TEMASEK
JUNIOR COLLEGE

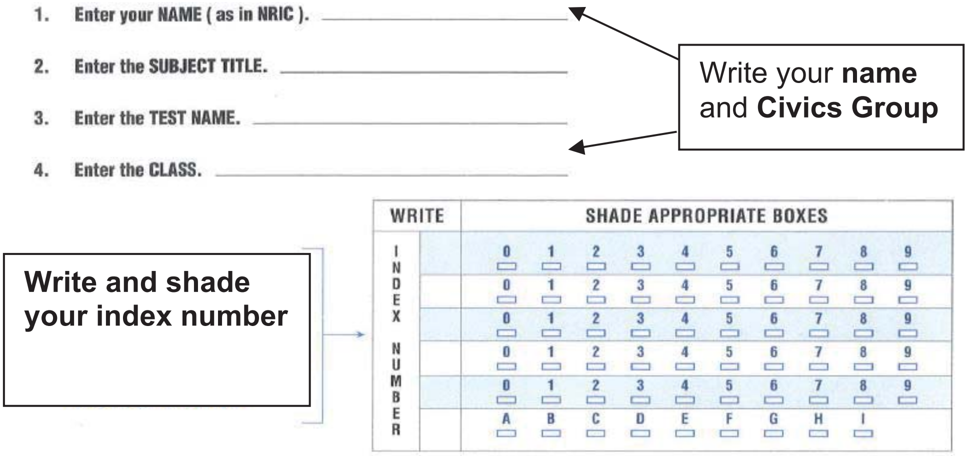
CHEMISTRY 9729/01

Paper 1 Multiple Choice **15th September 2017**
1 hour

Additional materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, glue or correction fluid.



1. Enter your NAME (as in NRIC). ______
2. Enter the SUBJECT TITLE. ______
3. Enter the TEST NAME. ______
4. Enter the CLASS. ______

WRITE	SHADE APPROPRIATE BOXES
INDEX NUMBER	0 1 2 3 4 5 6 7 8 9
	0 1 2 3 4 5 6 7 8 9
	0 1 2 3 4 5 6 7 8 9
	0 1 2 3 4 5 6 7 8 9
	0 1 2 3 4 5 6 7 8 9
	A B C D E F G H I

Write your **name** and **Civics Group**

Write and shade your index number

There are **thirty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.
Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this booklet.
The use of an approved scientific calculator is expected, where appropriate.

This document consists of **13** printed pages.

1 The reaction between aluminium powder and anhydrous barium nitrate is used as the propellant in some fireworks. Nitrogen gas is one of the products formed.

Which volume of nitrogen, measured under room conditions, is produced when 1 g of anhydrous barium nitrate reacts with an excess of aluminium?

A 86.9 cm^3 **B** 91.8 cm^3 **C** 174 cm^3 **D** 184 cm^3

2 Which statements about relative molecular mass are correct?

1 It is the mass of one mole of the molecule.

2 It is the ratio of the average mass of a molecule to the mass of a ^{12}C atom.

3 It is the sum of the relative atomic masses of all the atoms within the molecule.

A 1, 2 and 3

B 2 and 3 only

C 2 only

D 3 only

3 The Claus process recovers sulfur from the gaseous hydrogen sulfide found in raw natural gas and from the crude oil refinery by-product gases.

reaction I $2H_2S(g) + 3O_2(g) \rightarrow 2H_2O(l) + 2SO_2(g)$

reaction II $2H_2S(g) + SO_2(g) \rightarrow 2H_2O(l) + 3S(s)$

Which statement about the Claus process is correct?

A SO_2 is a reducing agent.

B SO_2 behaves as a catalyst.

C H_2S is oxidised in the reaction.

D Reaction II is a disproportionation reaction.

4 A stream of gaseous, doubly-charged calcium ions was passed between 2 oppositely charged plates. Analysis of the deflection shows that these ions deflected at an angle of 20.0°.

Under the same electric field, an unknown gaseous ion $\mathbf{X}^+$ is deflected at an angle of 5.08°.

What is the atomic number of **X**?

A 34 **B** 45 **C** 46 **D** 79

5 Which of the following species do not have all atoms that lie on the same plane?

A CH_2CH_2 **B** I_3^- **C** XeF_4 **D** $BeCl_4^{2-}$

6 In which pair of compounds does the first compound have higher boiling point than the second compound?

A HI, HF

B MgO, NaC*l*

C CH_4, SiH_4

D *trans*-$C_2H_2Cl_2$, *cis*-$C_2H_2Cl_2$

7 A sample of m g of an organic compound is vaporised in a gas syringe and occupies *V* cm^3 at *T* K and *p* atm.

What is the relative molecular mass of the compound?

A $$\frac{m \times 24000 \times T}{p \times V \times 293}$$

B $$\frac{m \times 24000 \times (T+293)}{p \times V \times 273}$$

C $$\frac{m \times 24000 \times 293 \times p}{V \times T}$$

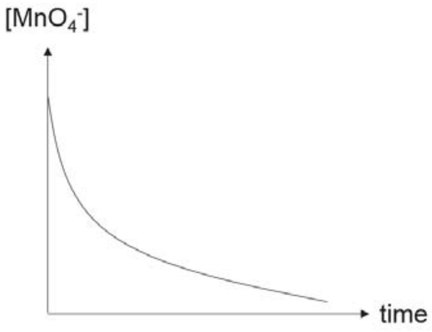
D $$\frac{m \times 24000 \times 293 \times p}{V \times (T+273)}$$

8 An autocatalytic reaction is one whereby the products catalyses the reaction. One such reaction is the reaction between ethanedioate and manganate(VII) anions.

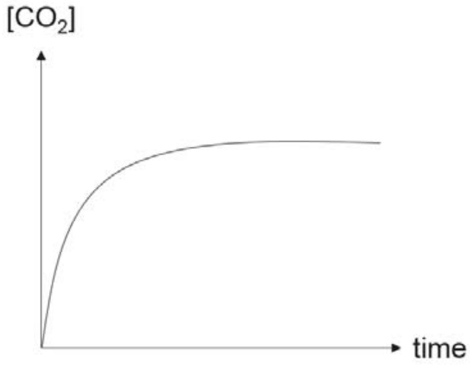
$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

Which of the following graphs would be obtained for an autocatalytic reaction?

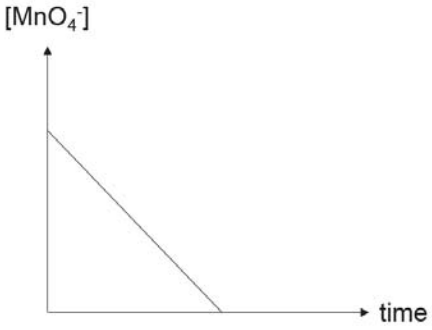
A



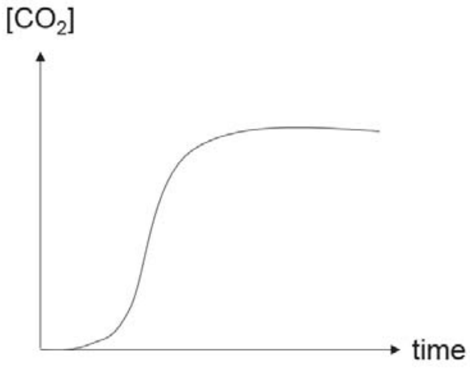
B



C



D



9 Molecular bromine, Br_2 reacts with methanoic acid, HCOOH slowly in an open beaker to produce aqueous hydrogen bromide and carbon dioxide gas.

$$Br_2(aq) + HCOOH(aq) \rightarrow 2HBr(aq) + CO_2(g)$$

Which of the following methods is **not** suitable for studying the kinetics of this reaction?

A Measuring the conductivity of the solution over time.

B Measuring the change in pressure of the reaction over time.

C Measuring the change in colour intensity of the mixture over time.

D Measuring the changes of pH of the solution over time.

10 When bromine vapourises at 58.8°C, 30.9 kJ mol^{-1} of heat was required.

What is the entropy change when 32 g of bromine is vapourised?

A -18.6 J K^{-1}

B +18.6 J K^{-1}

C -93.1 J K^{-1}

D +93.1 J K^{-1}

11 Compound **E** is a hydrocarbon. When 0.47 g of **E** was completely burnt in air, the heat produced raised the temperature of 200 g of water by 26.4 °C.

Given that the standard enthalpy change of combustion of **E** is –3290 kJ mol^{-1}, which of the following could be **E**?

1 $CH_2{=}CHCH_2CH_3$

2 $(CH_3)_2C{=}CHCH_3$

3 C_5H_{10}

A 1 only

B 3 only

C 1 and 2

D 2 and 3

12 Two equilibria are shown below.

reaction I $X_2(g) + \frac{1}{2}Y_2(g) \rightleftharpoons X_2Y(g)$

reaction II $2X_2Y(g) \rightleftharpoons 2X_2(g) + Y_2(g)$

The numerical value of K_c for reaction I is 2.
Under the same conditions, what is the numerical value of K_c for reaction II?

A $\frac{1}{2}$ **B** $\frac{1}{\sqrt{2}}$ **C** $\frac{1}{4}$ **D** -2

13 Consider the following equilibrium system:

$$\mathbf{P}(s) + \mathbf{Q}(g) \rightleftharpoons \mathbf{R}(g) + 3\mathbf{S}(s) \qquad \Delta H = +ve$$

0.500 mol each of **P** and **Q** were placed in a 1 dm^3 container. At equilibrium, 0.100 mol of **R** was formed.

Which of the following statement is **not** correct?

A The value of K_c is 0.25.

B K_p increases with increasing temperature.

C Increasing the pressure will not affect the equilibrium.

D Adding **P** causes the position of equilibrium to shift to the right.

14 Which of the following mixtures does not act as a buffer solution?

A 10 cm^3 of 1 mol dm^{-3} HCl and 5 cm^3 of 1 mol dm^{-3} $Mg(CH_3CH_2COO)_2$

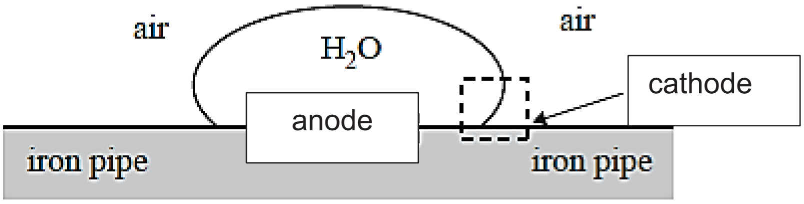
B 20 cm^3 of 1 mol dm^{-3} Na_2CO_3 and 20 cm^3 of 1 mol dm^{-3} $NaHCO_3$

C 20 cm^3 of 1 mol dm^{-3} HCl and 20 cm^3 of 2 mol dm^{-3} $CH_3CH_2NH_2$

D 10 cm^3 of 1 mol dm^{-3} NaOH and 20 cm^3 of 1 mol dm^{-3} NH_4Cl

15 Iron pipes are used to transport natural gas to cities. Corrosion occurs when water droplets sit on the outer surface of the iron pipes.

Miniature galvanic cells are created, with regions such as those shown below, that act as anodes and cathodes.



Which of the following is incorrect?

A The reaction at the cathode is $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$.

B The reaction at the anode is $Fe \rightarrow Fe^{2+} + 2e^-$.

C The corrosion of iron is inhibited at low pH.

D Corrosion can be prevented by connecting it to a magnesium bar buried in the ground.

16 Copper minerals often contain magnesium and silver as impurities. An impure copper rod is purified by electrolysis using a constant current. After 1 hour, the mass of one electrode decreased by 19.0 g while the mass of the other electrode increased by 17.8 g.

Which of the following statements is correct?

1 The decreased in mass is due to the oxidation of copper, magnesium and silver.

2 The increase in mass is due to copper being formed.

3 Doubling the mass of the impure copper rod under the same set of operating conditions double the mass of the copper deposited.

A 2 only

B 1 and 2

C 1 and 3

D 2 and 3

17 Consider the oxides of period 3 elements.

Which factor generally decreases across the period?

A Covalent character

B Melting point

C pH when mixed with water

D Solubility in aqueous NaOH

18 Which property of the Group 2 elements or their compounds increases with increasing atomic number?

A Reducing power of the metal

B Magnitude of the enthalpy change of hydration of the metal ion

C Acidity of an aqueous solution of the chloride

D Tendency to form complex ions

19 The table shows the results of experiments in which the halogens X_2, Y_2, and Z_2 were added to separate aqueous solutions containing X^-, Y^- and Z^- ions.

	X^-(aq)	Y^-(aq)	Z^-(aq)
X_2	No reaction	No reaction	No reaction
Y_2	X_2 formed	No reaction	Z_2 formed
Z_2	X_2 formed	No reaction	No reaction

Which set contains the ions X^-, Y^- and Z^- in order of their decreasing strength as a reducing agent?

	Strongest	$\longrightarrow$	Weakest
A	X^-	Y^-	Z^-
B	X^-	Z^-	Y^-
C	Y^-	Z^-	X^-
D	Z^-	X^-	Y^-

20 K_{stab}, is an equilibrium constant for the formation of a complex in solution.

Consider the following reaction

$$[M(H_2O)_6]^{m+}(aq) + nL^-(aq) \rightleftharpoons [M(H_2O)_{6-n}L_n]^{(m-n)+}(aq) + nH_2O(l)$$

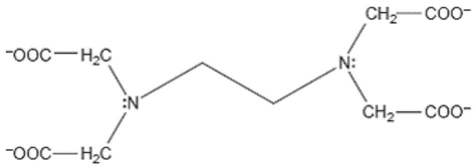
The K_{stab}, of the reaction, taking the concentration of water as being constant, is

$$K_{stab} = \frac{[[M(H_2O)_{6-n}L_n]^{(m-n)+}]}{[[M(H_2O)_6]^{m+}][L^-]^n}$$

The following table shows the colour and the value of K_{stab} of some iron complexes.

complex	**colour**	K_{stab}
$[Fe(SCN)(H_2O)_5]^{2+}$(aq)	deep red	1×10^2
$[FeF_6]^{3-}$(aq)	colourless	2×10^{15}
$[Fe(CN)_6]^{3-}$(aq)	orange-yellow	1×10^{31}
$[Fe(edta)]^{2-}$(aq)	colourless	2×10^{14}
$[Fe(edta)]^-$(aq)	yellow	1×10^{25}

The structure of $edta^{4-}$ is as follows:



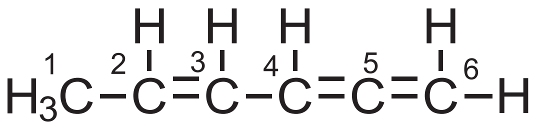
Which of the following statements is true?

A $[Fe(SCN)(H_2O)_5]^{2+}$(aq) absorbs red light.

B Addition of $edta^{4-}$ to a solution containing $[FeF_6]^{3-}$(aq) does not produce any colour change.

C Addition of KCN(aq) to a solution containing $[Fe(SCN)(H_2O)_5]^{2+}$(aq) produces an orange-yellow solution.

D Addition of Cl_2(aq) to a solution of Fe^{2+}(aq) produces a yellow solution which remains yellow when KF(aq) is added.

21 

$$\mathrm{H_3\overset{1}{C}-\overset{\overset{H}{|}}{\underset{2}{C}}=\overset{\overset{H}{|}}{\underset{3}{C}}-\overset{\overset{H}{|}}{\underset{4}{C}}=\underset{5}{C}=\overset{\overset{H}{|}}{\underset{6}{C}}-H}$$

Which bond is present in the compound above?

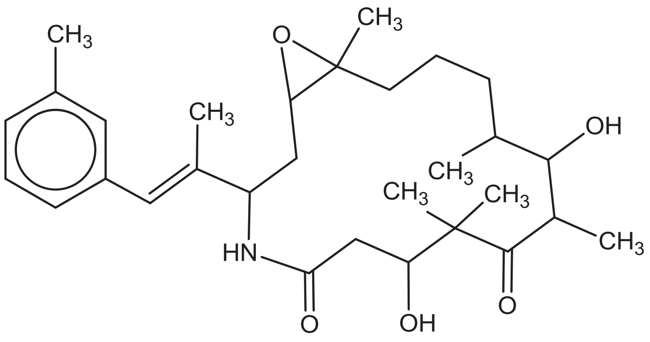
A a σ bond formed by sp^3 - sp^3 overlap between C3 and C4

B a σ bond formed by sp^2 - sp overlap between C4 and C5

C a σ bond formed by sp^2 - sp^2 overlap between C5 and C6

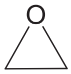
D a π bond formed by sp^2 – sp^2 overlap between C2 and C3

22 Compound **X** is an analogue of Ixabepilone which is an anticancer agent currently in clinical development.



compound **X**

Compound **X** was reacted with $NaBH_4$ in methanol.

In this reaction, the  ring remains unaltered.

What is the maximum number of stereoisomers in the product of this reaction?

A 2^7 **B** 2^8 **C** 2^9 **D** 2^{10}

23 Which of the following reactions will give an optically inactive mixture?

1 2–bromo-2-methylbutane heated with aqueous KOH

2 3-bromo-3-methylhexane heated with alcoholic NaOH

3 But–1–ene reacted with HBr dissolved in organic solvent

4 Butanone reacted with HCN, trace amount of NaOH

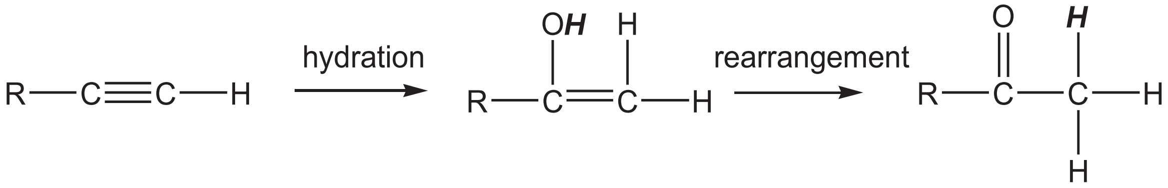
A 1 & 3

B 3 & 4

C 1, 2 & 3

D All of the above

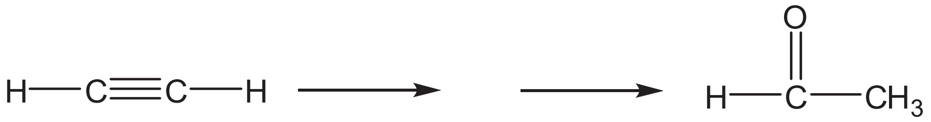
24 An alkyne ($C\equiv C$) undergoes hydration in a similar mechanism as an alkene. However, the formation of enol (C=C-OH) is unstable and would undergo rearrangement to form a carbonyl compound.



$$R-C\equiv C-H \xrightarrow{\text{hydration}} R-\overset{OH}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-H \xrightarrow{\text{rearrangement}} R-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-H$$

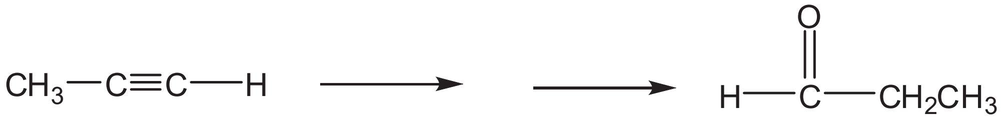
Which compound will **not** be formed when the following alkynes undergo hydration?

A



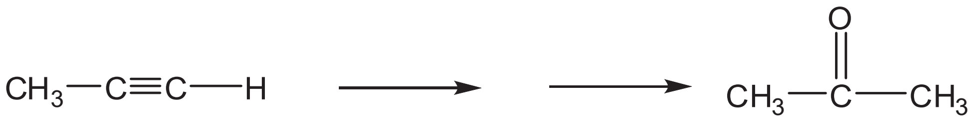
$$H-C\equiv C-H \longrightarrow \longrightarrow H-\overset{O}{\overset{\|}{C}}-CH_3$$

B



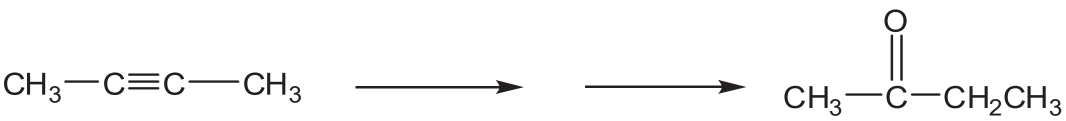
$$CH_3-C\equiv C-H \longrightarrow \longrightarrow H-\overset{O}{\overset{\|}{C}}-CH_2CH_3$$

C



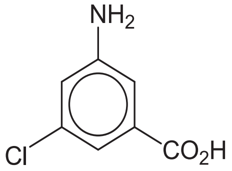
$$CH_3-C\equiv C-H \longrightarrow \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

D



$$CH_3-C\equiv C-CH_3 \longrightarrow \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_2CH_3$$

25 A student wishes to synthesise compound **Q** from benzene.



Q

Which of the following routes would give the maximum yield of **Q**?

