1.2dm^3 ≡ 1H_2 ≡ 1ROH
→ **F** contains only 1 **alcohol.**

F **does not undergo strong oxidation** with $K_2Cr_2O_7$
→ **F** contains a **tertiary alcohol.**

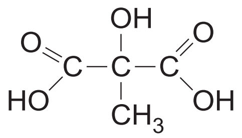
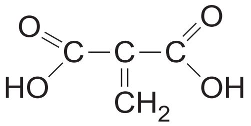
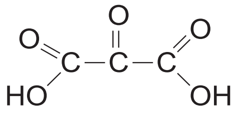
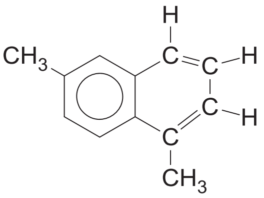
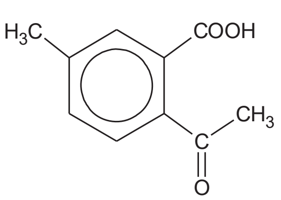
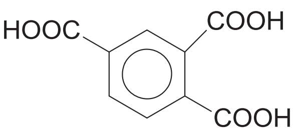
F undergoes **elimination** with excess concentrated sulfuric acid to give **I**, $C_4H_4O_4$
→ **F** contains an **alcohol.**

I further oxidises to give **J,** $C_3H_2O_5$, and an inorganic by-product
→ **I** contains 4 **carboxylic acid** and **CO_2** is the by-product

H undergoes **mild oxidation** with iodoform
→ **H** contains a **terminal methyl ketone**
(since it is an [O] product, it cannot be a methyl carbinol)

H dissolves in aqueous sodium hydroxide.
→ **H** contains an **acidic group** (i.e. – COOH)

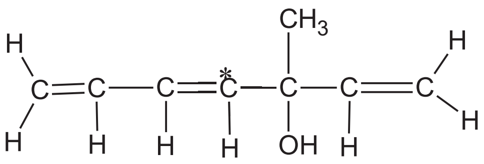
L is an oxidised product
→ **L** contains a **tricarboxylic acid** and the inorganic product is **CO_2**.

		
G	**I**	**J**
		
K	**H**	**L**

Note : methyl group can be on any position

(ii) State the type(s) of stereoisomerism shown by compound **F** and give one further piece of relevant information about it. [2]

F:



Enantiomerism:
F has **no plane of symmetry. OR**
F **rotates plane polarised light. OR**
F has a pair of **non-superimposable images.**

Cis-trans:
Restricted rotation about C=C OR
two different substituents about each C on C=C

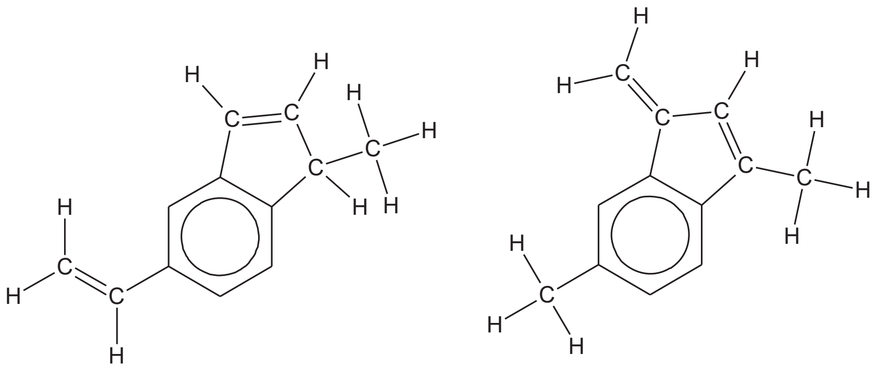
(iii) Hence, predict the total number of isomers shown by **F**. [1]

no of enantiomers present = **4**

(iv) When compound **K** undergoes prolonged heating with $KMnO_4$ to give **L**, **K** exhibits **two** types of constitutional isomerism.

Name the specific types of isomerism shown by compound **K** and hence, draw the **displayed formulae** of the isomers. [3]

Positional and Chain isomerism



[Total : 20]

SERANGOON JUNIOR COLLEGE
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME	
CLASS	

CHEMISTRY
JC2 Preliminary Examination
Paper 4 Practical

9729/04
25 Aug 2017
2 hr 30 min

Candidates answer on the Question Paper

Additional Materials:

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Give details of the practical shift and laboratory in the boxes provided.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough work.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages ______

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

Shift
Laboratory

For Examiner's Use	
1	
2	
3	
4	
TOTAL	**/ 55**

1 You are to determine the concentration of aqueous copper(II) sulfate by titration. The concentration of Cu^{2+} ions in a solution can be found by reaction with an excess of aqueous iodide ions to produce iodine. The amount of iodine formed can be found by titration with thiosulfate ions, $S_2O_3^{2-}$.

FB 1 is aqueous copper(II) sulfate, $CuSO_4$.
FB 2 is 0.100 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$.
FB 3 is aqueous potassium iodide, KI.
starch indicator

(a) Method

(i) 1. Fill the burette with **FB 2**.
2. Using a pipette, transfer 25.0 cm^3 of **FB 1** into a conical flask.
3. Use an appropriate measuring cylinder, transfer 10 cm^3 of **FB 3** to the same conical flask.
4. Titrate this mixture with **FB 2** until the colour of the mixture changes from brown to yellow-brown. An off-white precipitate will also be present in the flask throughout the titration.
5. Add 5 drops of starch indicator.
6. Continue the titration until the blue-black colour of the starch-iodine complex just disappears leaving the off-white precipitate.
7. Record your titration results in the space provided below. Make certain that your recorded results show the precision of your working.
8. Repeat points **1** to **7** as necessary until consistent results are obtained.

Results

Initial burette reading / cm^3	0.00	0.00
Final burette reading / cm^3	25.10	25.10
Volume of **FB 2** used / cm^3	25.10	25.10

[5]

(ii) From your titrations, obtain a suitable volume of **FB 2** to be used in your calculations. Show clearly how you obtained this volume.

Volume of FB 2 = $\dfrac{25.10 + 25.10}{2} = 25.10\ \text{cm}^3$

volume of **FB 2** = ...[1]

(b) (i) The equations for the formation of iodine and its reaction with thiosulfate ions are given below.

$$2Cu^{2+} + 4I^- \rightarrow 2CuI + I_2$$
$$I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$$

Calculate the amount of thiosulfate ions, $S_2O_3^{2-}$, present in the volume of **FB 2** in **(a)(ii)**.

amount of $S_2O_3^{2-}$ = $\frac{0.1 \times (a)(ii)}{1000} = \frac{0.1 \times 25.10}{1000}$ = 2.51×10^{-3} mol

amount of $S_2O_3^{2-}$ = ...[1]

(ii) Using the equations above, calculate the amount of Cu^{2+} ions present in 25.0 cm^3 of **FB 1**.

$2S_2O_3^{2-} \equiv I_2 \equiv 2Cu^{2+}$

amount of Cu^{2+} = (b)(i) = 2.51×10^{-3} mol

amount of Cu^{2+} = ...[1]

(iii) Calculate the concentration, in mol dm^{-3}, of copper(II) sulfate in **FB 1**.

concentration of $CuSO_4$ = $\frac{(b)(ii) \times 1000}{25.0} = \frac{2.51 \times 10^{-3} \times 1000}{25.0}$
= 0.100 mol dm^{-3}

concentration of $CuSO_4$ = ...[1]

(c) Two students repeated the experiment but each obtained different values for the concentration of $CuSO_4$.

The students each suggested possible improvements.

Student 1 suggested that a larger volume of potassium iodide, **FB 3**, should be added. Student 2 suggested that the contents of the conical flask should be filtered before titration.

Comment on the effectiveness of **each** of these possible improvements.
Explain your answers.

Student 1 No effect because KI (FB 3) already in excess.

Student 2 Not effective because some iodine stays on the filter paper.

[2]

(d) The maximum error in each burette reading is ±0.05 cm^3.
The maximum error in each titration is therefore ±0.10 cm^3.
The 25.0 cm^3 pipette used in this titration, is labelled with an error of ±0.06 cm^3.

Explain why the maximum error when 25.0 cm^3 of solution is run from a pipette is only ±0.06 cm^3 and not ±0.12cm^3.

………………………………………………………………………………………………...