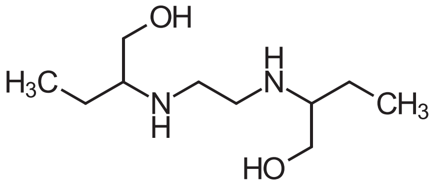
A Alkylation → nitration → chlorination → reduction → oxidation

B Nitration → alkylation → oxidation → chlorination → reduction

C Alkylation → oxidation → nitration → reduction → chlorination

D Chlorination → nitration → reduction → alkylation → oxidation

26 Ethambutol (EMB) is commonly used as first line drugs in tuberculosis treating regimes.



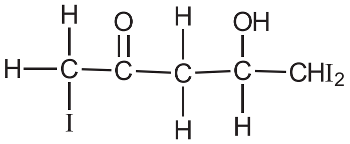
EMB

How many moles of hydrogen gas will be produced when one mole of EMB reacts with sodium?

A 1.0 **B** 2.0 **C** 3.0 **D** 4.0

27 Which of the following compound gives a yellow precipitate with alkaline aqueous iodine?

A

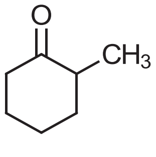


$CH_2I-CO-CH_2-CH(OH)-CHI_2$

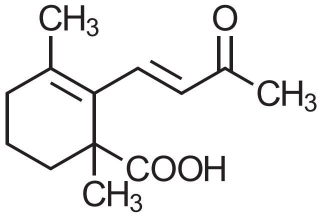
B CH_3OH

C CH_3CONH_2

D



28 Compound **Y** is a derivative of β-ionone, which is an important contributor of the aroma of roses.



Compound **Y**

What is the correct number of H atoms incorporated per molecule of Compound **Y** when Compound **Y** is reacted with each of the following reducing agents?

	Reducing agent	Number of hydrogen atoms incorporated per molecule of Compound **Y**
1	H_2 / Ni	6
2	LiA/H_4 in dry ether	8
3	$NaBH_4$ in ethanol	2

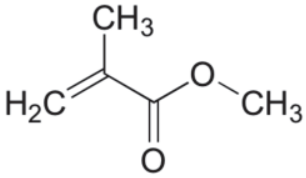
A 1 is correct only

B 1 and 3 is correct

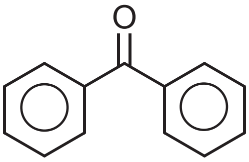
C 2 and 3 is correct

D 1,2,3 is correct

29 Methyl methacrylate and benzophenone are common ingredients found in nail polishes.



Methyl methacrylate



benzophenone

Which of the following reagents cannot be used to distinguish between these two compounds?

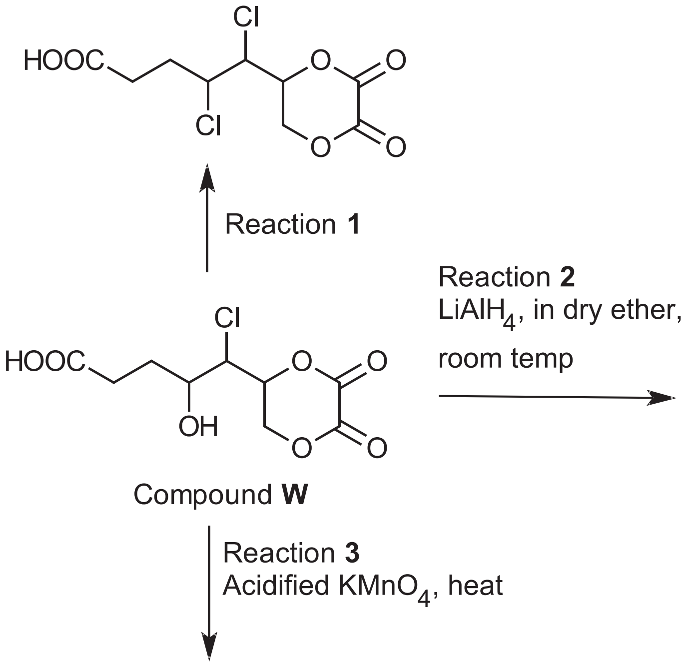
A Acidified $K_2Cr_2O_7$

B 2,4-dinitrophenylhydrazine

C Tollens' Reagent

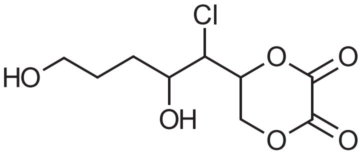
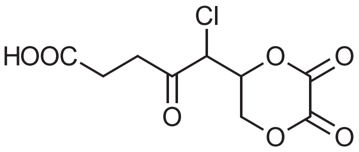
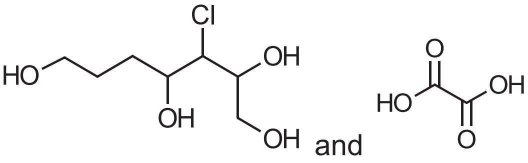
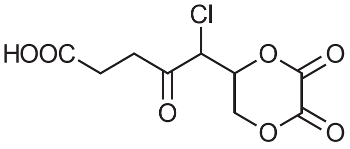
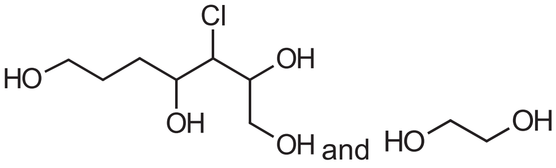
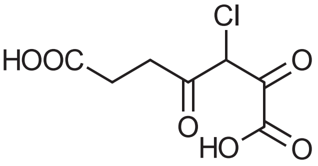
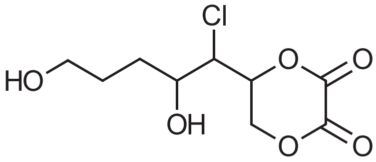
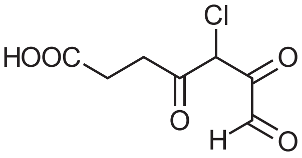
D Bromine water

30 The diagram below shows a reaction scheme of compound **W**.



Compound **W**

Which of the following shows the correct products of Reactions **2** and **3** and the type of reaction for Reaction **1**?

	Reaction 1	Product(s) of Reaction 2	Product of Reaction 3
A	Nucleophilic substitution		
B	Nucleophilic addition		
C	Nucleophilic substitution		
D	Nucleophilic addition		

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PRELIMINARY EXAMINATIONS
HIGHER 2

CANDIDATE NAME

CIVICS GROUP /

CENTER NUMBER S

INDEX NUMBER

CHEMISTRY
9729/02

Paper 2 Structured Questions **11 September 2017**

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Civics Group, centre number, index number and name on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

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 brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	/ 22
2	/ 15
3	/ 21
4	/ 8
5	/ 9
Paper 1	/ 30
Paper 3	/ 80
Total	

This document consists of 18 printed pages

Answer **all** the questions

1 Silver chloride is an important photosensitive inorganic material widely used in photographic applications. It is industrially produced by mixing solutions of silver nitrate and sodium chloride.

$$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s) \qquad \Delta H_{ppt}^{\ominus} = -65.7 \text{ kJ mol}^{-1},\ \Delta S_{ppt}^{\ominus} = -34.3 \text{ J mol}^{-1} \text{ K}^{-1}$$

(a) **(i)** Suggest whether a lower or higher temperature should be used to increase the yield of silver chloride. Explain your answer. [2]

(ii) Calculate $\Delta G^{\ominus}$ of the precipitation of $AgCl$. [1]

(iii) In view of your answer in **(a)(ii)**, comment on the solubility of silver chloride in water. [1]

(b) **(i)** Lattice energies are not measured directly. The value calculated using Hess' Law and the Born-Haber cycle is the experimental lattice energy. [3]

Using $\Delta H_{ppt}^{\ominus}$ of AgC*l*(s), the following data and relevant data from the *Data Booklet*, calculate the experimental lattice energy of AgC*l*(s).

standard enthalpy change of formation of $Ag^+(aq)$	+106 kJ mol^{-1}
standard enthalpy change of formation of $Cl^-(aq)$	–167 kJ mol^{-1}
standard enthalpy change of atomisation of Ag(s)	+285 kJ mol^{-1}
first electron affinity of chlorine	–349 kJ mol^{-1}

The theoretical value of lattice energies are calculated using the distances between the cations and anions in the crystal structure, and the charge on each ion.

The table below shows the numerical values of experimental and theoretical lattice energies for sodium chloride and silver fluoride.

compound	experimental value/ kJ mol^{-1}	theoretical value/ kJ mol^{-1}
NaC*l*	-771	-766
AgF	-967	-953

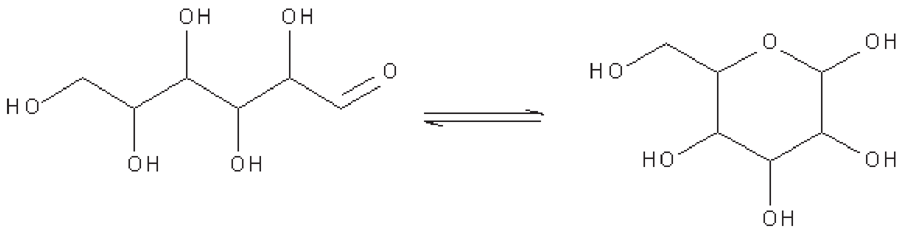
(ii) It can be seen that the experimental and theoretical values for sodium chloride and silver fluoride are quite similar. [1]

However, the theoretical value for the *silver chloride* is significantly less exothermic than the experimental value.

Suggest a reason for this.

(c) Explain, with the aid of equations, why silver chloride is soluble in aqueous ammonia while silver iodide does not dissolve in aqueous ammonia. [3]

(d) **(i)** Most of the energy our bodies need comes from carbohydrates and fat. Starch is broken down into glucose,$C_6H_{12}O_6$. Glucose exist mainly in cyclic forms with a small percentage in open chains. [1]



open-chain cyclic

State what you would observe when glucose is added to an alkaline solution of ammoniacal silver(I) nitrate.

Glucose is transported to the cells to react with oxygen via a series of steps to form carbon dioxide, water and energy.

(ii) Write a balanced equation for the reaction of glucose with oxygen. [1]

(iii) Using data from the Data Booklet, calculate the amount of energy released per mole of glucose using the **cyclic** structure. [2]

(iv) The literature value for the amount of energy released per mole of glucose is – 2800 kJ. [1]

Apart from bond energies are average values, suggest another reason for the difference between this value and that calculated in **(d)(iii)**.

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____

Like carbohydrates, fats are metabolised into carbon dioxide and water and when subjected to combustion in a bomb calorimeter. The reaction of tristearin, $C_{57}H_{110}O_6$, a typical fat is as follows:

$$C_{57}H_{110}O_6 + \frac{163}{2} O_2 \rightarrow 57\ CO_2 + 55\ H_2O \quad \Delta H^\ominus = -37760\ \text{kJ mol}^{-1}$$

The fuel value is the energy when one gram of the material undergoes combustion. The table below shows the fuel value of carbohydrates and protein and the food label of a cup noodle:

	Fuel value / kJ g^{-1}
Carbohydrate	17
Fat (Tristearin)	To be calculated
Protein	17

Nutrition Facts
Serving Size 1 container (70g)

Amount Per Serving	
Calories 310	Calories from Fat 100
	% Daily Value*
Total Fat 12g	**18%**
Saturated Fat	**25%**
Trans Fat	
Cholesterol 0mg	**0%**
Sodium 1010mg	**42%**
Total Carbohydrate 44g	**15%**
Dietary Fiber 4g	**16%**
Sugars 4g	
Protein 8g	

(v) Determine the fuel value of tristearin and hence deduce if tristearin or carbohydrate is a better source of energy. (M_r of tristearin = 890) [2]

(vi) During reading or watching television, the average adult uses about 7 kJ/min. How many minutes of such activity can be sustained by the energy supplied by a serving of cup noodle (considering only the total fat, total carbohydrate and total protein content)? [1]

(e) In the body, glucose is also converted to energy via alcoholic fermentation. This process has been used in making beer and the side products such as esters contribute greatly to the taste and aroma of the beer. [3]

Ethyl acetate can be formed as follows

$$CH_3CO_2H + CH_3CH_2OH \rightleftharpoons CH_3CO_2CH_2CH_3 + H_2O$$

1.51 mol of CH_3CO_2H and 1.66 mol of CH_3CH_2OH was allowed to reach equilibrium in a 100 cm^3 solution. 10 cm^3 of the equilibrium mixture was extracted and large amounts of cold water was added to quench the reaction. The mixture was then titrated with 22.40 cm^3 of 2 mol dm^{-3} NaOH.

Calculate the K_c for the formation of ethyl acetate.

[Total: 22]

2 **(a)** In 1887, the Swedish scientist Svante Arrhenius postulated that acids and bases dissociate in water to form hydrogen ions, H^+, and hydroxide ions, OH^-, respectively.

(i) Suggest a limitation of the Arrhenius concept of acids and bases. [1]

A theory proposed by Danish chemist J.N. Brønsted and British chemist T.M. Lowry overcame the shortcomings of the Arrhenius theory.

(ii) Using the Brønsted–Lowry model, nitric acid can be either a Brønsted–Lowry acid or base. Write equations to show how nitric acid *reacts* as a Brønsted–Lowry acid and a Brønsted–Lowry base respectively. [2]

As an acid

As a base

(b) The following table compares the K_a values of two three-carbon carboxylic acids.

Acid	Formula	K_{a1}	K_{a2}
Propanoic	$CH_3CH_2CO_2H$	1.35×10^{-5}	—
Malonic	$HO_2CCH_2CO_2H$	1.41×10^{-3}	2.00×10^{-6}

Suggest a reason why K_{a1} of malonic acid is higher than

(i) K_a of propanoic acid [1]

(ii) K_{a2} of malonic acid [1]

(iii) 25 cm^3 of 0.10 mol dm^{-3} of NaOH is gradually added to 10 cm^3 of 0.10 mol dm^{-3} malonic acid. Calculate the pH of the mixture when the following volumes of NaOH has been added. [3]

- 0 cm^3 [considering only K_{a1} of malonic acid]

- 5 cm^3

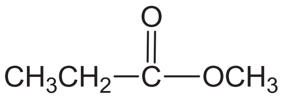
- 15 cm^3

- 25 cm^3

(iv) Using your answers in **(b)(iii)**, sketch the pH-volume added curve when 25 cm^3 of 0.10 mol dm^{-3} NaOH is gradually added to 10 cm^3 of 0.10 mol dm^{-3} malonic acid. [2]

(v) Suggest an indicator for the first equivalence point. [1]

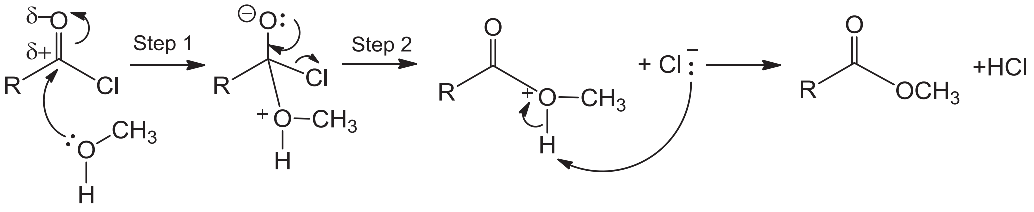
(c) Compound **A** can be directly synthesised from propanoic acid or propanoyl chloride via condensation.



$CH_3CH_2-C(=O)-OCH_3$

Compound **A**

The formation of compound **A** from propanoyl chloride occurs via the mechanism shown below.



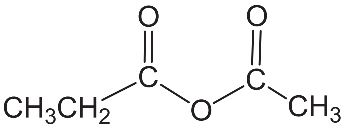
where R = CH_3CH_2—

(i) Name the reactions in step 1 and step 2. [2]

Step 1 ________________________________

Step 2 ________________________________

Compound **B** is a carboxylic acid anhydride that reacts similarly to an acyl chloride.



Compound **B**

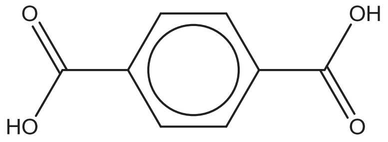
(ii) Compound **B** reacts with methanol that has been labelled with ^{18}O isotope to form compound **A**. [1]

Write an equation for the reaction showing clearly the location of the ^{18}O atom in the product. The formula of methanol can be written as $CH_3{}^{18}OH$.

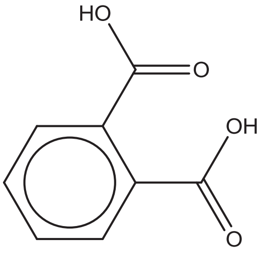
(iii) Draw the structure of another neutral product formed in the reaction. [1]

[Total: 15]

3 Terephthalic acid (TPA) and phthalic acid (PA) both have the molecular formula $C_6H_4(COOH)_2$. While TPA is used principally to make clothing and plastic bottles, PA has limited commercial application. The structures of TPA and PA are shown below.



TPA



PA

Some physical properties of TPA and PA are shown in the table below:

	TPA	PA
Appearance	White crystal	White crystal
Melting point	300 °C	207 °C
Boiling point	Decomposes	Decomposes

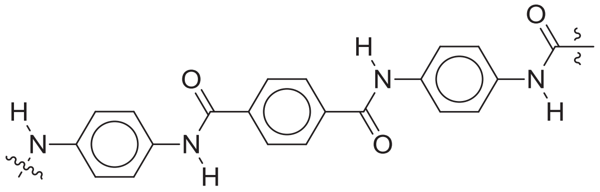
(a) Explain why TPA has a higher melting point than PA. [2]

(b) **(i)** TPA can be reduced to a diol for the synthesis of a renewable polymer.

Draw the structure of this diol and illustrate with a diagram, its interaction with water. [3]

(ii) Hence, explain why the diol in **(i)** is soluble in water. [1]

One common derivative of TPA is terephthaloyl chloride. Terephthaloyl chloride reacts with another monomer in a polymerisation reaction to form a synthetic fiber, commonly known as Kevlar®. A short chain of the Kevlar® polymer is shown below.



A strand of Kevlar® polymer

(c) **(i)** Name the type of reaction for this polymerisation reaction and suggest the structure of the other monomer to form the Kevlar® polymer. [2]

Type of reaction:

Structure of monomer:

(ii) In selecting a suitable material for the manufacture of bulletproof armour, it is necessary to ensure that the material does not shatter upon high impact force from a bullet.

With reference to the structures of gold and fluorite, CaF_2, explain why gold is more suitable for the lining of bulletproof armour. [2]

(d) **(i)** Define second ionisation energy of aluminium. [1]

(ii) Explain why the second ionisation energy of aluminium is higher than that of silicon. [1]

(e) Many chemical reactions such as the reaction between peroxodisulfate and iodide ions occur very slowly at room temperature.

$$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$$

One way to speed up rate of reaction is to use a homogeneous catalyst.

(i) Explain why the reaction between $S_2O_8^{2-}$ and I^- has a high activation energy. [1]

(ii) A solution of iron(II) ions can be used to catalyse the reaction between $S_2O_8^{2-}$ and I^-.

Using appropriate equations, outline the catalytic role of Fe^{2+} in the $S_2O_8^{2-}$ and I^- reaction. Hence, explain with the aid of a Boltzmann distribution curve, how Fe^{2+} speeds up the rate of the reaction. [5]

A kinetics study was conducted on the reaction of $S_2O_8^{2-}$ and I^- to determine the rate equation. Varying volumes of $S_2O_8^{2-}$ and I^- were added to a mixture containing sodium thiosulfate and starch indicator, followed by topping up with suitable volume of water.

As the reaction of $S_2O_8^{2-}$ and I^- proceeds, the iodine produced will be consumed by the thiosulfate. When all thiosulfate is reacted, the remaining iodine will react with the starch indicator, forming a blue-black complex. The rate of reaction is determined by the time taken for the blue-black colouration to appear.