The mark on the pipette was only read once.
………………………………………………………………………………………………...

[1]

(e) Considering the maximum errors from pipette and burette, calculate the total percentage error in one titration.

error from pipette = $\frac{0.06}{25.0} \times 100\%$ = 0.24%

% error from burette = $\frac{2 \times 0.05}{25.70 (volume\ from\ 1\ titration)} \times 100\%$ = 0.39%

Total % error = 0.24 + 0.39 = 0.63%

[2]
[Total: 14]

2 You are to determine the enthalpy change of reaction, ΔH, for the reaction shown below.

$$Cu(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + H_2(g)$$

Since copper is an unreactive metal it does not react directly with dilute acids. You will therefore need to find the enthalpy change of reaction for two reactions that do occur. The equations for these two reactions are below.

$Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$ **Reaction 1**

$Mg(s) + CuSO_4(aq) \rightarrow MgSO_4(aq) + Cu(s)$ **Reaction 2**

You will carry out experiments to find the enthalpy changes for each of **Reaction 1** and **Reaction 2** and use these values to calculate the enthalpy change for the reaction of copper with sulfuric acid.

TURN OVER FOR EXPERIMENTAL METHOD

Determining the enthalpy change for Reaction 1

$Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$ **Reaction 1**

I (a) Method

FB 4 is 1.00 mol dm^{-3} sulfuric acid, H_2SO_4.
FB 5 is magnesium powder, Mg.

Read through the method before you start any practical work and prepare a suitable table for your results.

1. Weigh the stoppered weighing bottle containing **FB 5**. Record the mass.
2. Support the styrofoam cup in the 250cm^3 beaker.
3. Use the measuring cylinder to transfer 25cm^3 of **FB 4** into the styrofoam cup.
4. Measure the temperature of **FB 4** in the styrofoam cup and start the stop watch. Record this temperature as being the temperature at time = 0.
5. Measure, and record, the temperature of this **FB 4** every half minute for 2 minutes.
6. At time = 2.5 minutes, add **FB 5** to the acid and stir carefully to reduce acid spray.
   Caution : Inhalation of the fumes may cause choking.
7. Measure the temperature of the mixture in the cup at time = 3 minutes and then every half minute up to time = 7 minutes.
8. Continue stirring occasionally throughout this time.
9. Weigh the weighing bottle that had contained **FB 5**. Record the mass.
10. Calculate and record the mass of **FB 5** added to the sulfuric acid.
11. Discard the used styrofoam cup.

Mass of weighing bottle and FB 5 before transfer /g	
Mass of weighing bottle and residual FB 5 /g	
Mass of FB 5 used /g	0.195

Time / min	Temperature / °C
0	
0.5	
1.0	
1.5	
2.0	
2.5	
3.0	
3.5	
4.0	
4.5	
5.0	
5.5	
6.0	
6.5	
7.0	

[5]

(b) **(i)** On the grid below plot a graph of temperature (*y*-axis) against time (*x*-axis).

[2]

(ii) Complete the graph by inserting **two**, **straight** lines of best fit:

- one to show the temperature up to time = 2.5 minutes,
- one to show the temperature after time = 2.5 minutes.

[1]

(iii) From your graph, use the two straight lines of best fit to calculate the change in temperature at time = 2.5 minutes.

temperature change = ……………………………………[1]

(c) Calculations

(i) In the reaction in **(a)**, the sulfuric acid was in excess. Without carrying out any additional tests, what observation could you have made during your experiment to confirm this?

All the magnesium / solid dissolved / disappeared or all solid / Mg has gone / been used up or no solid / Mg left

[1]

(ii) Calculate the energy change that occurred during the reaction in **(a)**.

[Assume that 4.2 J is needed to raise the temperature of 1.0cm^3 of solution by 1.0°C.]

Energy change = 25 × 4.2 × b(iii) = XXX J

energy change = ……………………………………[1]

(iii) Use your answer to **(ii)** to calculate the enthalpy change, in kJ mol^{-1}, for the reaction between sulfuric acid and magnesium.

[A_r : Mg, 24.3]

$$Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g) \quad \textbf{Reaction 1}$$

$$\Delta H = -\frac{(ii) \times 24.3}{1000 \times \text{mass of Mg}} = -\text{ xxx kJ mol}^{-1}$$

enthalpy change for **Reaction 1** = ……………………………………[1]

Determining the enthalpy change for Reaction 2

$$Mg(s) + CuSO_4(aq) \rightarrow MgSO_4(aq) + Cu(s) \quad \textbf{Reaction 2}$$

(d) Method

FB 6 is 1.00 mol dm^{-3} copper(II) sulfate, $CuSO_4$.
FB 7 is magnesium powder, Mg.

Read through the method before you start any practical work and prepare a suitable table for your results.

1. Weigh the weighing bottle containing **FB 7**. Record the mass.
2. Support the styrofoam cup in the 250cm^3 beaker.
3. Use the measuring cylinder to transfer 25cm^3 of **FB 6** into the styrofoam cup.
4. Measure the temperature of **FB 6** in the styrofoam cup and record the temperature.
5. Add the **FB 7** to the **FB 6** in the cup and stir the mixture constantly.
6. Measure and record the maximum temperature reached during the reaction.

7. Calculate and record the maximum temperature change that occurred during the reaction.
8. Weigh the weighing bottle that had contained **FB 7**. Record the mass.
9. Calculate and record the mass of **FB 7** added to the copper(II) sulfate.
10. Empty the contents of the styrofoam cup into the bottle labelled **waste**.

Mass of weighing bottle and FB 7 before transfer /g	
Mass of weighing bottle and residual FB 7 /g	
Mass of FB 7 used /g	

Initial temperature / °C	
Maximum temperature / °C	
Maximum temperature change /°C	

[2]

(e) **Calculations**

(i) Show, using a suitable calculation, that the copper(II) sulfate was in excess in the reaction.

[A_r : Mg, 24.3]

Amount of $CuSO_4$ = $\frac{25 \times 1}{1000}$ = 0.025 mol

Amount of Mg = $\frac{\text{mass of FB 7}}{24.3}$ = xxx mol

Hence $CuSO_4$ is in excess.

[1]

(ii) Hence, calculate the enthalpy change, in kJ mol^{-1}, for the reaction between magnesium and copper(II) sulfate.

[Assume that 4.2 J is needed to raise the temperature of 1.0cm^3 of solution by 1.0°C.]

$Mg(s) + CuSO_4(aq) \rightarrow MgSO_4(aq) + Cu(s)$ **Reaction 2**

$\Delta H = \frac{25 \times 4.2 \times \Delta T}{\text{amt of Mg from (i)}}$ = xxx kJ mol^{-1}

enthalpy change for **Reaction 2** = ……………………………………[1]

Enthalpy change for Reaction 3

Reaction 3 is shown below.

$Cu(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + H_2(g)$ **Reaction 3**

(f) Use your values for the enthalpy changes for **Reactions 1** and **2** to calculate the enthalpy change for **Reaction 3**.

$Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$ **Reaction 1**

$Mg(s) + CuSO_4(aq) \rightarrow MgSO_4(aq) + Cu(s)$ **Reaction 2**

Show clearly how you obtained your answer.

(If you were unable to calculate the enthalpy changes for **Reactions 1** and **2**, you should assume that the value for **Reaction 1** is – 444 kJ mol^{-1} and that the value for **Reaction 2** is – 504 kJ mol^{-1}. Note: these are not the correct values.)

$$\begin{tikzcd} MgSO_4(aq) + Cu(s) + H_2SO_4(aq) \arrow[rr, "\Delta H \text{ reaction 3}"] & & CuSO_4(aq) + H_2(g) + MgSO_4(aq) \\ & Mg(s) + CuSO_4(aq) + H_2SO_4(aq) \arrow[ul, "\Delta H \text{ reaction 2}"] \arrow[ur, "\Delta H \text{ reaction 1}"'] & \end{tikzcd}$$

ΔH reaction 3 = ΔH reaction 1 − ΔH reaction 2 = xxx

enthalpy change for **Reaction 3** = ...[1]

(g) **(i)** The method you used to determine the enthalpy change for **Reaction 1** was more accurate than the method you used to determine the enthalpy change for **Reaction 2**. Suggest why the method used for **Reaction 2** was less accurate. Explain your answer.