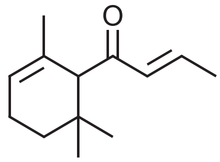
Experiment	Volume of KI / cm^3	Volume of $Na_2S_2O_8$ / cm^3	Volume of $Na_2S_2O_3$ / cm^3	Volume of water / cm^3	Time for blue-black colour / s
1	10	20	10	10	50
2	5	20	10	15	100
3	30	10	10	0	33
4	20	40	20	20	x

(iii) Determine the order of reaction with respect to iodide and peroxodisulfate. [2]

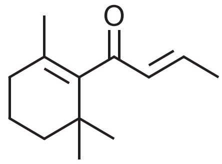
(iv) Hence, deduce the time taken for the blue-black colouration to appear for experiment 4. [1]

[Total: 21]

4 Rose ketones, damascenones, were discovered as active ingredients in the characteristic smell of Bulgarian rose oil. α-damascenone and β-damascenone were later discovered to give female perfumes such as *Dior's Poison* their unusual and distinctive fragrance.

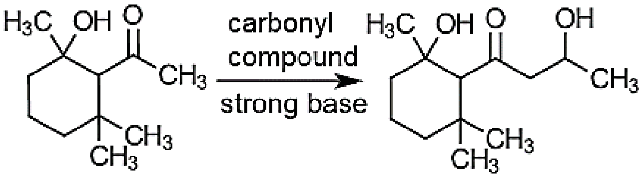


α-damascenone



β-damascenone

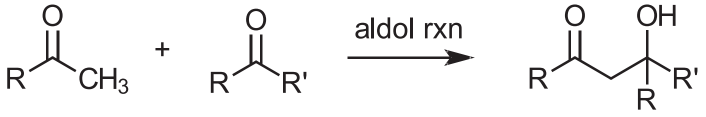
In the synthesis of damascenones in the laboratory, it was found that compound **A** is a possible precursor which could be synthesised from compound **B** via an aldol reaction.



Compound **B** Compound **A**

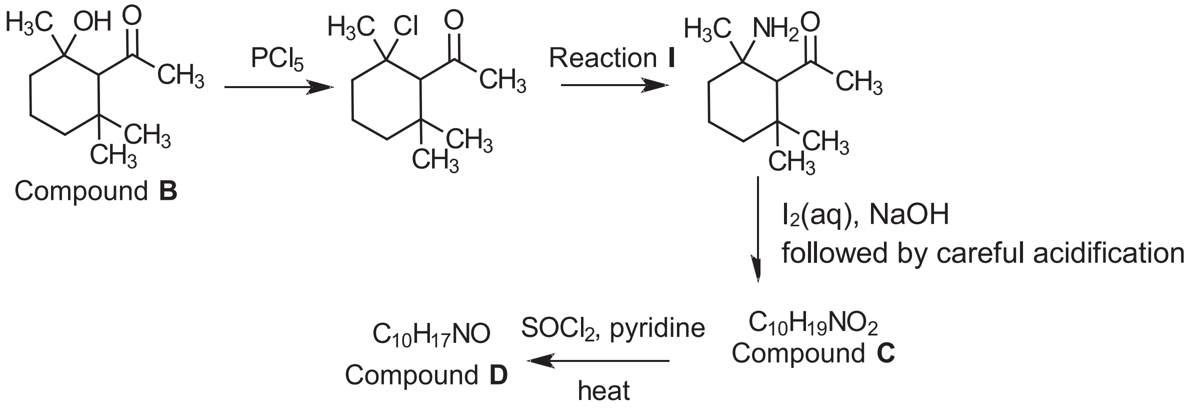
(a) State the reagent and condition required to convert compound **A** to either α-damascenone or β-damascenone. [1]

(b) With reference to an example of aldol reaction shown below, suggest an identity of the carbonyl compound reacting with compound **B** to form compound **A**.



[1]

Compound **B** can undergo a series of chemical reactions as shown in the flow chart below.

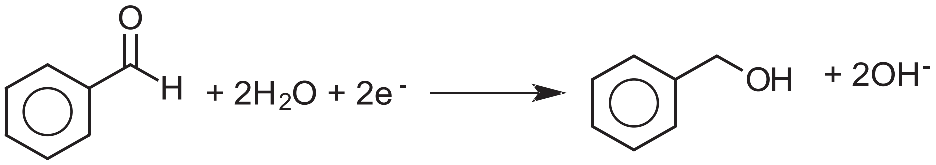


(c) State the reagents and conditions for Reaction **I**. [1]

(d) Draw the structural formulae of compounds **C** and **D**. [2]

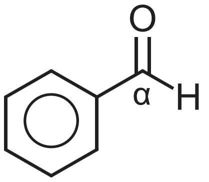
Benzaldehyde, in the presence of sodium hydroxide, undergoes the cannizzaro reaction to give benzoate ion and phenylmethanol.

(e) The ion-electron half-equation of benzaldehyde forming phenylmethanol is shown below.



Construct the ion-electron half equations for the reaction of benzaldehyde forming benzoate ion and hence, construct an overall balanced equation for the reaction. [2]

(f) Using changes in oxidation states of the carbon labelled α in benzaldehyde, state and explain the type of reaction that benzaldehyde undergoes in **(e)**. [1]



[Total: 8]

5 Organic compound **P** (M_r = 144) can be found in most leather products and is used as a mould inhibitor. **P** has the following composition by mass:

C: 50.04% H: 5.56% O: 44.40%

(a) (i) Determine the molecular formula of **P**. [2]

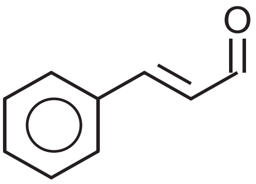
P exhibits stereoisomerism and it decolourises aqueous bromine. On heating one mole of **P** with dilute acid, two organic products **Q**, $C_4H_4O_4$ and **R** (M_r = 32) are obtained. The mole ratio of **Q** to **R** is 1:2. Vigorous effervescence was observed when **Q** reacted completely with sodium carbonate in equimolar proportions.

(ii) Draw the displayed formula of **Q**. [1]

(iii) State the functional groups present in **P**. [1]

(iv) Hence state the type of stereoisomerism exhibited by **P**. Draw and label the stereoisomers. [2]

(b) Another mould inhibitor, cinnamaldehyde has the structure shown below. [3]



Reaction of cinnamaldehyde with HBr produces a mixture that is optically inactive. Explain this observation.

[Total: 9]

TEMASEK
JUNIOR COLLEGE

CHEMISTRY **9729/03**
Paper 3 Free Response **13th September 2017**
2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Graph Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, index number, name and civics group on all the work you hand in.
Write in dark blue or black pen.
You may use a HB pencil for any diagrams or graphs.
Do not use staples, paper clips, 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 brackets [ ] at the end of each question or part question.

This document consists of **14** printed pages and **2** blank pages.

Section A

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

1 Calcium carbonate is found in rocks and is the main component of pearls and the shells of eggs, snails and many marine organisms. It is the active ingredient in agricultural lime and is also medicinally used as a calcium supplement or as an antacid.

(a) **(i)** Describe and explain the trend in thermal stability of the Group 2 carbonates. [3]

(ii) Determine the minimum temperature for the spontaneous decomposition of calcium carbonate, given that $\Delta H = +178.5 \text{ kJ mol}^{-1}$ and $\Delta S = +163.2 \text{ J K}^{-1} \text{ mol}^{-1}$. [2]

(b) Limestone is predominantly calcium carbonate, a slightly soluble salt with a K_{sp} value of 3.3×10^{-9}. This rocky material began accumulating in the Earth over 400 million years ago. The Howe Caverns in the USA is a relatively young limestone cave which began forming 800 000 years ago.

(i) Determine the solubility of calcium carbonate. [1]

The principal cave-forming process is explained below.

Gaseous CO_2 is in equilibrium with aqueous CO_2 in surface water.

$CO_2(g) \rightleftharpoons CO_2(aq)$ ----- **(1)**

As surface water trickles through cracks in the ground, it meets soil-trapped air which contains higher levels of CO_2 (P_{CO_2} = 100 Pa) and hence $[CO_2(aq)]$ increases.

When this CO_2-rich water contacts limestone, more $CaCO_3$ dissolves. As a result, more rock is carved out, more water flows in and over centuries a cave is formed.

$CaCO_3(s) + CO_2(aq) + H_2O(l) \rightleftharpoons Ca^{2+}(aq) + 2HCO_3^-(aq)$ ----- **(2)**

(ii) Show that the atmospheric partial pressure of CO_2, P_{CO_2}, is 40.5 Pa. You may assume air contains 0.04% by volume CO_2. [1]

(iii) State and explain whether CO_2 in the atmosphere or soil-trapped air is behaving less ideally. [2]

Stalactites and stalagmites are rock formations that hang from ceiling of caves and rise from the floor of caves, respectively. They are formed when surface water seeps through rock and drips from the ceiling of a cave.

(iv) With reference to equilibria **(1)** and **(2)**, explain the formation of stalactites and stalagmites in limestone caves. [3]

(v) Suggest a reason why some of these rock formations can appear reddish brown or bluish green. [1]

Lakes bounded by limestone-rich soil are less likely to be impacted by acid rain. Limestone dissolves sufficiently in lake water to form a buffer system capable of mitigating the effect of acid rain.

(vi) Suggest, with the aid of an equation, how the buffer system will maintain the pH of the lake water.

[1]

Acidification due to acid rain of lakes and rivers poses a serious environmental problem. The concentration of carbonate ions in these water is small due to the high acidity, hence affecting the survivability of some marine organisms.

(vii) Suggest a reason why the survivability of some marine organisms is affected.

[1]

(c) Emission from power stations using coal, which contains sulfur, as fuel has significant environmental consequences. One of the components is sulfur dioxide, which can be oxidised by atmospheric hydroxyl radical to sulfur trioxide.

(i) Write a balanced equation to explain how sulfur trioxide contribute to acid rain.

[1]

Current power plants are fitted with flue-gas desulfurization devices. These devices heat powdered limestone in air to remove sulfur dioxide from the gases produced during coal combustion. One of the products is calcium sulfate.

(ii) Write a balanced equation for the reaction that had taken place.

[1]

(d) Sulfur and aluminium can both react with chlorine.

Aluminium chloride is a white solid that sublimes while sulfur tetrachloride, SCl_4, is an unstable pale yellow solid. Both react with water but formed different products.

(i) Predict the shape of sulfur tetrachloride, using a diagram where appropriate. Suggest the bond angle(s) in the molecule.

[2]

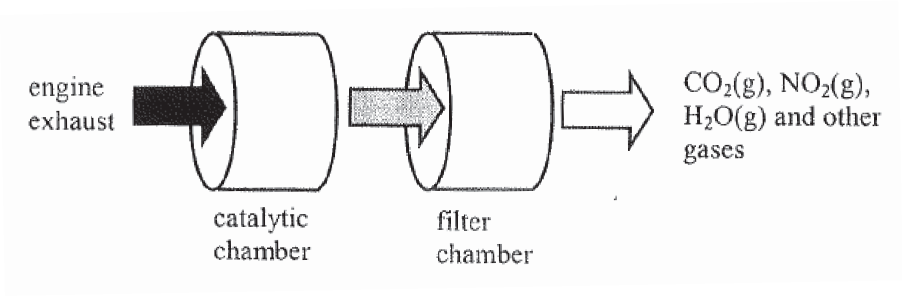
(ii) Describe and explain, with the aid of equations, the reaction of aluminium chloride with water. Suggest the pH of the resulting solution.

[3]

[Total: 22]

2 The exhaust of heavy-duty diesel engines contains a significant amount of particulate matter (PM) and harmful gases such as nitrogen oxides. A Continuous Regenerating Trap (CRT) is a device which is designed for use in exhaust systems of buses and lorries running on diesel to remove PM and some of the harmful gases. A second catalytic converter is usually installed to remove the oxides of nitrogen.

The diagram below shows how a CRT works:



(a) **(i)** Explain, with the aid of equations, why oxides of nitrogen are present in the engine exhaust.

[2]

(ii) State one harmful effect of nitrogen oxides on the environment.

[1]

(iii) State two harmful gases that are also present in the engine exhaust. Use chemical equations to show how these two gases can be removed in the catalytic chamber of a CRT.

[2]

A CRT is an automated, self-regenerating device which does not require cleaning of the filter. In a CRT, the carbon, which is the most abundant element in PM, is trapped onto the filter and is then removed by one of the harmful gases.

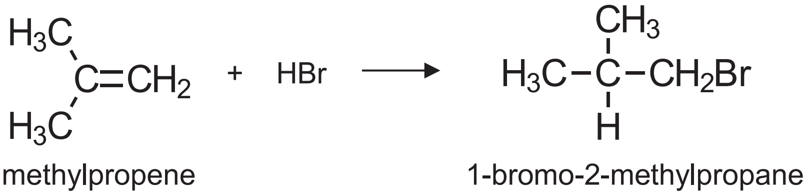
(iv) Explain, with the aid of an equation, how the carbon trapped on the filter of a CRT can be removed. Hence explain why the filter need not be cleaned.

[2]

(v) Suggest why buses and lorries equipped with CRT should not run on diesel with high sulfur content.

[1]

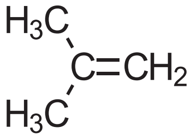
(b) In the reaction of HBr to alkenes such as methylpropene, scientists discovered that impurities such as peroxides, R-O-O-R, greatly increased the amount of anti-Markovnikov addition product as shown below.



The above reaction is explained by the 4 step free radical addition mechanism as described below.

Step 1: The reaction is initiated by the formation of RO• radicals.
Step 2: This is followed by the reaction of the RO• radical with HBr to give bromine radical.
Step 3: The bromine radical adds to the alkene via the cleaving of the pi bond.
Step 4: The radical obtained from Step 3 reacts with HBr to form the anti-Markovnikov product.

(i) Use the information given above to draw out the full mechanism for the reaction. You are advised to use structural formulae for all species, such as



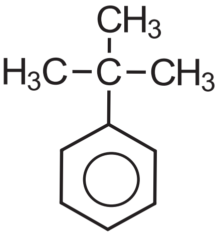
for methylpropene, so that it is clear which bonds are broken and which are formed. Indicate any unpaired electrons by a dot and use  to represent movement of an electron.

[4]

(ii) Unlike HBr, HC*l* does not undergo free radical addition to alkenes, even in the presence of peroxides. Explain this observation by quoting relevant values from the Data Booklet to substantiate your answer.

[2]

Tertiary butylbenzene is a colourless liquid widely used as a solvent for organic synthesis and also as a polymer linking agent.



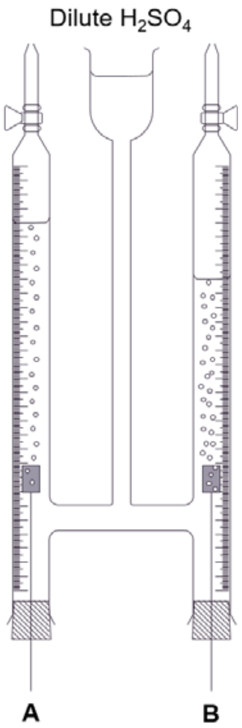
t-butylbenzene

(iii) Using 1-bromo-2-methylpropane as the starting material, suggest a 3-stage synthesis of t-butylbenzene. You should state the reagents and conditions needed for each step, and show clearly the structure of any intermediate compounds.

[3]

[Total: 17]

3 The following setup was carried out for the electrolysis of dilute sulfuric acid under room conditions, using platinum electrodes. A steady current of 2 A was applied for 1 minute through the circuit. The ratio of volume of gas produced at electrodes **A** and **B** is 1:2.



(a) **(i)** Write the half-equations for the reactions occurring at **A** and **B**. Label the polarity of each electrode clearly.

[2]

(ii) Calculate the volume of gas produced at **A** after 1 minute.

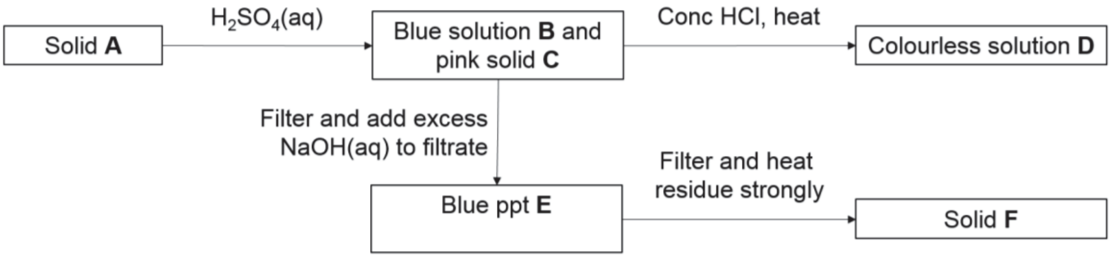
[1]

(iii) A student repeated the same experiment above, but using a copper electrode at **A** this time.

Suggest the volume of gas produced at **A** and explain your answer.

[2]

(b) Solid **A,** which is formed when a copper complex reacts with an aldehyde, is subjected to the following reactions.



Suggest the identities of **A** to **F**.

[6]

(c) Compounds **V** and **W** are gaseous hydrocarbons of empirical formulae CH_2 and CH_3 respectively. When 10 cm^3 of **V** and 10 cm^3 of **W** were completely burnt in 150 cm^3 of oxygen, the total gaseous volume decreased by 55 cm^3. After shaking the residual gases with aqueous sodium hydroxide, the total gaseous volume decreased by another 60 cm^3. When compound **V** is heated with acidified potassium manganate(VII), compound **X**, C_3H_6O, is formed.

(i) Suggest the molecular formula of **W**.

[1]

(ii) Suggest the structures of compounds **V** and **X**. Explain your answers.

[4]

(d) Compounds **Y** and **Z** are isomers of molecular formula $C_4H_7O_2Cl$. When **Y** and **Z** are added to separate portions of water, solutions are formed with pH values of 0.5 and 2.5 respectively. White precipitate is observed when aqueous silver nitrate is added to **Y**, but not **Z**. Both **Y** and **Z** gives yellow precipitate when warmed with aqueous sodium hydroxide and iodine.

Suggest the structures of compounds **Y** and **Z**. Explain your answers.

[5]

[Total: 21]

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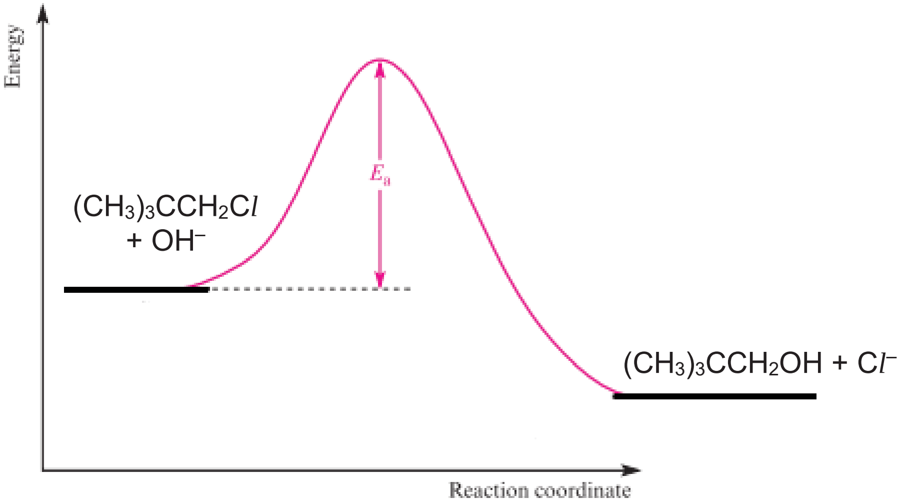
Section B

Answer **one** question from this section.

4 **(a)** Halogenoalkanes commonly undergo nucleophilic substitution reactions. On the basis of experimental observations developed over a 70-year period, two mechanisms for nucleophilic substitutions have been proposed.

In the kinetics study of the hydrolysis of 1-chloro-2,2-dimethylpropane, $(CH_3)_3CCH_2Cl$, the energy-profile diagram of the reaction was proposed below:



(i) With reference to the energy profile diagram, describe the mechanism of the reaction between 1-chloro-2,2-dimethylpropane and hydroxide ions. The mechanism should include curly arrows to show the movement of electrons and all charges.

[2]

(ii) A student decided to verify the mechanism deduced in **(a)(i)** for the hydrolysis reaction of 1-chloro-2,2-dimethylpropane.

The following results were obtained and you may consider the overall [NaOH(aq)] to remain virtually constant at 0.10 mol dm^{-3} throughout the experiment.

Time/ min	Experiment 1 $[(CH_3)_3CCH_2Cl]$/ mol dm^{-3}
0	0.0100
40	0.0070
80	0.0049
120	0.0034
160	0.0024
200	0.0017
240	0.0012

Using appropriate axes, plot a graph of $[(CH_3)_3CCH_2Cl]$ against time and use your graphs to deduce the order with respect to the concentration of the 1-chloro-2,2-dimethylpropane, showing your working clearly.