- Lower ΔH and so higher % error
- No correction made for loss of heat on cooling
- Some bubbles / gas / H2 in reaction 2 so wrong reaction taking place
- Not all Mg reacts / reaction does not go to completion in 2 (so not all energy released).
- Reaction 2 slower so more heat loss

[1]

(ii) A student suggested that the accuracy of the method used for **Reaction 2** could be improved by using a larger volume of copper(II) sulfate. Is this a correct suggestion? Give a reason for your answer.

No, since (larger volume of solution means) smaller ΔT OR
Yes, since there would be a smaller T rise so less heat would be lost.

[1]

[Total : 19]

3 Qualitative Analysis

At each stage of any test, you are to record details of the following.

- Colour changes seen
- The formation of any precipitate
- The solubility of such precipitates in an excess of the reagent added

Where gases are released, they should be identified by a test, described in the appropriate place in your observations.

You should indicate clearly at what stage in a test a change occurs.
No additional tests for ions present should be attempted.

FB 8 is a solution containing 2 cations and 1 anion.

(a)

Test	Procedure	Observation
1	To 1 cm depth of **FB 8** in a test tube, add aqueous ammonia until it is in excess.	• (grey) Green ppt formed, insoluble in excess NH_3. • Green ppt turned brown on contact with air
2	To 1 cm depth of **FB 8** in a **boiling tube**, add aqueous sodium hydroxide until it is in excess. Then heat the boiling tube gently with care. Keep the mixture for **Test 3**.	• Green ppt formed, insoluble in excess NaOH. • Gas evolved that turned moist red litmus paper blue. • Green ppt turned brown (grey) upon heating.
3	To the mixture from **Test 2**, add 1 cm depth of aqueous hydrogen peroxide. Shake the boiling tube gently.	• Ppt / solid turned brown / red-brown. • Effervescence observed. Gas evolved relights a glowing splint / glows brighter.
4	To 1 cm depth of **FB 8** in a test tube, add aqueous barium chloride, followed by dilute hydrochloric acid.	• White ppt formed, insoluble in HC*l*.

[4]

(b) Using your observations above, identify the ions in **FB 8**. Give evidence to support your conclusion.

Fe^{2+}: From Tests 1 and 2, green ppt formed, turned brown on contact with air, insoluble in excess NaOH and NH_3

NH_4^+: From Test 2, gas evolved that turned moist red litmus paper blue when warmed with NaOH.

SO_4^{2-}: From Test 4, white ppt formed when $BaCl_2$ is added, insoluble in HCl.

[3]

(c) What type of reaction has taken place in **Test 3**? Explain your answer.

Redox reaction.

Explanation:

- Iron(II) ions converted / oxidised to iron(III) ions
- Hydrogen peroxide converted / reduced to oxygen gas.
- Hydrogen peroxide decomposed to give oxygen gas

[1]

(d) **FB 9** is an aqueous solution, containing one cation and one anion.
Carry out the following tests in test-tubes.
Complete the table by recording your observations.

Test	Procedure	Observations
5	To 1 cm depth of **FB 9**, add aqueous sodium hydroxide until it is in excess.	• No ppt formed.
6	To 1 cm depth of **FB 9**, add a piece of magnesium ribbon.	• Effervescence observed. • Gas evolved extinguished lighted splint with a 'pop' sound.
7	To 1 cm depth of **FB 9** in a test tube, add 2 drops of aqueous silver nitrate, followed by aqueous ammonia until in excess.	• White ppt formed, soluble in NH_3 (aq) to form a colourless solution.

[2]

(e) Using your observations above, identify the ions in **FB 9**. Give evidence to support your conclusion.

H^+: hydrogen gas evolved, extinguished lighted splint with 'pop' sound.
Cl^-: White ppt formed, soluble in NH_3 (aq) to form a colourless solution.

[2]
[Total: 12]

4 Many transition metal complex ions are coloured. It is possible to use this property to determine the concentration of a solution of a coloured ion. A few cm^3 of the solution is placed inside a *spectrometer*.

A *spectrometer* measures the amount of light that is absorbed when a specific wavelength of visible light is shone through a coloured solution. It does this by comparing the amount of light passing through the sample with the amount of light passing through the pure solvent. The amount of light absorbed is expressed as an absorbance value, The more concentrated the solution, the higher the absorbance value.

Beer-Lambert's Law states that the absorbance values, A, is directly proportional to the concentration of absorbing species, c, as shown below. The general Beer-Lambert's Law is usually written as,

$$A = \varepsilon c l$$

Where ε is the molar extinction coefficient and l is the path length, which is usually 1.0cm.

This equation can be used to calculate the absorbance value when the concentration of copper(II) ions is known.

You may assume that you are provided with the following in the subsequent parts of the question.

- **FB1** from Question 1
- solid hydrated copper(II) sulfate, $CuSO_4.5H_2O$;
- access to a spectrometer and instructions for its use;
- graph paper;
- the apparatus and chemicals normally found in a school or college laboratory.

(a) The spectrometer is set to use the wavelength of light that is absorbed most strongly by the copper(II) ions.

Suggest a colour in the visible spectrum from which a suitable wavelength of light might be chosen. Explain your answer.

Orange. Cu^{2+} is blue in colour. Hence, it will absorb colours that are complementary to **blue.**

[1]

(b) Spectrometry can be used to determine the concentration of a solution of aqueous copper(II) sulfate. A series of known, but different, concentrations of copper(II) sulfate is prepared. A spectrometer is used to measure the absorbance of each solution.

According to Beer-Lambert's Law, a graph of absorbance against concentration is then plotted. This graph is known as *calibration* line.

The experiment is then repeated using a solution of unknown concentration. By comparing the absorbance of this solution with the calibration line, the concentration of copper(II) ions in the unknown solution can be determined.
Propose a simple plan on how you would prepare

- a 100.0cm^3 of 1.00 moldm^{-3} standard aqueous copper(II) sulfate;
- a suitable range of diluted solutions of accurate concentrations

You are to show detailed calculations and suitable tables (where appropriate) in your answer.

(i) a 100.0cm^3 of 1.00 moldm^{-3} standard aqueous copper(II) sulfate;

Preparation of the 100 cm^3 of 1.00 mol dm^{-3} aqueous copper (II) sulfate standard solution

Amount of $CuSO_4.5H_2O$ needed = (100/1000) x 1 = 0.100
Mass of $CuSO_4.5H_2O$ needed = 0.100 x (63.4+32.1+16x4+5x18) = 24.95 g

1. Weigh accurately about **24.95 g** of $CuSO_4.5H_2O$ using a clean, dry weighing bottle using a mass balance by recording the mass of the $CuSO_4.5H_2O$ and weighing bottle as shown in the table below.

Mass reading table

Mass of weighing bottle with $CuSO_4.5H_2O$ / g	***x***
Mass of **empty** weighing bottle / g	***y***
Mass of $CuSO_4.5H_2O$ / g	***x - y***

2. Transfer the weighed solid into a 100 cm^3 beaker and dissolve it using distilled water and stir.

3. Transfer the solution and washings into a **100 cm^3 volumetric flask**.

4. Reweigh the empty weighing bottle and record its mass.

5. Make up to the mark with distilled water and shake well to obtain a homogeneous solution.

(ii) a suitable range of diluted solutions of accurate concentrations, keeping the total volume of each solution to be constant at 20.00cm^3

Preparation of a suitable range of diluted standard solutions

6 different solutions with different concentrations of $CuSO_4$ (aq) were prepared, as shown in the following table:

Table 2

Solution	**Volume of 1.0 moldm^{-3} of $CuSO_4$ (aq) / cm^3**	**Volume of deionized water / cm^3**	**Total volume / cm^3**	**[$CuSO_4$] / mol dm^{-3}**	Absorbance value
1	20.00	0.00	20.00	1.000	
2	10.00	10.00	20.00	0.500	
3	5.00	15.00	20.00	0.250	
4	2.50	17.50	20.00	0.125	
5	1.50	18.50	20.00	0.075	
6	0.50	19.50	20.00	0.025	

1. To prepare 0.500 mol dm^{-3} of $CuSO_4$ (aq), add 10.00 cm^3 of 1.00 mol dm^{-3} $CuSO_4$ standard solution into a 50 cm^3 beaker using a burette.

2. Using a separate burette, add 10.00 cm^3 of deionised water into the beaker and stir using a glass rod to obtain a homogenous solution.