[4]

(iii) Given the general rate equation as

$$\text{Rate} = k' [(CH_3)_3CCH_2Cl]^x$$

Using your answer in **(a)(ii),** calculate the rate constant k', stating its units.

[2]

(iv) When the experiment was repeated at the same temperature, the concentration of NaOH was doubled and the concentration of 1-chloro-2,2-dimethylpropane was monitored against time. The same graph was obtained as Experiment 1.

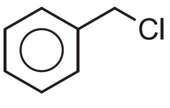
Deduce the order of reaction with respect to the concentration of hydroxide ion.

[1]

(v) Using your answers in **(a)(ii)** and **(a)(iv)**, explain if the student should agree with the proposed mechanism for the reaction in **(a)(i)**.

[1]

(b) (Chloromethyl)benzene is a primary alkyl halide.

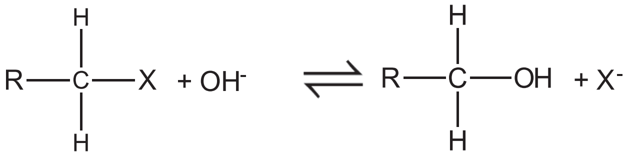


(Chloromethyl)benzene

Suggest a reason why (chloromethyl)benzene undergoes substitution via S_N1 mechanism.

[1]

(c) Different alkyl halides would have different reactivity towards nucleophilic substitution.



$$RCH_2X + OH^- \rightleftharpoons RCH_2OH + X^-$$

where X^- is a leaving group

The difference in reactivity is dependent on the stability of the leaving group. The more stable the halide ion, the better the leaving group. The pK_a values of HX is given below.

Halide (X)	pK_a (HX)
F	+3
Cl	–7
Br	–9
I	–10

(i) Suggest the relationship between pK_a of HX and the stability of the halide ion.

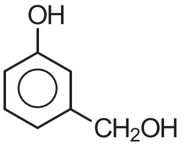
[1]

(ii) Iodomethane and chloromethane are separately reacted with hydroxide ions. Using your answer in **(c)(i)**, explain why iodomethane reacts at a faster rate.

[1]

(d) Chlorinated phenols have gained an increasing use as fungicides, herbicides, insecticides, and precursors in the synthesis of other pesticides since the early 1930s.

It can be easily synthesised from its precursor **A** using aqueous chlorine.

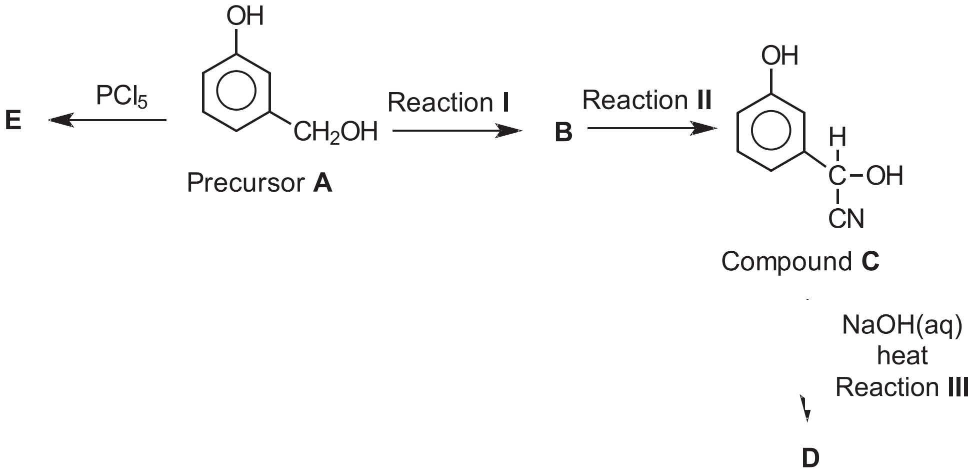


Precursor **A**

(i) Write a balanced equation for the reaction between precursor **A** and aqueous chlorine.

[1]

(ii) Precursor **A** undergoes a series of reactions shown in the reaction scheme below.



State the reagent and condition for Reaction **I** and **II**, and hence draw the structures of **B**, **D** and **E**.

[5]

(iii) Reaction **III** can be used as a distinguishing test between compound **C** and precursor **A**. State the observation for this distinguishing test.

[1]

[Total: 20]

5 **(a)** Describe and explain the relative thermal stabilities of the hydrogen halides down the group.

[2]

(b) Potassium chlorochromate (VI), $KCrClO_3$, was made using concentrated hydrochloric acid and potassium dichromate(VI).

$$K_2Cr_2O_7 + 2HCl \rightarrow 2KCrClO_3 + H_2O$$

Chlorine gas may be evolved as a side product. It was found that chlorine gas will not be produced if dilute hydrochloric acid was used instead.

Use data from the *Data Booklet* to explain why this is so.

[2]

(c) **(i)** Vanadium is a transition element that exhibits variable oxidation states.

Explain why vanadium has the ability to form compounds with different oxidation states.

[1]

(ii) A Latimer diagram shown below summarises the standard electrode potential data of vanadium complexes in acidic medium.

$$\begin{tikzcd}
VO_3^- \arrow[r, "+1.00\text{ V}"] \arrow[rr, bend left, "x"] & VO^{2+} \arrow[r, "+0.34\text{ V}"] & V^{3+}
\end{tikzcd}$$

x, the standard electrode potential of converting VO_3^- to V^{3+}, is **not** the summation of +1.00 V and +0.34 V. It can be calculated from $\Delta G^{\ominus}$.

Write a half-equation for the conversion of VO_3^- to V^{3+}.

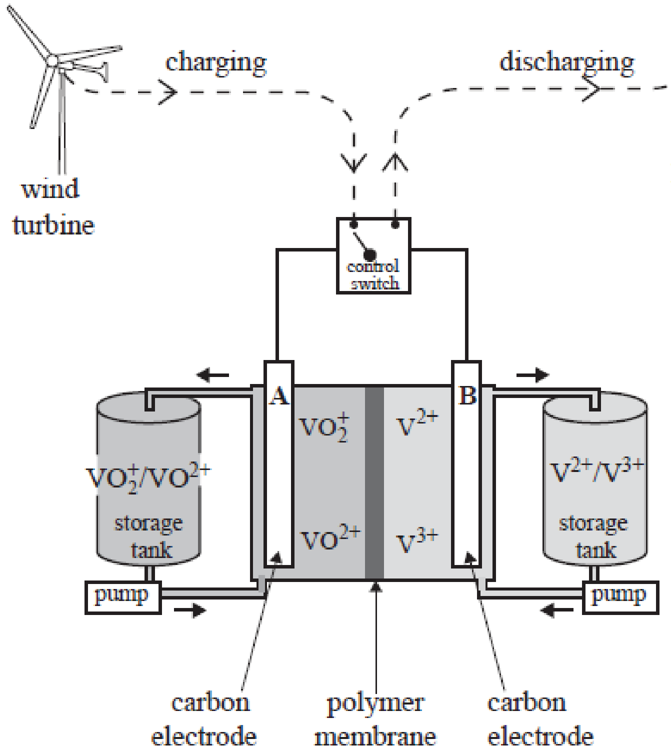
[1]

(iii) Calculate x, given that $\Delta G^{\ominus}$ for the conversion of VO_3^- to V^{3+} is -129000 J mol^{-1}.

[1]

(d) A vanadium redox battery is used to store electrical energy generated at a wind farm in Tasmania. The battery supplies electricity to the power grid as required through a control switch.

The diagram below shows the structure of a cell in a vanadium redox battery. The reactants are dissolved in an acidic solution, stored in large tanks and pumped through the cell. The cell is recharged using electricity generated by the wind turbines. A polymer membrane allows the movement of particular ions.



(i) State the polarity of electrode **A** when the cell is **discharging.** Explain your answer. [2]

(ii) Write an equation for the reaction that occurs when the cell is being **recharged**. [1]

(e) Nitrogen containing compounds such as ammonia and amines are common ligands found in transition metal complexes.

(i) Explain the relative basicities of ammonia, methylamine, dimethylamine and trimethylamine in the gaseous phase. [2]

(ii) Amides, such as ethanamide, are nitrogen containing compounds that do not exhibit basic properties like amines.

Explain why amides are neutral. [1]

(f) In 1893, Alfred Werner proposed the octahedral configuration of transition metal complexes. He was able to interpret isomeric properties using extensive studies on the octahedral cobalt complexes.

The following table gave information of two cobalt complexes **A** and **B** which are isomers of each other.

	Complex	Colour of solid	Does the complex have a dipole moment
A	$CoCl_2(NH_3)_4^+$	Violet	Yes
B	$CoCl_2(NH_3)_4^+$	Green	No

(i) Suggest structures for the cobalt complexes **A** and **B**.

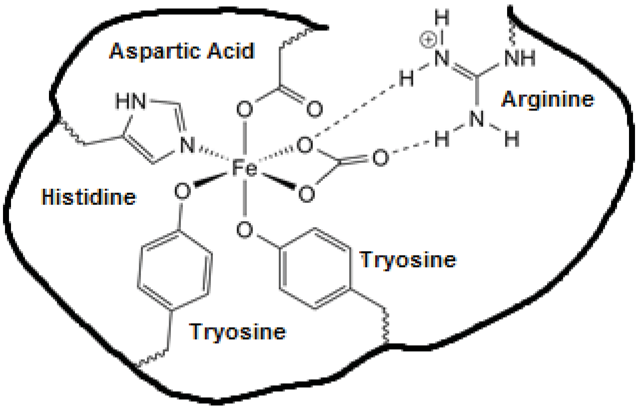
[2]

(ii) The crystal field theory can be used to explain colour of transition metal complexes.

Describe, using the shape and orientation of the d orbitals, the splitting of degenerate d orbitals into two energy levels in octahedral complexes.

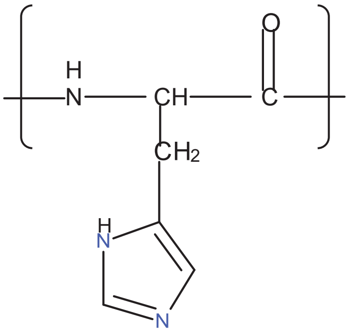
[3]

(g) R-groups on amino acids residues on protein act as ligands in biological systems. *Transferrin* is a protein in the blood that transports iron from food to the rest of the body.

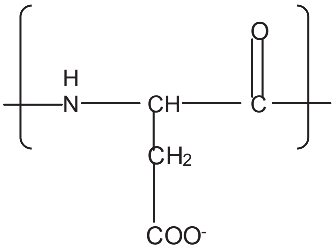


binding sites of *Transferrin*

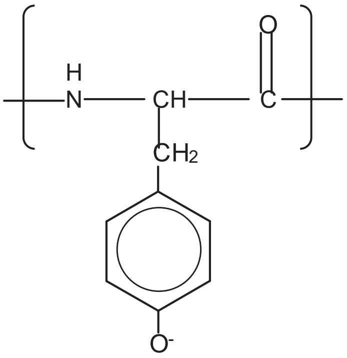
Transferrin binds to iron(III) via tryosine, histidine and aspartic acid residues as shown below.



Histidine residue
Side chain pK_a = 6.00



Aspartic acid residue
Side chain pK_a = 3.65



Tyrosine residue
Side chain pK_a = 10.07

The key to controlling uptake and release iron(III) is the change in pH. At pH 7.4, free transferrin binds to iron(III) to form the iron-transferrin complex. When the pH is lowered from 7.4 to 5.5, free iron(III) ions will be released from the protein binding site.

(i) Draw the structural formula of the tyrosine residue at its most stable state at pH 5.5.

[1]

(ii) Suggest how the decrease in pH releases iron(III) from the protein complex.

[1]

[Total: 20]

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TEMASEK
JUNIOR COLLEGE

2017 JC2 PRELIMINARY EXAMINATIONS
HIGHER 2

CANDIDATE NAME

CIVICS GROUP /

CENTRE NO. / INDEX NO. /

CHEMISTRY **9729/04**

Paper 4 Practical **28 August 2017**

2 hours 30 minutes

Candidates answer on the Question Paper.

READ THESE INSTRUCTIONS FIRST

Write your Civics Group and name on all the work you hand in.
Give details of the practical shift and laboratory where appropriate, in the boxes provided.
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.
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 14 and 15.
At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

Shift
Laboratory

For Examiner's Use	
1	/ 15
2	/ 24
3	/ 16
Total	/ 55

This document consists of 15 printed pages.

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

1 **Determination of change in oxidation number of a transition metal ion, M^{2+}**

You are to determine, by titration, the change in oxidation number of a transition metal ion, $\mathbf{M}^{2+}$, when reacted with acidified potassium manganate(VII).

FA 1 is 0.0200 mol dm^{-3} potassium manganate(VII), $KMnO_4$
FA 2 is 0.0470 mol dm^{-3} transition metal salt, $\mathbf{M}SO_4$
FA 3 is 1.00 mol dm^{-3} sulfuric acid, H_2SO_4

(a) Method

(i)
1. Fill the burette with **FA 1.**
2. Using a pipette, transfer 25.0 cm^3 of **FA 2** into the conical flask.
3. Using a measuring cylinder, transfer 25.0 cm^3 of **FA 3** to the same conical flask.
4. Carry out as many accurate titrations as necessary to obtain consistent results. Add **FA 1** until the contents of the conical flask turns a permanent pale pink colour.
5. Record below, in a table form, all of your burette readings and the volume of **FA 1** added in each accurate titration.

Results

[6]

(ii) From your titrations, obtain a suitable volume of **FA 1** to be used in your calculations. Show clearly how you obtained this volume.

25.0 cm^3 of **FA 2** required ______________ cm^3 of **FA 1** [1]

(b) **Calculations**

Show your working and appropriate significant figures in the final answer to **each** step of your calculations.

(i) Calculate the amount of potassium manganate(VII) present in the volume of **FA 1** calculated in **(a)(ii)**.

amount of $KMnO_4$ = ______________________ [1]

(ii) Determine the amount of **M**SO_4 in 25.0 cm^3 of **FA 2**.

amount of **M**SO_4 in 25.0 cm^3 = ______________________ [1]

(iii) Use your answer to **(b)(i)** and **(b)(ii)** to calculate the number of moles of **M**SO_4 that react with 1 mole of $KMnO_4$

amount of **M**SO_4 = ______________________ [1]

(iv) Two possible equations for the reaction of acidified $KMnO_4$ with **M**SO_4 are shown below:

Equation 1: $2KMnO_4 + 10\mathbf{M}SO_4 + 8H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5\mathbf{M}_2(SO_4)_3 + 8H_2O$
Equation 2: $2KMnO_4 + 5\mathbf{M}SO_4 + 8H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5\mathbf{M}(SO_4)_2 + 8H_2O$

State and explain which of the above two equations is consistent with your answer in **(b)(iii)**.

____

____

____

____ [1]

(v) Use your answer in **(b)(iv)** to state the oxidation number of the transition metal **M** in the product of the reaction.

[1]

(c) **(i)** A student suggested that using a burette to measure 25.0 cm^3 of **FA 2** would give a more accurate result than using a pipette. The percentage error of a 25.0 cm^3 pipette is 0.24%.

Calculate the percentage error of using a burette and deduce if the above claim by the student is correct.

[2]

(ii) Another student decided to use a 25.0 cm^3 pipette instead of a measuring cylinder to measure the volume of **FA 3** in **Step 3**.

State and explain whether this alteration will improve the accuracy of the experimental results.

[1]

[Total: 15]

2 Determination of the enthalpy change of neutralisation, ΔH_n

You are to determine the enthalpy change for the neutralisation reaction given below.

$$HA(aq) + NaOH(aq) \rightarrow NaA(aq) + H_2O(l)$$

FA 4 is 1.80 mol dm^{-3} HA
FA 5 is aqueous sodium hydroxide, NaOH

(a) **Method**

Read through the instructions carefully and prepare a table below for your results before starting any practical work.

1. Support the styrofoam cup in the 250 cm^3 beaker.
2. Rinse and fill the burette with **FA 4**.
3. Use the measuring cylinder to transfer 25 cm^3 of **FA 5** into the styrofoam cup.
4. Place the thermometer in the styrofoam cup and record the temperature of the solution. Tilt the cup if necessary to ensure the thermometer bulb is fully immersed.
5. Run 5.00 cm^3 of **FA 4** into the cup. Stir, and record the new temperature of the solution and the volume of **FA 4** added.
6. Run a second 5.00 cm^3 of **FA 4** into the cup. Stir and record the new temperature and the total volume of **FA 4** added.
7. Continue adding **FA 4** in 5.00 cm^3 portions. Stir and record each new temperature and total volume of **FA 4** until a total of 45.00 cm^3 has been added.

Results

[2]

(b) **(i)** Plot a graph of temperature (*y*-axis) against total volume of **FA 4** added (*x*-axis) on the grid below. The temperature axis should allow you to include a point at least 2 °C greater than the maximum temperature recorded.

Draw two best-fit lines connecting all the plotted points with

- an increasing trend
- a decreasing trend.

[3]

(ii) Extrapolate the two lines until they cross.
The intersection gives the maximum temperature, T_{max}, at equivalence point.
Use your graph to determine the following and show clearly on your graph how you obtained these answers.

- Maximum temperature at the equivalence point, $T_{max,}$
- Maximum temperature change at the equivalence point, $\Delta T_{max.}$
- Total volume of **FA 4** added at the equivalence point, $V_{eq.}$

T_{max} = ______________

ΔT_{max} = ______________

$V_{eq.}$ = ______________

[3]

(c) Explain the shapes of your graph lines before the equivalence point and after the equivalence point.

(i) Before the equivalence point

[2]

(ii) After equivalence point

[1]

(d) **Calculations**
Show your working and appropriate significant figures in the final answer to **each** step of your calculations.

(i) Calculate the number of moles of HA present in the volume of **FA 4** recorded in **(b)**.

Amount of HA = ______________________

(ii) Using your answers in **(b)**, calculate the heat energy produced when **FA 4** neutralised 25 cm^3 of sodium hydroxide.
(Assume that **4.2 J** of heat energy changes the temperature of 1.0 cm^3 of solution by 1 °C.)

Heat energy produced = ______________________

(iii) Calculate the enthalpy change of neutralisation, in kJ mol^{-1}, for the reaction below.

$$HA(aq) + NaOH(aq) \rightarrow NaA(aq) + H_2O(l)$$

Enthalpy change = ______________________

[6]

(e) Apart from using a thermometer calibrated to a greater level of precision, suggest one other improvement that could be made to the **method** carried out in **(a)**.

____

____

____

[1]

Planning

The enthalpy change of solution of solid NaOH can be calculated using the enthalpy change of neutralisation of aqueous NaOH with aqueous HC*l*, ΔH$_1$ and the enthalpy change of reaction of solid NaOH with aqueous HC*l*, ΔH$_2$.

(f) Given that the enthalpy change of neutralisation of aqueous NaOH with aqueous HC*l* is –57.0 kJ mol^{-1}, construct an energy cycle and show how it can be used to determine the enthalpy change of solution of NaOH.

[1]

(g) You are to plan an experiment to determine the enthalpy change of reaction of solid NaOH with aqueous HC*l*, ΔH$_2$. You are provided with the following reagents and the usual laboratory apparatus.

Reagents : 50 cm^3 1 mol dm^{-3} HC*l* solution
sodium hydroxide solid

Your plan should include

- calculation to show the appropriate mass of solid sodium hydroxide to be used.
- a sequence of numbered steps, the details of the experimental procedure including the measurements to be taken and tabulation of measurements and results.
- calculation of the enthalpy change of reaction of solid NaOH with HC*l* (aq).

(Assume that **4.2 J** of heat energy changes the temperature of 1.0 cm^3 of solution by 1 °C.)
[Ar Na: 23.0, H:1.0; O:16.0]

[5]

[Total:24]

3 You are provided with the solid **FA 6** and solution **FA 7**.

You are to perform the tests below and record your observations in the spaces provided. Your answers should include

- details of colour changes and precipitates formed;
- the names of any gases evolved **and** details of the test used to identify each one.

You should indicate clearly at what stage in a test a change occurs.

If it appears that no reaction has taken place this should be clearly recorded.

Rinse and reuse test-tubes where possible.

Marks are **not** given for chemical equations.

No additional or confirmatory tests for ions present should be attempted.

Candidates are reminded that definite deductions may be made from tests where there appears to be no reaction.

(a) **FA 6** contains one cation and one anion.

	Test	*Observation*
(i)	To half a spatula-full of **FA 6** in a test-tube add excess dilute sulfuric acid. Keep the solution for test **(iii)** and **(iv)**.	
(ii)	Place a spatula-full of **FA 6** in a test-tube and heat strongly.	
(iii)	To 1 cm depth of the solution from **(i)** in a test-tube, add a few drops of aqueous sodium hydroxide Then add excess aqueous sodium hydroxide.	

(iv)	To 1 cm depth of the solution from **(i)** in a test-tube, add a few drops of aqueous ammonia. Then add excess aqueous ammonia.	

The cation present in **FA 6** is ______________________

The anion present in **FA 6** is ______________________

FA 7 contains one cation and two anions.

	Test	*Observations*
(v)	To 1 cm depth of **FA 7** in a test-tube, add a few drops of aqueous sodium hydroxide. Then add excess aqueous sodium hydroxide. Warm the mixture.	
(vi)	To 1 cm depth of **FA 7** in a test-tube, add a few drops of aqueous ammonia Then add excess aqueous ammonia.	
(vii)	To 1 cm depth of **FA 7** in a test-tube, add aqueous silver nitrate, followed by aqueous ammonia.	
(viii)	To half a spatula-full of **FA 6** in a test-tube, add 3 cm depth of **FA 7**.	
	Then add 1 cm depth of aqueous sodium thiosulfate.	

One anion present in **FA 7** is ____________________

With reference to tests **(v)**, **(vi)** and **(viii)**, suggest the identity of the cation present in **FA 7**.

The second anion is suspected to be the sulfate ion.

(ix) Suggest a test to verify the presence of sulfate ion in **FA 7**. Carry out the test and record your results in the space below.

[11]

(b) **FA 8** is a solution that contains the Cr^{3+}, Mg^{2+} and Cl^{-} ions.

Plan a sequence of steps by which the three ions could be separated so that each ion is present in a separate precipitate. For each of the steps, you are to specifiy the location of the ions.

You may assume that the usual bench reagents and apparatus are available for use.

[5]

[Total: 16]

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

anion	*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)	SO_2 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) Colours 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

A: 7 B: 9
C: 8 D: 6

2017 JC2 Prelim H2 CHEMISTRY MCQ Worked Solution

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
B	D	C	A	D	B	A	D	B	B	D	C	D	A	C
16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
A	C	A	B	C	B	C	D	B	B	A	A	B	C	C

1 Answer: B

Since $Ba(NO_3)_2 \equiv N_2$, M_r of $Ba(NO_3)_2$ = 261.3
No. of moles of N_2 = No. of moles of $Ba(NO_3)_2$
$= \frac{1}{261.3} = 3.83 \times 10^{-3}$ mol
Volume of $N_2 = 3.83 \times 10^{-3} \times 24000 = 91.8$ cm^3

2 Answer: D

Definition – Relative molecular mass is the average mass of one molecule of an element or compound on a scale on which one atom of the ^{12}C isotope of carbon has a mass of 12 units.

Option **1** is incorrect. Relative molecular mass is a ratio.
Option **2** is incorrect. It should be the ratio of the average mass of a molecule to <u>1/12</u> the mass of a ^{12}C atom.
Option **3** is correct.

3 Answer: C

A is incorrect as SO_2 is an oxidizing agent and oxidises H_2S in reaction.
B is incorrect as SO_2 is the intermediate and is not regenerated in the reaction.
C is correct as H_2S (oxidation state of sulfur is -2) is oxidized to S (oxidation state 0).
D is incorrect as reaction II is a comproportionation reaction.

4 Answer: A

Angle of deflection $\theta \propto q/m$. So $\theta_{Ca}m_{Ca}/q_{Ca} = \theta_X m_X/q_X$
Mass of X = 20(40.1)/2 / 5.08 = 79 (Se)
Atomic number of **X** = 34

5 Answer: D

A: Ethene is a planar molecule which has all atoms on the plane

B: Tri-iodide has 3 lone pairs and 2 bond pairs, hence the ion is linear and all atoms lie on the same plane

C: XeF_4 has 4 bond pairs and 2 lone pairs, hence shape is square planar and all atoms lie on the same plane

D: $BeCl_4^{2-}$ has a total of 4 bond pairs (2 covalent bonds and 2 dative bonds) around Be atom. The shape is tetrahedral.

6 Answer: B

A: HF has hydrogen bonding between its molecules and hence require a larger energy to overcome compared to pd-pd between HI molecules.

B: MgO has a higher boiling point. MgO has a higher lattice energy than NaC*l* due to larger charge and smaller ionic radii of Mg^{2+} and O^{2-} ion compared to Na^+ and Cl^-.

C: SiH_4 has a higher boiling point as its M_r is larger than CH_4 and thus the id-id interactions are stronger and more extensive than CH_4.

D: *trans*-$C_2H_2Cl_2$ has a lower boiling point as it has no net dipole moment so the molecule is non-polar and only has id-id interactions between the molecules. *cis*-$C_2H_2Cl_2$ has pd-pd interaction between the molecules and more energy is needed to overcome the stronger pd-pd interactions.

7 Answer: A

PV = nRT
At r.t.p,
R = PV/nT = (1 atm x 24000 cm^3)/(1 mol x 293K)

M_r = mRT / PV = (m x T x 24000) / (p x V x 293)

8 Answer: D

A & C: Wrong as the concentration of manganate would decrease slowly at the start of the reaction before decreasing more quickly as more Mn^{2+} catalyst is generated.

B: Wrong as the volume of CO_2 cannot be increasing rapidly at the start of the reaction due to slow rate of reaction.

9 Answer: B

A: HBr will complete dissociate to give free H^+ ions and Br^- ions. Since there is a change in the number of ions as the reaction progresses, so conductivity of the solution increases over time and can be monitored using a conductivity meter.

B: Although CO_2 gas is produced, the reaction is done at atmospheric pressure and not in a closed system, so pressure of the system will not change over time.

C: Br_2(aq) is reddish-brown and all the products are colourless, so the intensity of the solution would decolourise over time.

D: As the reaction progresses, more HBr (a strong acid) is produced, so concentration of H^+ would increase over time and can be monitoring by quenching and titration against standard NaOH.

10 Answer: B

No. of moles of bromine = 32/(79.9 x 2) = 0.200 mol

When bromine vapourises, ΔG = 0 since it is an equilibrium reaction.

$\Delta H = T\Delta S$

$\Delta S = \Delta H/T = (30.9 \times 10^3 \times 0.2)/(58.8 + 273)$

$= 18.6$ J K^{-1}

11 Answer : D

Heat released when **E** is burnt = 200 x 4.18 x 26.4

= 22070 J

No. of moles of **E** = 22076 ÷ (3290 x 10^3)

= 0.00671 mol

M_r of **E** = 0.47/0.00671

= 70 (C_5H_{10})

Option 1 is incorrect as it is short of a CH_2. Options 2 & 3 are isomers of C_5H_{10}.

12 Answer : C

From reaction I,
$K_c = \frac{[X_2Y]}{[X_2][Y_2]^{\frac{1}{2}}} = 2$

For reaction II,
$K_c' = \frac{[X_2]^2[Y_2]}{[X_2Y]^2} = \frac{1}{K_c^{\ 2}} = \frac{1}{4}$

13 Answer : D

A:	P	+	Q	$\rightleftharpoons$	R	+	3S
Initial amt/mol	-		0.5		0		-
Change in amt/mol	-		-0.1		+0.1		-
Eqm amt/mol	-		0.4		0.1		-

$K_c = \frac{[R]}{[Q]} = \frac{0.1}{0.4} = 0.25.$

B: When temperature increases, the forward reaction is favoured by Le Chatelier’s Principle to absorb heat. At equilibrium, there will be greater no. of moles of R and lesser no. of moles of S. Thus, K_p increases.

C: There is equal number of moles of gas on both sides of the equation. Increasing pressure will not affect equilibrium.

D: **P** is a solid and is not included in the equilibrium constant. Changing its concentration will not affect the equilibrium.

14 Answer: A

Buffers are formed when roughly equal amount of the conjugate acid-base pair is present.

A is not a buffer as the resultant mixture only contains $CH_3CH_2CO_2H$ from the reaction between HCl and $CH_3CH_2CO_2^-$.
B is buffer as it contains HCO_3^- and CO_3^{2-}.
C is a buffer as $CH_3CH_2NH_2$ is in excess and $CH_3CH_2NH_3^+$ is formed from the reaction between $CH_3CH_2NH_2$.
D is a buffer as NH_4^+ is in excess and NH_3 is formed from the reaction between NH_4^+ and NaOH.

15 Answer: C

A & B: During rusting, oxygen is being reduced to hydroxide ions and iron being oxidised to iron(II) ions.

C: $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ +1.23 V

$E^{\ominus}_{cell}$ = +1.23 – (-0.44) = +1.67 V

Since $E^{\ominus}_{cell} > 0$, the reaction is spontaneous. Hence, it is not inhibited a low pH.

D: $E^{\ominus}_{Fe2+/Fe}$ = - 0.44 V $E^{\ominus}_{Mg2+/Mg}$ = -2.38 V

Since $E^{\ominus}_{Mg2+/Mg}$ is more negative than $E^{\ominus}_{Fe2+/Fe}$, magnesium will be oxidised instead of iron. Hence, magnesium acts as a sacrificial metal and prevents corrosion.

16 Answer: A

1: $E^{\ominus}_{Cu2+/Cu}$ = +0.34 V $E^{\ominus}_{Mg2+/Mg}$ = -2.38 V
$E^{\ominus}_{Ag+/Ag}$ = +0.80 V

At the anode, copper is preferentially oxidised over water to form copper(II) ions. As $E^{\theta}(Mg^{2+}/Mg)$ is more negative than $E^{\theta}(Cu^{2+}/Cu)$, magnesium will also be preferentially oxidised.

Ag will not be oxidised as $E^{\theta}(Ag^+/Ag)$ is more positive than $E^{\theta}(Cu^{2+}/Cu)$. Ag will be collected below the anode as ‘anode sludge’.

The decreased in mass at the anode is due to oxidation of copper and magnesium. Silver is not being oxidised but is collected as anode sludge.

2: At the cathode, only copper(II) ions were reduced to copper. As $E^{\theta}(Mg^{2+}/Mg)$ is more negative than $E^{\theta}(Cu^{2+}/Cu)$, magnesium will not be preferentially reduced together with copper.

3: The amount of copper deposited is dependent on the magnitude of the current and time in which the current was supplied. It is not affected by the size of the electrode.

17 Answer: C

A The covalent character increase across the period.
B The melting point increase then decrease across the period.
C The pH change from basic to neutral to acidic across the period.
D Only Al_2O_3, P_4O_{10} and SO_3 are soluble in NaOH, so there is actually no trend.

18 Answer: A

The charge density decreases with increasing atomic no., hence the tendency to form complexes, acidity of the aqueous chloride solution (because ease of hydrolysis decreases) and magnitude of hydration energy decreases

The reduction potential becomes more negative with increasing atomic no., hence the metal’s reducing power increases.

19 Answer: B

Since X^- can react with both Y_2 and Z_2 in the process forming X_2, it is the strongest reducing agent.

Since Y^- cannot react with both X_2 and Z_2 to form Y_2, it is the weakest reducing agent.

20 Answer: C

A is incorrect. For the complex to be red it must have absorbed blue light (complementary colour).

B is incorrect. $[FeF_6]^{3-}(aq)$ is colourless when $edta^{4-}$ is added. $[Fe(edta)]^{-}(aq)$ is formed and solution will turn yellow. *(Charge on edta is 4-).*

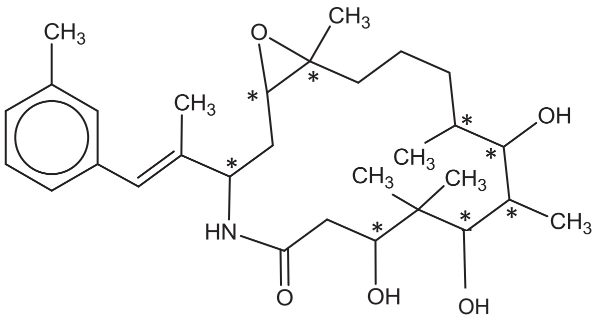
C is correct. $[Fe(CN)_6]^{3-}(aq)$ has a greater K_{stab} hence is more likely to be formed thus SCN^- and H_2O ligands will be displaced. The solution will turn orange yellow.

$E^{\theta}_{Cl_2/Cl^-} = +1.36V$
$E^{\theta}_{Fe^{3+}/Fe^{2+}} = +0.77V$
D is incorrect. Cl_2 will oxidise Fe^{2+} to Fe^{3+} turning the solution yellow. Upon addition of F^- the solution will turn colourless as $[FeF_6]^{3-}(aq)$ has a greater K_{stab}.

21 Answer: B

A: a σ bond formed by $sp^2 – sp^2$ overlap between C3 and C4
C: a σ bond formed by $sp – sp^2$ overlap between C5 and C6
D: a π bond formed by p – p overlap between C2 and C3

22 Answer: C



Since there are 8 chiral centers and 1 C=C that can exhibit cis-trans isomerism, no. of stereoisomers = 2^9.

23 Answer: D

1. Tertiary halogenoalkane undergoes S_N1 reaction with aqueous KOH. Formation of carbocation that is planar about the positively charged carbon. The nucleophile OH^- can attack the positively charged C from top and bottom with equal probability resulting in a racemic mixture that is optically not active.
2. Elimination of HBr results in alkenes that are optically not active.
3.Electrophilic addition of HBr to alkene results in formation of intermediate carbocation that will give racemic products.
4.The nucleophile CN^- attacks the planar carbonyl carbon in butanone from top and bottom with equal probability forming a racemic mixture.

24 Answer: B

$CH_3–C{\equiv}C–H$ will give CH_3COCH_3

25 Answer: B

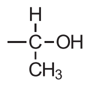
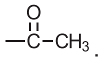
A: Alkylation followed by nitration will place the alkyl and nitro gps at 1,2 or 1,4 positions. Thus the $–CO_2H$ gp and $–NH_2$ will not be at 1,3 position.
C: The last chlorination step results in –Cl at position 2 or 4 from $–NH_2$ gp.
D: Chlorination followed by nitration results in nitro gp placed at positions 2 or 4 from –Cl gp.

26 Answer: A

2 –OH groups in 1 mol of EMB react with Na to give 1 mol of H_2 gas.

$2\ R\text{-}OH + 2Na \rightarrow 2\ RO^-Na^+ + H_2$

27 Answer: A

Positive test with tri-iodomethane test means  $–\overset{\displaystyle H}{\underset{\displaystyle CH_3}{C}}–OH$ or  $–\overset{\displaystyle O}{\overset{\|}{C}}–CH_3$.

The H-atoms in the $-CH_3$ group in the methyl alcohol and methyl ketone group when replaced by iodine atoms, are still tri-iodomethane test positive.

28 Answer: B

Compound **Y** has 2 C=C, 1 COOH and 1 ketone functional group. Every functional group in Compound **Y** that gets reduced would have 2 H atoms incorporated per molecule of Compound **Y**.

	Reducing agent	No. of hydrogen atoms incorporated per molecule of Compound **Y**	Functional group reduced
1	H_2 / Ni	6	2C=C + 1 ketone
2	LiA/H_4 in dry ether	**<u>4</u>**	1 ketone and 1 – COOH group
3	$NaBH_4$ in ethanol	2	1 ketone group

29 Answer: C

Option A: Orange dichromate turns green for methyl methacrylate as ester bond cleave and the primary alcohol part of the ester gets oxidised. Orange dichromate remains orange for benzophenone.

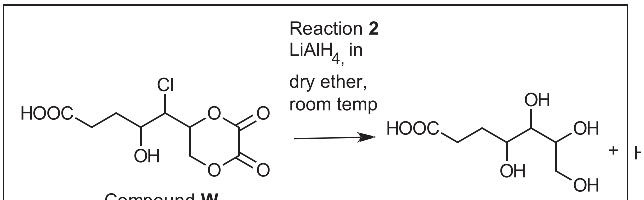
Option B: orange ppt formed for benzophenone and no orange ppt formed for methyl methacrylate.

Option C: Tollen's reagent is negative for both compounds as both compounds do not have an aldehyde functional group.

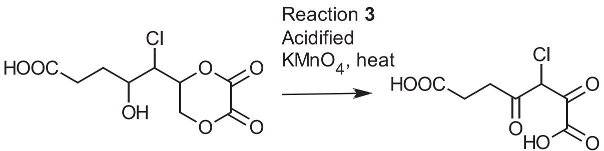
Option D: reddish-brown bromine water decolourise for methyl methacrylate due to C=C. Reddish brown bromine remain for benzophenone.

30 Answer: C

Reaction 1 – conversion of alcohol to halogenoalkane: nucleophilic substitution



Compound **W**



Compound **W**

TEMASEK
JUNIOR COLLEGE

PRELIMINARY EXAMINATIONS
HIGHER 2

CANDIDATE NAME										
CIVICS GROUP			/							
CENTER NUMBER	S					INDEX NUMBER				

CHEMISTRY
9729/02

Paper 2 Structured Questions **11 September 2017**

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Civics Group, centre number, index number and name on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

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 brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	/ 22
2	/ 15
3	/ 21
4	/ 8
5	/ 9
Paper 1	/ 30
Paper 3	/ 80
Total	

This document consists of 18 printed pages

Answer **all** the questions

1 Silver chloride is an important photosensitive inorganic material widely used in photographic applications. It is industrially produced by mixing solutions of silver nitrate and sodium chloride.

$$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s) \qquad \Delta H_{ppt}^{\ominus} = -65.7\ kJ\ mol^{-1},\ \Delta S_{ppt}^{\ominus} = -34.3\ J\ mol^{-1}\ K^{-1}$$

(a) **(i)** Suggest whether a lower or higher temperature should be used to increase the yield of silver chloride. Explain your answer. [2]

- **A lower temperature should be used.**
- **By Le Chatelier's Principle, the system will favour the forward exothermic reaction to counteract the lowered temperature. Hence, the position of equilibrium shifts to the right increasing the yield of silver chloride.**

(ii) Calculate $\Delta G^{\ominus}$ of the precipitation of $AgCl$. [1]

- $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$

  $= -65.7 - (298)(-34.3/1000)$

  $= -55.5\ kJ\ mol^{-1}$

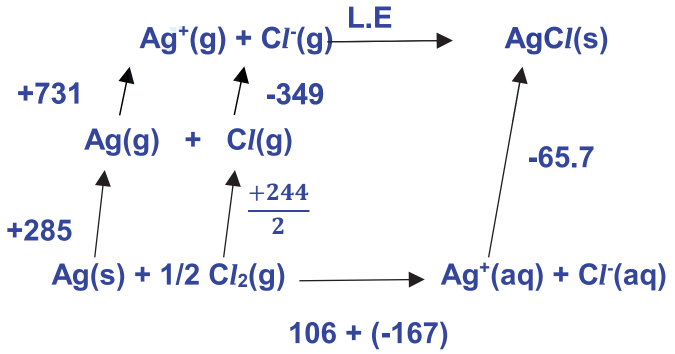
(iii) In view of your answer in **(a)(ii)**, comment on the solubility of silver chloride in water. [1]

- **Since $\Delta G^{\ominus}$ is negative, precipitation is spontaneous. Hence, AgCl is insoluble/sparingly soluble in water.**

(b) **(i)** Lattice energies are not measured directly. The value calculated using Hess' Law and the Born-Haber cycle is the experimental lattice energy. [3]

Using $\Delta H_{ppt}^{\ominus}$ of $AgCl(s)$, the following data and relevant data from the *Data Booklet*, calculate the experimental lattice energy of $AgCl(s)$.

standard enthalpy change of formation of $Ag^+(aq)$	+106 kJ mol^{-1}
standard enthalpy change of formation of $Cl^-(aq)$	–167 kJ mol^{-1}
standard enthalpy change of atomisation of Ag(s)	+285 kJ mol^{-1}
first electron affinity of chlorine	–349 kJ mol^{-1}



- **cycle with state symbols**

By Hess' Law,
• +285 + 731 + 122 – 349 + L.E = +106 – 167 – 65.7
L.E = • - 916 kJ mol^{-1}

The theoretical value of lattice energies are calculated using the distances between the cations and anions in the crystal structure, and the charge on each ion.

The table below shows the numerical values of experimental and theoretical lattice energies for sodium chloride and silver fluoride.

compound	experimental value/ kJ mol^{-1}	theoretical value/ kJ mol^{-1}
NaC*l*	-771	-766
AgF	-967	-953

(ii) It can be seen that the experimental and theoretical values for sodium chloride and silver fluoride are quite similar. [1]

However, the theoretical value for the *silver chloride* is significantly less exothermic than the experimental value.

Suggest a reason for this.

• The theoretical value of lattice energy is based on the assumption that AgC*l* is ionic. However, there is some covalent character in AgC*l* due to the large size of C*l*$^-$ ion which can be polarised by Ag$^+$.

(c) Explain, with the aid of equations, why silver chloride is soluble in aqueous ammonia while silver iodide does not dissolve in aqueous ammonia. [3]

•

$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq)$ --------------------(1)

•NH_3 forms a stable soluble complex $[Ag(NH_3)_2]^+$ with the free Ag^+ ion causing $[Ag^+(aq)]$ to decrease.

•

$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$ ----------------(2)

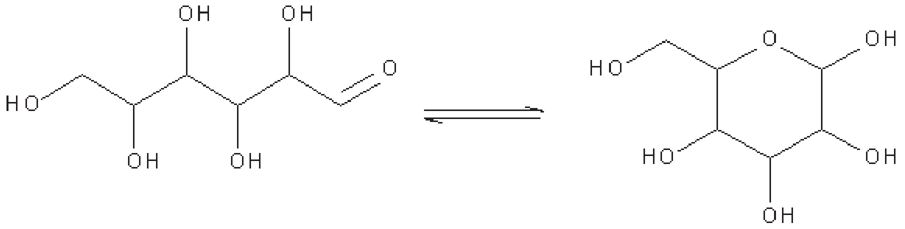
By Le Chatelier's Principle, the position of equilibrium in (2) shifts left to counteract the decrease in the $[Ag^+(aq)]$.

•

The ionic product $[Ag^+][Cl^-]$ decreases to a value lower than the K_{sp} of AgC*l* and AgC*l* dissolves.

The K_{sp} of AgI is much lower than K_{sp} of AgCl. The ionic product is still easily exceeded even with the decrease in $[Ag^+(aq)]$ and hence it does not dissolve.

(d) **(i)** Most of the energy our bodies need comes from carbohydrates and fat. Starch is broken down into glucose,$C_6H_{12}O_6$. Glucose exist mainly in cyclic forms with a small percentage in open chains. [1]



open-chain cyclic

State what you would observe when glucose is added to an alkaline solution of ammoniacal silver(I) nitrate.

• Silver mirror is observed.

Glucose is transported to the cells to react with oxygen via a series of steps to form carbon dioxide, water and energy.

(ii) Write a balanced equation for the reaction of glucose with oxygen. [1]

• $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$

(iii) Using data from the Data Booklet, calculate the amount of energy released per mole of glucose using the **cyclic** structure. [2]

Using the cyclic structure of glucose,

Bond-breaking	**Bond-Forming**
5 x C – C	**12 x C = O**
5 x O – H	**12 x O – H**
7 x C – H	
7 x C – O	
6 x O = O	

• Energy released
= +(5 x 350 + 5 x 460 + 7 x 410 + 7 x 360 + 6 x 496) – (12 x 805 + 12 x 460)
= • - 2760 kJ mol^{-1}

(iv) The literature value for the amount of energy released per mole of glucose is – 2800 kJ. [1]

Apart from bond energies are average values, suggest another reason for the difference between this value and that calculated in **(d)(iii)**.

• The ΔH calculated using bond energies applies for the reactants and products in the gaseous phase but the reaction involves liquid H_2O rather than gaseous H_2O.

Like carbohydrates, fats are metabolised into carbon dioxide and water and when subjected to combustion in a bomb calorimeter. The reaction of tristearin, $C_{57}H_{110}O_6$, a typical fat is as follows:

$$C_{57}H_{110}O_6 + \frac{163}{2} O_2 \rightarrow 57\ CO_2 + 55\ H_2O \quad \Delta H^{\ominus} = -37760 \text{ kJ mol}^{-1}$$

The fuel value is the energy when one gram of the material undergoes combustion. The table below shows the fuel value of carbohydrates and protein and the food label of a cup noodle:

	Fuel value / kJ g^{-1}
Carbohydrate	17
Fat (Tristearin)	To be calculated
Protein	17

Nutrition Facts

Serving Size 1 container (70g)

Amount Per Serving

Calories 310	Calories from Fat 100
	% Daily Value*
Total Fat 12g	**18%**
Saturated Fat	**25%**
Trans Fat	
Cholesterol 0mg	**0%**
Sodium 1010mg	**42%**
Total Carbohydrate 44g	**15%**
Dietary Fiber 4g	**16%**
Sugars 4g	
Protein 8g	

(v) Determine the fuel value of tristearin and hence deduce if tristearin or carbohydrate is a better source of energy. (M_r of tristearin = 890) [2]

No. of moles of tristearin in 1 g = 1/890 = 1.12×10^{-3} mol
• Fuel value of tristearin = $1.12 \times 10^{-3} \times 37760$ = 42.4 kJ/g

OR

Since mass of 1 mol tristearin is 890 g
Fuel value = -37760/890 = 42.4 kJ/g

• Since more energy is produced per gram, tristearin is a better source of energy than carbohydrate.

(vi) During reading or watching television, the average adult uses about 7 kJ/min. How many minutes of such activity can be sustained by the energy supplied by a serving of cup noodle (considering only the total fat, total carbohydrate and total protein content)? [1]

Total energy provided by cup noodle = 12 x 42.4 + 44 x 17 + 8 x 17
= 1390 kJ

• No. of minutes that can be sustained by energy = 1390/7
= 199 min

[Turn over

(e) In the body, glucose is also converted to energy via alcoholic fermentation. This process has been used in making beer and the side products such as esters contribute greatly to the taste and aroma of the beer. [3]

Ethyl acetate can be formed as follows

$$CH_3CO_2H + CH_3CH_2OH \rightleftharpoons CH_3CO_2CH_2CH_3 + H_2O$$

1.51 mol of CH_3CO_2H and 1.66 mol of CH_3CH_2OH was allowed to reach equilibrium in a 100 cm^3 solution. 10 cm^3 of the equilibrium mixture was extracted and large amounts of cold water was added to quench the reaction. The mixture was then titrated with 22.40 cm^3 of 2 mol dm^{-3} NaOH.

Calculate the K_c for the formation of ethyl acetate.

$NaOH \equiv CH_3CO_2H$

No. of moles of CH_3CO_2H in 10 cm^3 = (22.40/1000) x 2
= 0.0448 mol

• No. of moles of CH_3CO_2H in 100 cm^3 = 0.0448 x 10
= 0.448 mol

•	CH_3CO_2H +	CH_3CH_2OH $\rightleftharpoons$	$CH_3CO_2CH_2CH_3$ +	H_2O
Initial amount/mol	**1.51**	**1.66**	**0**	**0**
Change in amount/mol	**-1.06**	**-1.06**	**+1.06**	**+1.06**
Eqm amount/mol	**0.448**	**0.600**	**1.06**	**1.06**

$$\bullet\ K_c = \frac{[\mathrm{CH3CO2CH2CH3}\ ][\mathrm{H2O}]}{[\mathrm{CH3CO2H}][\mathrm{CH3CH2OH}]}$$

$$= \frac{(\frac{1.06}{0.1})(\frac{1.06}{0.1})}{(\frac{0.448}{0.1})(\frac{0.6}{0.1})}$$

= 4.18

[Total: 22]

2 **(a)** In 1887, the Swedish scientist Svante Arrhenius postulated that acids and bases dissociate in water to form hydrogen ions, H^+, and hydroxide ions, OH^-, respectively.

(i) Suggest a limitation of the Arrhenius concept of acids and bases. [1]

Accept any of the answers below
- **It applies only to aqueous solutions.**
- **It does not adequately explain why such compounds as ammonia are bases.**
- **The hydrogen ion, H^+, exists as hydronium ion, H_3O^+, in water.**

A theory proposed by Danish chemist J.N. Brønsted and British chemist T.M. Lowry overcame the shortcomings of the Arrhenius theory.

(ii) Using the Brønsted–Lowry model, nitric acid can be either a Brønsted–Lowry acid or base. Write equations to show how nitric acid *reacts* as a Brønsted–Lowry acid and a Brønsted–Lowry base respectively. [2]

- **Acting as acid: $HNO_3 + NaOH \rightarrow NaNO_3 + H_2O$**
- **Acting as base: $HNO_3 + H_2SO_4 \rightarrow H_2NO_3^+ + HSO_4^-$**

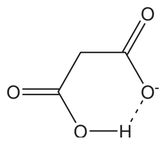
(b) The following table compares the K_a values of two three-carbon carboxylic acids.

Acid	Formula	K_{a1}	K_{a2}
Propanoic	$CH_3CH_2CO_2H$	1.35×10^{-5}	—
Malonic	$HO_2CCH_2CO_2H$	1.41×10^{-3}	2.00×10^{-6}

Suggest a reason why K_{a1} of malonic acid is higher than

(i) K_a of propanoic acid [1]

- **This is due to the stabilisation of the monoanion by hydrogen bonding with the unionised $-CO_2H$ group.**



(ii) K_{a2} of malonic acid [1]

- **The stabilising hydrogen bonding in the monoanion of malonic acid would be destroyed by the ionisation of the second $-CO_2H$ group.**

or

- **The removal of an H^+ from $HO_2CCH_2CO_2^-$ that already carries a negative charge would be electrostatically unfavourable.**

(iii) 25 cm^3 of 0.10 mol dm^{-3} of NaOH is gradually added to 10 cm^3 of 0.10 mol dm^{-3} malonic acid. Calculate the pH of the mixture when the following volumes of NaOH has been added. [3]

- 0 cm^3 [considering using K_{a1} of malonic acid]
- 5 cm^3
- 15 cm^3
- 25 cm^3

Volume of NaOH added = 0 cm^3 (Initial pH)

$K_{a1} = 1.41 \times 10^{-3}$ mol dm^{-3}

$[H^+] = \sqrt{1.41 \times 10^{-3} \times 0.10} = 0.0118$ mol dm^{-3}

- **pH = -lg $[H^+]$ = -log 0.0118 = 1.93**

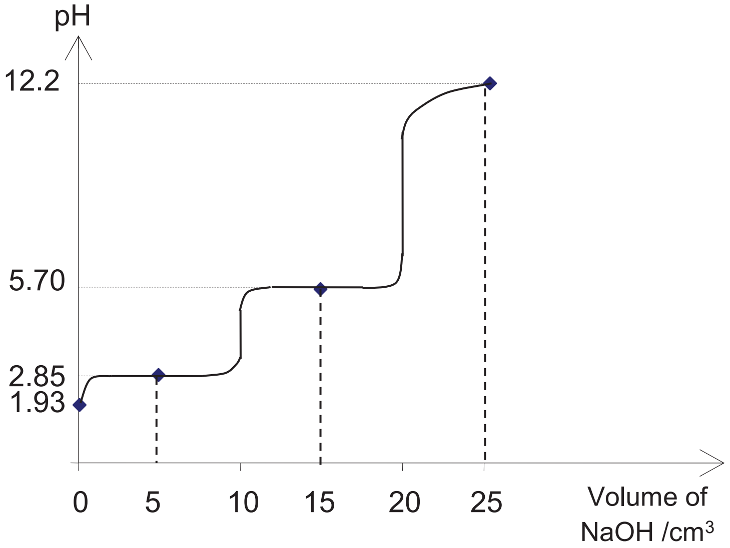
Volume of NaOH added = 5 cm^3 and 15 cm^3 (Maximum buffering)

- **pH at 5 cm^3 = pK_{a1} = -lg 1.41×10^{-3} = 2.85**
  pH at 15 cm^3 = pK_{a2} = -lg 2.00×10^{-6} = 5.70

Volume of NaOH added = 25 cm^3 (Excess NaOH added)
Volume of excess NaOH added = 25 -20 = 5 cm^3
No. of moles of excess NaOH = $\frac{5}{1000}$ **x 0.10 = 5.00 x 10^{-4} mol**
Total volume of solution = 10 + 25 = 35 cm^3
$[OH^-]$ = $\frac{5.00\times10^{-4}}{\frac{35}{1000}}$ **= 0.0143 mol dm^{-3}**
pOH = -log $[OH^-]$ = 1.85

- **pH = 14 – pOH = 12.2**

(iv) Using your answers in **(b)(iii)**, sketch the pH-volume added curve when 25 cm^3 of 0.10 mol dm^{-3} NaOH is gradually added to 10 cm^3 of 0.1 mol dm^{-3} malonic acid. [2]

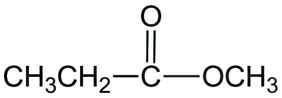


•• Correct shape of graph, correct volumes of NaOH indicated, proper labelling of axes and pH

(v) Suggest an indicator for the first equivalence point. [1]

- **Screened methyl orange or methyl orange**

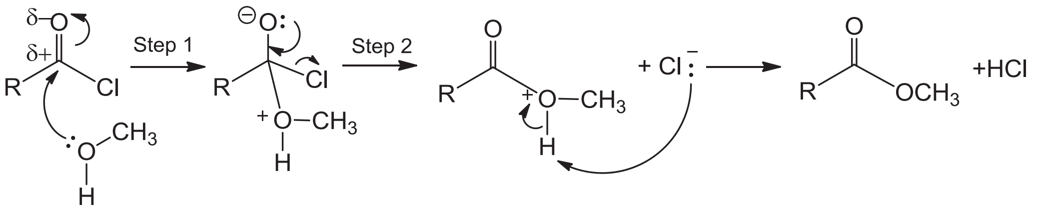
(c) Compound **A** can be directly synthesised from propanoic acid or propanoyl chloride via condensation.



$$CH_3CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OCH_3$$

Compound **A**

The formation of compound **A** from propanoyl chloride occurs via the mechanism shown below.

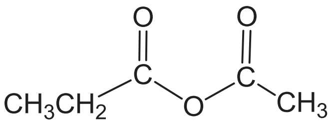


where R = CH_3CH_2—

(i) Name the reactions in step 1 and step 2. [2]

- **Step 1: Nucleophilic addition**
- **Step 2: Elimination**

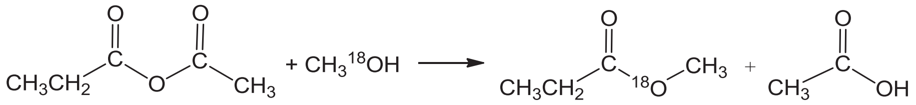
Compound **B** is a carboxylic acid anhydride that reacts similarly to an acyl chloride.



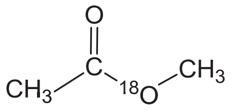
Compound **B**

(ii) Compound **B** reacts with methanol that has been labelled with ^{18}O isotope to form compound **A**. [1]

Write an equation for the reaction showing clearly the location of the $^{1(}$O atom in the product. The formula of methanol can be written as $CH_3{}^{18}OH$.

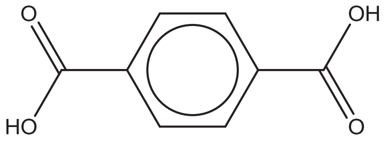
- 

(iii) Draw the structure of another neutral product formed in the reaction. [1]

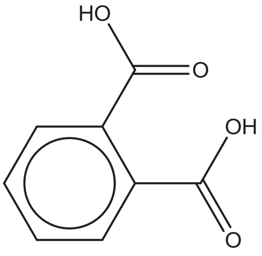
- 

[Total: 15]

3 Terephthalic acid (TPA) and phthalic acid (PA) both have the molecular formula $C_6H_4(COOH)_2$. While TPA is used principally to make clothing and plastic bottles, PA has limited commercial application. The structures of TPA and PA are shown below.



TPA



PA

Some physical properties of TPA and PA are shown in the table below:

	TPA	PA
Appearance	White crystal	White crystal
Melting point	300 °C	207 °C
Boiling point	Decomposes	Decomposes

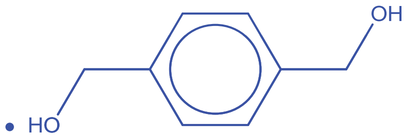
(a) Explain why TPA has a higher melting point than PA. [2]

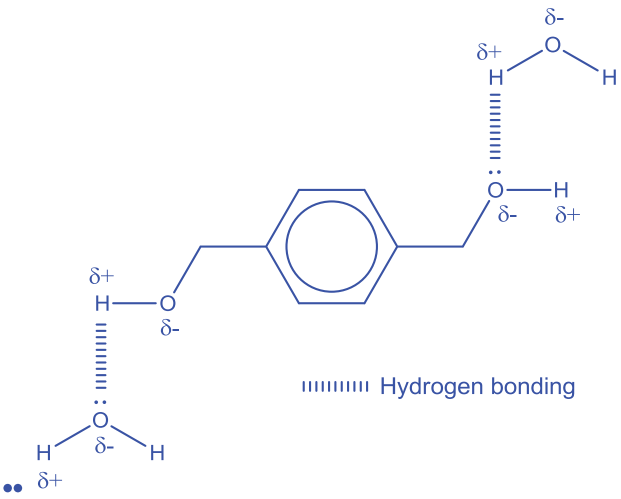
• Due to the close proximity of the 2 -COOH groups in PA, intramolecular hydrogen bonding occurs. This reduces the extent of intermolecular hydrogen bonding between PA molecules.

• In TPA, the 2 -COOH groups are further away hence only intermolecular hydrogen bonding occurs. Thus, more heat energy is needed to overcome the more extensive hydrogen bonding.

(b) **(i)** TPA can be reduced to a diol for the synthesis of a renewable polymer.

Draw the structure of this diol and illustrate with a diagram, its interaction with water. [3]

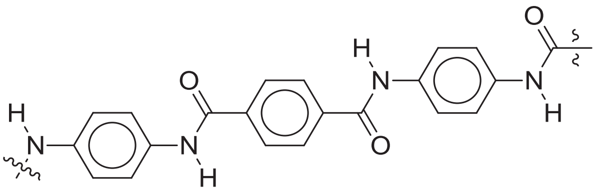




(ii) Hence, explain why the diol in **(i)** is soluble in water. [1]

• Formation of hydrogen bonds between the diol and water <u>releases sufficient energy to overcome the hydrogen bonding between diol molecules and hydrogen bonding between water molecules</u>.

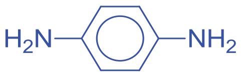
One common derivative of TPA is terephthaloyl chloride. Terephthaloyl chloride reacts with another monomer in a polymerisation reaction to form a synthetic fiber, commonly known as Kevlar®. A short chain of the Kevlar® polymer is shown below.



A strand of Kevlar® polymer

(c) **(i)** Name the type of reaction for this polymerisation reaction and suggest the structure of the other monomer to form the Kevlar® polymer. [2]

• Condensation reaction

•


(ii) In selecting a suitable material for the manufacture of bulletproof armour, it is necessary to ensure that the material does not shatter upon high impact force from a bullet.

With reference to the structures of gold and fluorite, CaF_2, explain why gold is more suitable for the lining of bulletproof armour. [2]

• When hit with a high impact force, the <u>layers of close-packed gold atoms can slide over one another without breaking the non-directional metallic bonds</u>.

However, for an ionic compound CaF_2, a • high impact force would cause layers of ions to shift and causes ions to same charge to slide next to each other, forcing the layers to come apart and shatter.

(d) **(i)** Define second ionisation energy of aluminium. [1]

• 2nd IE of aluminium is the minimum amount of energy to completely remove 1 mole of valence electrons from 1 mole of ground state gaseous Al^+ ions to form 1 mole of gaseous Al^{2+} ions.

(ii) Explain why the second ionisation energy of aluminium is higher than that of silicon. [1]

Al^+: [Ne] $3s^2$

Si^+: [Ne] $3s^2$ $3p^1$

Si has a higher nuclear charge than Al. However, • 2nd IE of Al involves the removal of 3s electron which is more strongly attracted and closer to the nucleus than the removal of 3p electron for Si. Hence, more energy is needed to remove the 3s electron.

(e) Many chemical reactions such as the reaction between peroxodisulfate and iodide ions occur very slowly at room temperature.

$$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$$

One way to speed up rate of reaction is to use a homogeneous catalyst.

(i) Explain why the reaction between $S_2O_8^{2-}$ and I^- has a high activation energy. [1]

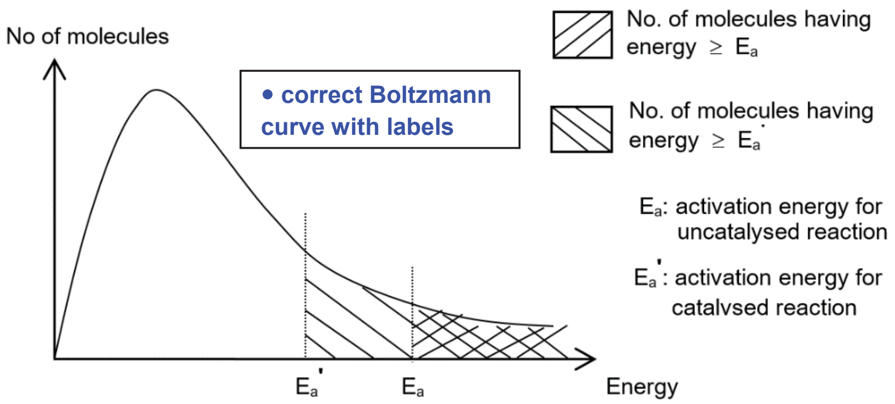
• The reaction involve the collision of 2 anions which would experience electrostatic repulsion upon contact with each other.

(ii) A solution of iron(II) ions can be used to catalyse the reaction between $S_2O_8^{2-}$ and I^-.

Using appropriate equations, outline the catalytic role of Fe^{2+} in the $S_2O_8^{2-}$ and I^- reaction. Hence, explain with the aid of a Boltzmann distribution curve, how Fe^{2+} speeds up the rate of the reaction. [5]

• $2Fe^{2+}(aq) + S_2O_8^{2-}(aq) \rightarrow 2SO_4^{2-}(aq) + 2Fe^{3+}(aq)$

• $2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$



$Fe2^{+}$ acts as a homogeneous catalyst that provides an • alternative pathway of lower activation energy than the uncatalysed reaction, through the formation of an intermediate Fe^{3+}.

• The number of reactant molecules having energy greater than or equal to the lower activation energy, E_a' increases significantly.

Hence the frequency of effective collisions increases and the rate increases.

A kinetics study was conducted on the reaction of $S_2O_8^{2-}$ and I^- to determine the rate equation. Varying volumes of $S_2O_8^{2-}$ and I^- were added to a mixture containing sodium thiosulfate and starch indicator, followed by topping up with suitable volume of water.

As the reaction of $S_2O_8^{2-}$ and I^- proceeds, the iodine produced will be consumed by the thiosulfate. When all thiosulfate is reacted, the remaining iodine will react with the starch indicator, forming a blue-black complex. The rate of reaction is determined by the time taken for the blue-black colouration to appear.

Experiment	Volume of KI / cm^3	Volume of $Na_2S_2O_8$ / cm^3	Volume of $Na_2S_2O_3$ / cm^3	Volume of water / cm^3	Time for blue-black colour / s
1	10	20	10	10	50
2	5	20	10	15	100
3	30	10	10	0	33
4	20	40	20	20	x

(iii) Determine the order of reaction with respect to iodide and peroxodisulfate. [2]

For expt 1 to 3, total volume is kept constant, so volume of reactant ∝ concentration.

Since thiosulfate is the limiting reagent and volume is constant, relative rate ∝ 1/t, so relative rates for expt 1, 2 and 3 are 0.02, 0.01 and 0.03.

• Comparing expt 1 and 2, when conc of KI decreases by 2 times, rate decreases by 2 times → 1st order with respect to I^-.

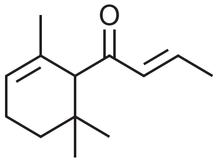
- **Comparing expt 1 and 3, when conc of KI increases by 3 times and conc of $Na_2S_2O_8$ decreases by 2 times, overall rate increases by 1.5 times (from 0.02 to 0.03) → 1st order with respect to $S_2O_8^{2-}$.**

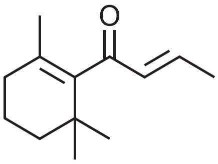
(iv) Hence, deduce the time taken for the blue-black colouration to appear for experiment 4. [1]

Since volume of all reactants double and total volume of mixture doubles, concentration of KI, $Na_2S_2O_8$ and $Na_2S_2O_3$ remain the same. Rate of reaction remains constant, so x = 50 s.

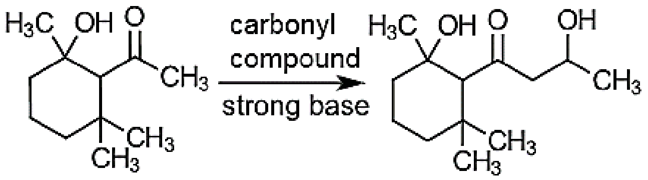
[Total: 21]

4 Rose ketones, damascenones, were discovered as active ingredients in the characteristic smell of Bulgarian rose oil. α-damascenone and β-damascenone were later discovered to give female perfumes such as *Dior's Poison* their unusual and distinctive fragrance.


α-damascenone


β-damascenone

In the synthesis of damascenones in the laboratory, it was found that compound **A** is a possible precursor which could be synthesised from compound **B** via an aldol reaction.

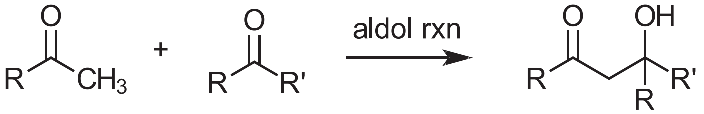


Compound **B** Compound **A**

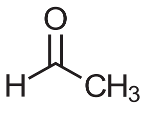
(a) State the reagent and condition required to convert compound **A** to either α-damascenone or β-damascenone. [1]

- Excess concentrated sulfuric acid, 180°C

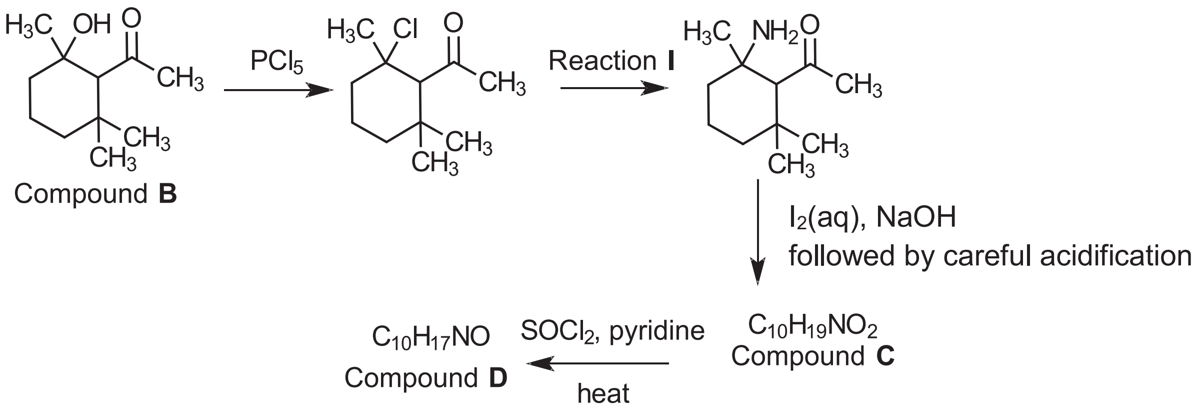
(b) With reference to an example of aldol reaction shown below, suggest an identity of the carbonyl compound reacting with compound **B** to form compound **A**.



[1]

-  ethanal

Compound **B** can undergo a series of chemical reactions as shown in the flow chart below.

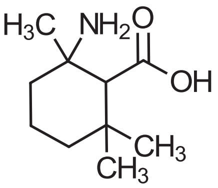


(c) State the reagents and conditions for Reaction **I**. [1]

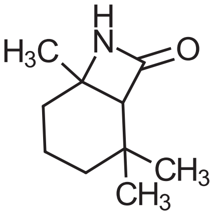
- Excess concentrated NH_3, heat in a sealed tube

(d) Draw the structural formulae of compounds **C** and **D**. [2]

- Compound **C**:

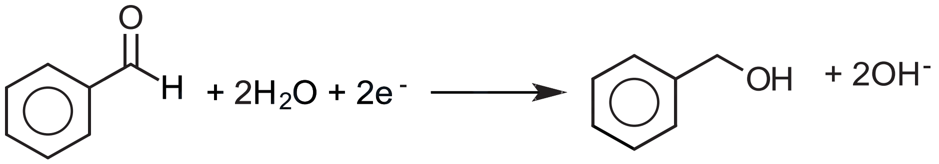


- Compound **D**:



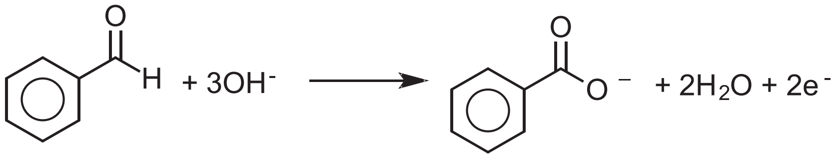
Benzaldehyde, in the presence of sodium hydroxide, undergoes the cannizzaro reaction to give benzoate ion and phenylmethanol.

(e) The ion-electron half-equation of benzaldehyde forming phenylmethanol is shown below.

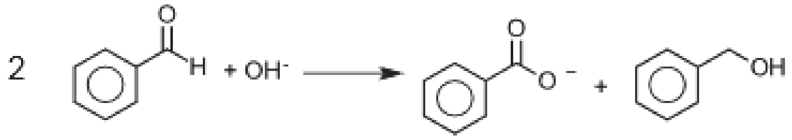


Construct the ion-electron half equations for the reaction of benzaldehyde forming benzoate ion and hence, construct an overall balanced equation for the reaction. [2]

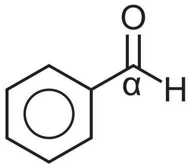
- **Oxidation:**



•Overall:



(f) Using changes in oxidation states of the carbon labelled α in benzaldehyde, state and explain the type of reaction that benzaldehyde undergoes in (e).



[1]

Disproportionation reaction.
The oxidation state of α-C in benzaldehyde changes from +1 to +3 (in benzoate ion) and –1 (in phenylmethanol) simultaneously.

[Total: 8]

5 **(a)** Organic compound **P** (M_r = 144) can be found in most leather products and is used as a mould inhibitor. P has the following composition by mass:

C: 50.04% H: 5.56% O: 44.40%

(i) Determine the molecular formula of **P**. [2]

	C	**H**	**O**
Mole ratio	**50.04/12**	**5.56/1**	**44.40/16**
	4.167	**5.56**	**2.775**
Simplest ratio	**1.50**	**2.00**	**1.00**
	3	**4**	**2**

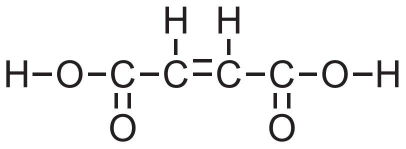
Empirical formula : $C_3H_4O_2$

$(C_3H_4O_2)_n$ = 144
36n + 4n + 32n = 144
n = 2

Molecular formula : $C_6H_8O_4$

P exhibits stereoisomerism and it decolourises aqueous bromine. On heating one mole of **P** with dilute acid, two organic products **Q**, $C_4H_4O_4$ and **R** (M_r = 32) are obtained. The mole ratio of **Q** to **R** is 1:2. Vigorous effervescence was observed when **Q** reacted completely with sodium carbonate in equimolar proportions. Vigorous effervescence was observed when **Q** reacted completely with sodium carbonate in equimolar proportions.

(ii) Draw the displayed formula of **Q**. [1]



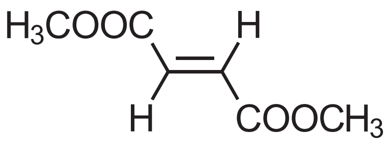
$$\mathrm{H{-}O{-}\underset{\underset{O}{\|}}{C}{-}\overset{\overset{H}{|}}{C}{=}\overset{\overset{H}{|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}O{-}H}$$

(iii) State the functional groups present in **P**. [1]

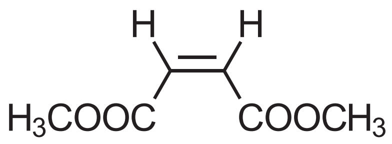
P : **alkene, ester**

(iv) Hence state the type of stereoisomerism exhibited by **P**. Draw and label the stereoisomers. [2]

Cis-trans isomerism

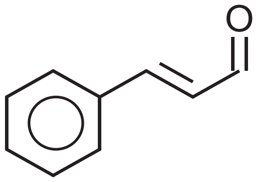


Trans



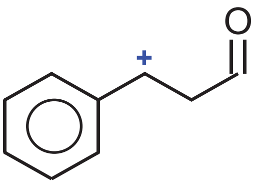
Cis

(b) Another mould inhibitor, cinnamaldehyde has the structure shown below. [3]

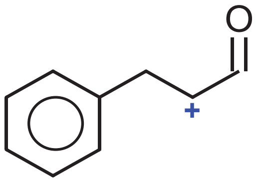


Reaction of cinnamaldehyde with HBr produces a mixture that is optically inactive. Explain this observation.

•Cinnamaldehyde undergoes <u>electrophilic addition</u> with HBr to form the intermediate carbocation,



or



which is planar about the C with the positive charge.
•The Br^- ion can then attack from both top and bottom of the plane with equal probability resulting in a racemic mixture.
•The resulting enantiomers rotate plane polarized light to equal extent but in opposite directions giving rise to an optically inactive mixture.

[Total: 9]

TEMASEK
JUNIOR COLLEGE

CHEMISTRY **9729/03**
Paper 3 Free Response **13th September 2017**
2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Graph Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, index number, name and civics group on all the work you hand in.
Write in dark blue or black pen.
You may use a HB pencil for any diagrams or graphs.
Do not use staples, paper clips, 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 brackets [ ] at the end of each question or part question.

This document consists of **14** printed pages and **2** blank pages.

Section A

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

1 Calcium carbonate is found in rocks and is the main component of pearls and the shells of eggs, snails and many marine organisms. It is the active ingredient in agricultural lime and is also medicinally used as a calcium supplement or as an antacid.

(a) **(i)** Describe and explain the trend in thermal stability of the Group 2 carbonates. [3]

- **Down the group, charge of the cation remains constant but ionic radius increases. Hence charge density of the cation decreases.**
- **(CO_3^{2-} ion is a large anion so is easily polarised but) Polarising power of cation decreases resulting in less distortion of the electron cloud of CO_3^{2-} ion, weakening the C-O covalent bond less.**
- **More energy needed to decompose the carbonate, hence down the Group, carbonates become more stable to heat, therefore decomposition temperature increases and thermal stability increases down the group.**

(ii) Determine the minimum temperature for the spontaneous decomposition of calcium carbonate, given that $\Delta H = +178.5$ kJ mol^{-1} and $\Delta S = +163.2$ J K^{-1} mol^{-1}. [2]

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

- **$\Delta H - T\Delta S < 0$**

$T > \Delta H / \Delta S$

$T > 178.5 \times 1000 / 163.2$

- **$T > 1090$ K (3 sig fig)**

(b) Limestone is predominantly calcium carbonate, a slightly soluble salt with a K_{sp} value of 3.3×10^{-9}. This rocky material began accumulating in the Earth over 400 million years ago. The Howe Caverns in the USA is a relatively young limestone cave which began forming 800 000 years ago.

(i) Determine the solubility of calcium carbonate. [1]

Let solubility of $CaCO_3$ be x.

$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$

$K_{sp} = x^2$

- **$x = 5.74 \times 10^{-5}$ mol dm^{-3}**

The principal cave-forming process is explained below.

Gaseous CO_2 is in equilibrium with aqueous CO_2 in surface water.

$CO_2(g) \rightleftharpoons CO_2(aq)$ ----- **(1)**

As surface water trickles through cracks in the ground, it meets soil-trapped air which contains higher levels of CO_2 (P_{CO_2} = 100 Pa) and hence [CO_2(aq)] increases.

When this CO_2-rich water contacts limestone, more $CaCO_3$ dissolves. As a result, more rock is carved out, more water flows in and over centuries a cave is formed.

$CaCO_3(s) + CO_2(aq) + H_2O(l) \rightleftharpoons Ca^{2+}(aq) + 2HCO_3^-(aq)$ ----- **(2)**

(ii) Show that the atmospheric partial pressure of CO_2, P_{CO_2}, is 40.5 Pa. You may assume air contains 0.04% by volume CO_2.

[1]

volume of gas α no of mole of gas (Avogadro's Law)

- **P_{CO_2} = 0.04/100 x 101325 = 40.5 Pa**

(iii) State and explain whether CO_2 in the atmosphere or soil-trapped air is behaving less ideally.

[2]

- **CO_2 in soil-trapped air will behave less ideally.**
- **As soil-trapped air will be under higher pressure the total volume occupied by the gas is reduced, the volume of the gas molecules becomes more significant compared with the total volume of the gas.**

Stalactites and stalagmites are rock formations that hang from ceiling of caves and rise from the floor of caves, respectively. They are formed when surface water seeps through rock and drips from the ceiling of a cave.

(iv) With reference to equilibria **(1)** and **(2)**, explain the formation of stalactites and stalagmites in limestone caves.

[3]

- **When the surface water drips from the ceiling, $CO_2(g)$ escape as it comes into contact with the atmosphere, which has a lower P_{CO_2}.**
- **By Le Chatelier's principle, equilibrium (1) shift to the left causing [$CO_2(aq)$] to decrease. Equilibrium (2) will be be shifted to the left to counter the decrease in [$CO_2(aq)$]**
- **$CaCO_3$ will then be precipitated out on the ceiling or on the floor resulting in the formation of stalactites and stalagmites.**

(v) Suggest a reason why some of these rock formations can appear reddish brown or bluish green.

[1]

- **It is likely due to the presence of transition metal ions like Fe^{3+} and Cu^{2+}.**

Lakes bounded by limestone-rich soil are less likely to be impacted by acid rain. Limestone dissolves sufficiently in lake water to form a buffer system capable of mitigating the effect of acid rain.

(vi) Suggest, with the aid of an equation, how the buffer system will maintain the pH of the lake water.

[1]

- **$CO_3^{2-}(aq) + H^+(aq) \rightarrow HCO_3^-(aq)$**

As the carbonate ions neutralise the H^+ from acid rain, there is negligible change in pH.

Acidification due to acid rain of lakes and rivers poses a serious environmental problem. The concentration of carbonate ions in these water is small due to the high acidity, hence affecting the survivability of some marine organisms.

(vii) Suggest a reason why the survivability of some marine organisms is affected. [1]

- **Carbonate ions, together with calcium ions, are the building blocks of their shells and skeletons.**

(c) Emission from power stations using coal, which contains sulfur, as fuel has significant environmental consequences. One of the components is sulfur dioxide, which can be oxidised by atmospheric hydroxyl radical to sulfur trioxide.

(i) Write a balanced equation to explain how sulfur trioxide contribute to acid rain. [1]

- **$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$**

Current power plants are fitted with flue-gas desulfurization devices. These devices heat powdered limestone in air to remove sulfur dioxide from the gases produced during coal combustion. One of the products is calcium sulfate.

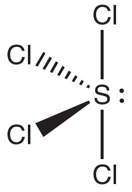
(ii) Write a balanced equation for the reaction that had taken place. [1]

- **$CaCO_3(s) + \frac{1}{2}O_2(g) + SO_2(g) \rightarrow CaSO_4(s) + CO_2(g)$**

(d) Sulfur and aluminium can both react with chlorine.

Aluminium chloride is a white solid that sublimes while sulfur tetrachloride, SCl_4, is an unstable pale yellow solid. Both react with water but formed different products.

(i) Predict the shape of sulfur tetrachloride, using a diagram where appropriate. Suggest the bond angle(s) in the molecule. [2]

- **See-saw, < 90° and < 120°**
- 

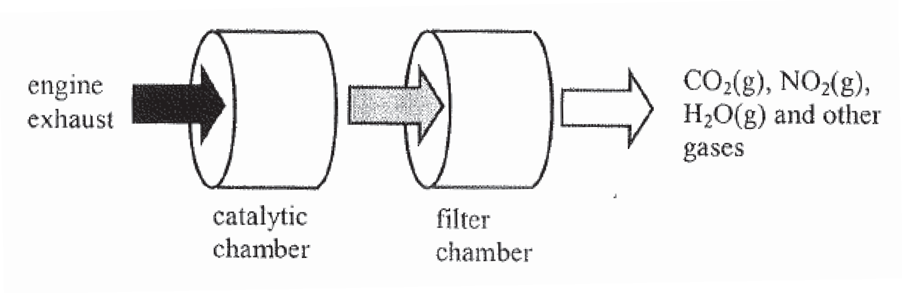
(ii) Describe and explain, with the aid of equations, the reaction of aluminium chloride with water. Suggest the pH of the resulting solution. [3]

- **Hydration: $AlCl_3(s) + 6H_2O(l) \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$**
  Hydrolysis: $[Al(H_2O)_6]^{3+}(aq) \rightleftharpoons [Al(H_2O)_5OH]^{2+}(aq) + H^+(aq)$
- **Hydrolysis is possible because Al^{3+} has a high charge density (small in size and highly charged) hence a high polarising power. It draws electrons away from its surrounding water molecules and weakens the O-H bond. It is easier for a H^+ ion to leave the water molecule.**
- **pH = 3**

[Total: 22]

2 The exhaust of heavy-duty diesel engines contains a significant amount of particulate matter (PM) and harmful gases such as nitrogen oxides. A Continuous Regenerating Trap (CRT) is a device which is designed for use in exhaust systems of buses and lorries running on diesel to remove PM and some of the harmful gases. A second catalytic converter is usually installed to remove the oxides of nitrogen.

The diagram below shows how a CRT works:



(a) **(i)** Explain, with the aid of equations, why oxides of nitrogen are present in the engine exhaust.

[2]

- **Under the high temperature condition of the internal combustion engine, atmospheric nitrogen reacts with oxygen to from oxides of nitrogen.**
- **$N_2(g) + O_2(g) \rightarrow 2NO(g)$**
  $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

(ii) State one harmful effect of nitrogen oxides on the environment.

[1]

- **Acid rain OR photochemical smog**

(iii) State two harmful gases that are also present in the engine exhaust. Use chemical equations to show how these two gases can be removed in the catalytic chamber of a CRT.

[2]

- **CO and hydrocarbons**
- **$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$**
  $C_xH_y(g) + (x + y/4)\ O_2(g) \rightarrow xCO_2(g) + y/2\ H_2O(l)$

A CRT is an automated, self-regenerating device which does not require cleaning of the filter. In a CRT, the carbon, which is the most abundant element in PM, is trapped onto the filter and is then removed by one of the harmful gases.

(iv) Explain, with the aid of an equation, how the carbon trapped on the filter of a CRT can be removed. Hence explain why the filter need not be cleaned.

[2]

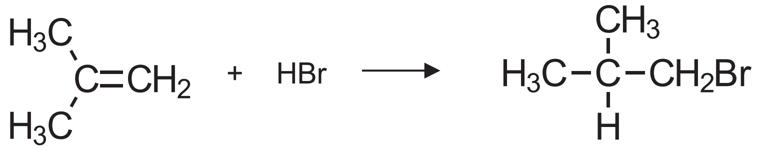
- **$C(s) + 2NO_2(g) \rightarrow CO_2(g) + 2NO(g)$ OR**
  $C(s) + 2NO(g) \rightarrow CO_2(g) + N_2(g)$ OR
  $2C(s) + 2NO_2(g) \rightarrow 2CO_2(g) + N_2(g)$
- **The carbon on the filter is oxidised by the oxides of nitrogen to form gaseous CO_2 and thus the filter need not be cleaned.**

(v) Suggest why buses and lorries equipped with CRT should not run on diesel with high sulfur content.

[1]

- **The sulfur will poison the catalyst rendering it ineffective.**

(b) In the reaction of HBr to alkenes such as methylpropene, scientists discovered that impurities such as peroxides, R-O-O-R, greatly increased the amount of anti-Markovnikov addition product as shown below.

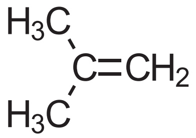


methylpropene 1-bromo-2-methylpropane

The above reaction is explained by the 4 step free radical addition mechanism as described below.

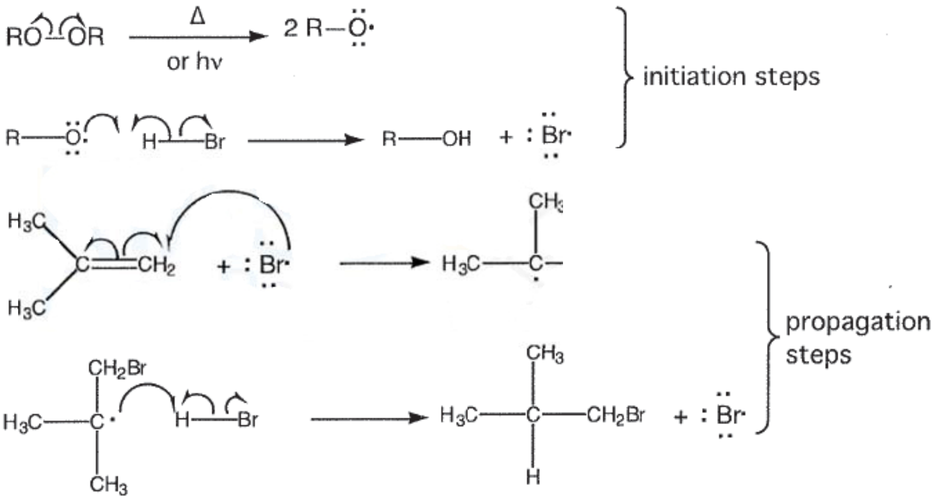
Step 1: The reaction is initiated by the formation of RO• radicals.
Step 2: This is followed by the reaction of the RO• radical with HBr to give bromine radical.
Step 3: The bromine radical adds to the alkene via the cleaving of the pi bond.
Step 4: The radical obtained from Step 3 reacts with HBr to form the anti-Markovnikov product.

(i) Use the information given above to draw out the full mechanism for the reaction. You are advised to use structural formulae for all species, such as



for methylpropene, so that it is clear which bonds are broken and which are formed. Indicate any unpaired electrons by a dot and use  to represent movement of an electron.

[4]

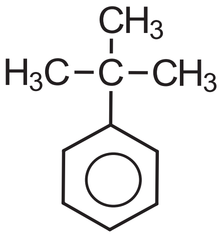


(ii) Unlike HBr, HC*l* does not undergo free radical addition to alkenes, even in the presence of peroxides. Explain this observation by quoting relevant values from the Data Booklet to substantiate your answer.

[2]

- **B.E H-Cl = 431 kJ mol^{-1}**
  B.E H-Br = 366 kJ mol^{-1}
- **The H—Cl bond is a stronger bond with better orbital overlap between H and Cl atoms. More energy is required to break the bond compared to HBr as shown by the bond energy values.**

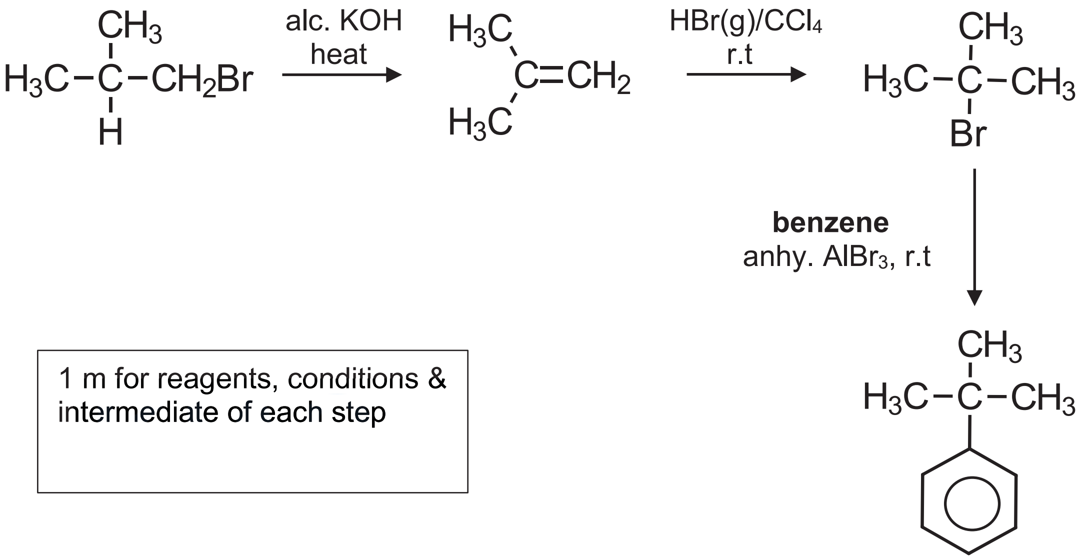
Tertiary butylbenzene is a colourless liquid widely used as a solvent for organic synthesis and also as a polymer linking agent.



t-butylbenzene

(iii) Using 1-bromo-2-methylpropane as the starting material, suggest a 3-stage synthesis of t-butylbenzene. You should state the reagents and conditions needed for each step, and show clearly the structure of any intermediate compounds.

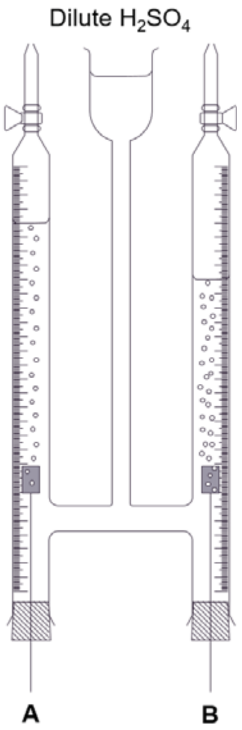
[3]



1 m for reagents, conditions & intermediate of each step

[Total: 17]

3 The following setup was carried out for the electrolysis of dilute sulfuric acid under room conditions, using platinum electrodes. A steady current of 2 A was applied for 1 minute through the circuit. The ratio of volume of gas produced at electrodes **A** and **B** is 1:2.



(a) **(i)** Write the half-equations for the reactions occurring at **A** and **B**. Label the polarity of each electrode clearly.

[2]

• Anode is A: $2H_2O \rightarrow O_2 + 4H^+ + 4e$ Polarity of electrode: +
• Cathode is B: $2H^+ + 2e \rightarrow H_2$ Polarity of electrode: -

(ii) Calculate the volume of gas produced at **A** after 1 minute.

[1]

Number of moles of electrons = It/F = 2x60/96500 = 1.24×10^{-3} mol
O_2 gas is produced at A. Since 4e ≡ O_2, amount of O_2 gas produced

= $1.24 \times 10^{-3} / 4 = 3.11 \times 10^{-4}$ mol
• Volume of O_2 gas = $3.11 \times 10^{-4} \times 24000 = 7.46$ cm^3

(iii) A student repeated the same experiment above, but using a copper electrode at **A** this time.

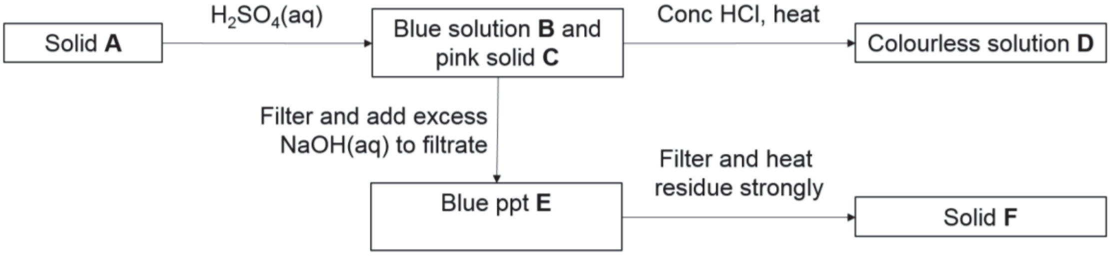
Suggest the volume of gas produced at **A** and explain your answer.

[2]

• Volume of gas at A = 0 cm^3.
$E^\ominus_{Cu^{2+}/Cu} = +0.34$ V

$E^\ominus_{O2/H2O} = +1.23$ V
Since the • standard reduction potential of Cu^{2+}/Cu is less positive than O_2/H_2O, the copper electrode would be preferentially oxidised instead of water. Hence, no gas is produced at A.

(b) Solid **A,** which is formed when a copper complex reacts with an aldehyde, is subjected to the following reactions.



Suggest the identities of **A** to **F**. [6]

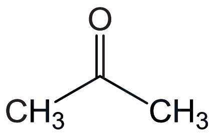
A: Cu_2O
B: $[Cu(H_2O)_6{}^{2+}]$(aq)
C: Cu
D: $[CuCl_2]^-$
E: $Cu(OH)_2$(s) OR $Cu(OH_2)(H_2O)_4$
F: CuO

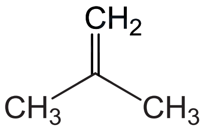
(c) Compounds **V** and **W** are gaseous hydrocarbons of empirical formulae CH_2 and CH_3 respectively. When 10 cm^3 of **V** and 10 cm^3 of **W** were completely burnt in 150 cm^3 of oxygen, the total gaseous volume decreased by 55 cm^3. After shaking the residual gases with aqueous sodium hydroxide, the total gaseous volume decreased by another 60 cm^3. When compound **V** is heated with acidified potassium manganate(VII), compound **X**, C_3H_6O, is formed.

(i) Suggest the molecular formula of **W**. [1]

- **C_2H_6**

(ii) Suggest the structures of compounds **V** and **X**. Explain your answers. [4]

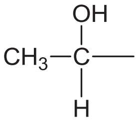
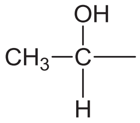
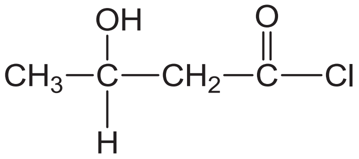
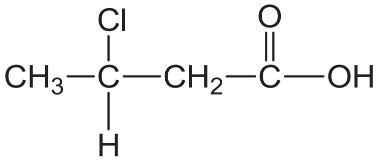
- **Since the total gaseous volume decreased by 60 cm^3 when shaken with NaOH, the volume of CO_2(g) is 60 cm^3. Compounds V and W contain a total of 6 carbon atoms.**
- **Since W is ethane, CH_3CH_3, V contains 4 carbons and is an alkene that undergoes strong oxidation with $KMnO_4$ to form X (C_3H_6O) and CO_2.**
- **X is** 

- **V is** 

(d) Compounds **Y** and **Z** are isomers of molecular formula $C_4H_7O_2Cl$. When **Y** and **Z** are added to separate portions of water, solutions are formed with pH values of 0.5 and 2.5 respectively. White precipitate is observed when aqueous silver nitrate is added to **Y**, but not **Z**. Both **Y** and **Z** gives yellow precipitate when warmed with aqueous sodium hydroxide and iodine.

Suggest the structures of compounds **Y** and **Z**. Explain your answers.

[5]

- Compound Y is an acyl chloride that undergoes hydrolysis in water, giving a solution of lower pH value since HCl is formed.
- Compound Z is a carboxylic acid as it gives an acidic solution upon partial dissociation of H^+ ions in water.
- Since white precipitate of AgCl is formed when Y is added to aqueous silver nitrate, Y is an acyl chloride.
- When warmed with alkaline medium, chloroalkane Z undergoes nucleophilic substitution to form  $CH_3-\overset{OH}{\underset{H}{C}}-$.
- Y undergoes oxidation with alkaline aqueous iodine and contains  $CH_3-\overset{OH}{\underset{H}{C}}-$.
- Y is  $CH_3-\overset{OH}{\underset{H}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-Cl$
- Z is  $CH_3-\overset{Cl}{\underset{H}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OH$

[7 marking points, maximum 5 marks]

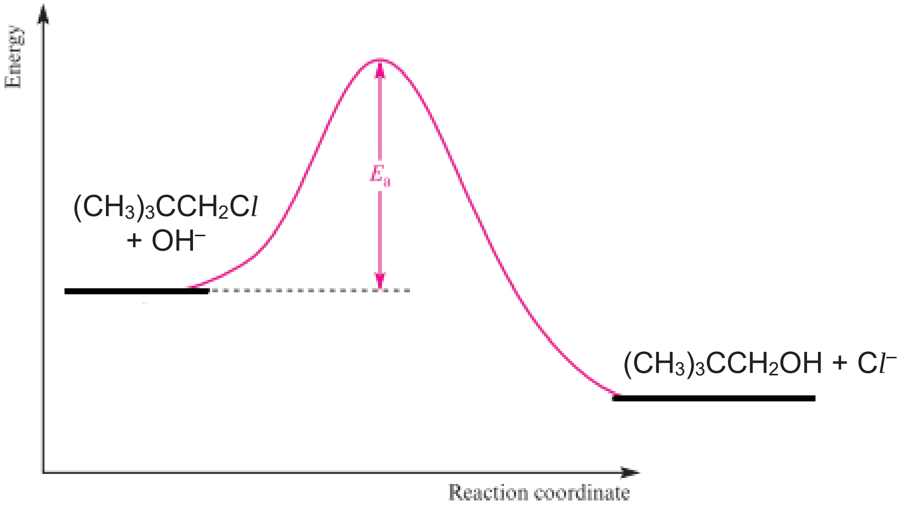
[Total: 21]

Section B

Answer **one** question from this section.

4 **(a)** Halogenoalkanes commonly undergo nucleophilic substitution reactions. On the basis of experimental observations developed over a 70-year period, two mechanisms for nucleophilic substitutions have been proposed.

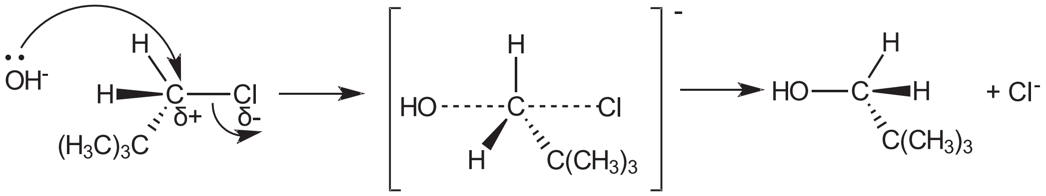
In the kinetics study of the hydrolysis of 1-chloro-2,2-dimethylpropane, $(CH_3)_3CCH_2Cl$, the energy-profile diagram of the reaction was proposed below:



(i) With reference to the energy profile diagram, describe the mechanism of the reaction between 1-chloro-2,2-dimethylpropane and hydroxide ions. The mechanism should include curly arrows to show the movement of electrons and all charges.

[2]

Energy profile diagram indicates S_N2 mechanism



•1m – shows inversion of configuration & correct transition state drawn
•1m – arrows, partial charges

(ii) A student decided to verify the mechanism deduced in **(a)(i)** for the hydrolysis reaction of 1-chloro-2,2-dimethylpropane.

The following results were obtained and you may consider the overall [NaOH(aq)] to remain virtually constant at 0.10 mol dm^{-3} throughout the experiment.

Time/ min	Experiment 1 $[(CH_3)_3CCH_2Cl]$/ mol dm^{-3}
0	0.0100
40	0.0070
80	0.0049
120	0.0034

160	0.0024
200	0.0017
240	0.0012

Using appropriate axes, plot a graph of $[(CH_3)_3CCH_2Cl]$ against time and use your graphs to deduce the order with respect to the concentration of the 1-chloro-2,2-dimethylpropane, showing your working clearly.

[4]

- **appropriate axes**
- **smooth curve drawn with accurate points plotted**

- **1st t ½ = 78 min; 2nd t ½ = 78 min (with workings line drawn on graph)**
- **Since t ½ is a constant, order of reaction is 1st order with respect to $[(CH_3)_3CCH_2Cl]$.**

(iii) Given the general rate equation as

$$\text{Rate} = k' [(CH_3)_3CCH_2Cl]^x$$

Using your answer in **(a)(ii),** calculate the rate constant k', stating its units.

[2]

$t_{1/2} = \frac{ln2}{k'}$ •k' = $\frac{ln2}{t_{1/2}} = \frac{ln2}{78} = 0.00889\ min^{-1}$ (•correct units)

(iv) When the experiment was repeated at the same temperature, the concentration of NaOH was doubled and the concentration of 1-chloro-2,2-dimethylpropane was monitored against time. The same graph was obtained as Experiment 1.

Deduce the order of reaction with respect to the concentration of hydroxide ion.

[1]

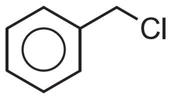
•When $[OH^-]$ doubles, the same graph was plotted means that the initial rate remains the same.
Since initial rate remains the same when concentration doubles, order of reaction is 0th order with respect to $[OH^-]$.

(v) Using your answers in **(a)(ii)** and **(a)(iv)**, explain if the student should agree with the proposed mechanism for the reaction in **(a)(i)**.

[1]

The student •should not agree with the proposed mechanism as the rate equation is rate = k $[(CH_3)_3CCH_2Cl]$, and thus only 1 molecule of $(CH_3)_3CCH_2Cl$ reacts in the rate-determining step.

(b) (Chloromethyl)benzene is a primary alkyl halide.