3. Repeat the above steps to obtain diluted solutions of different concentrations using the volumes in Table 2.

[5]

(c) Using the solutions prepared in **(b)**, the absorbance value of each copper(II) sulfate solution can be determined and hence a calibration line can be obtained via the spectrometer.

Describe a plan to determine the concentration of **FB 1**.

Your plan should include details of:

- calculation of the absorbance value for each copper(II) sulfate solution prepared in **(b)**, given ε of $CuSO_4$ is **2.81** mol^{-1} dm^3 cm^{-1}.
- a sketch of the calibration line you would expect to obtain;
- a brief outline of how the results would be obtained.
- how the calibration line would be used to determine the concentration of copper(II) ions in **FB 1**.

Table of results

Solution	**[$CuSO_4$] / mol dm^{-3}**	**Absorbance value**
1	1.000	2.81
2	0.500	1.41
3	0.250	0.70
4	0.125	0.35
5	0.075	0.21
6	0.025	0.07

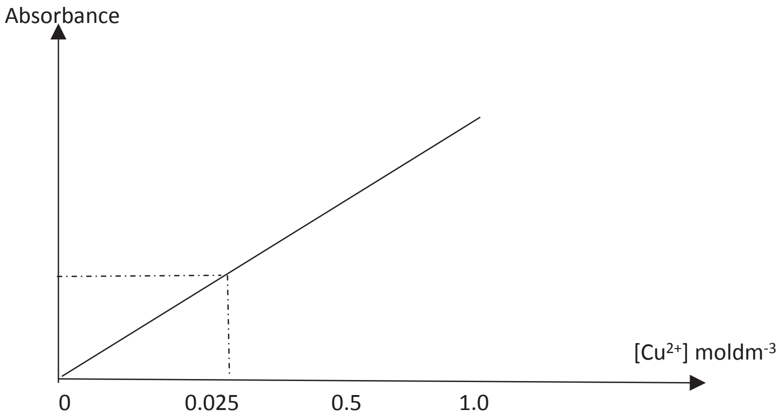
Using the spectrometer

1. Spectrometer is set up to absorb the wavelength of orange (600nm).

2. A few cm^3 of each of the 6 $CuSO_4$ solutions are run by the spectrometer and the absorbance values are recorded in Table 2.

3. Plot a graph of absorbance value versus [$CuSO_4$].

4. Draw the best-fit straight line passing through the origin. This is the calibration line.



Analysing solution FB1

1. Run a few cm^3 of **FB1** in the spectrometer and record the absorbance value, A_x.

2. Using the graph drawn earlier, a horizontal line is drawn from this value to intersect the calibration line. By drawing a vertical line from the intersection point, [Cu^{2+}] in **FB1** can be determined.

[3]

(d) Given that the absorbance for **FB 1** is 0.286, calculate the concentration of **FB 1**.

Applying Beer-Lambert's Law, $A = \varepsilon cl$

$0.286 = (2.81)(c)(1)$

c = **0.105 moldm^{-3}**

concentration of **FB 1** = ……………………………………[1]

[Total : 10]

Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	***reaction with***	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq),	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt., turning brown on contact with air insoluble in excess	green ppt., turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt., rapidly turning brown on contact with air insoluble in excess	off-white ppt., rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

ion	*reaction*
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, Cl^-(aq)	gives white ppt. with Ag^+(aq) (soluble in NH_3(aq))
bromide, Br^-(aq)	gives pale cream ppt. with Ag^+(aq) (partially soluble in NH_3(aq))
iodide, I^-(aq)	gives yellow ppt. with Ag^+(aq) (insoluble in NH_3(aq))
nitrate, NO_3^-(aq)	NH_3 liberated on heating with OH^-(aq) and Al foil
nitrite, NO_2^-(aq)	NH_3 liberated on heating with OH^-(aq) and Al foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, SO_4^{2-}(aq)	gives white ppt. with Ba^{2+}(aq) (insoluble in excess dilute strong acids)
sulfite, SO_3^{2-}(aq)	SO2 liberated with dilute acids; gives white ppt. with Ba^{2+}(aq) (soluble in dilute strong acids)

(c) Tests for gases

gas	*test and test result*
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	"pops" with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	*colour of element*	*colour in aqueous solution*	*colour in hexane*
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple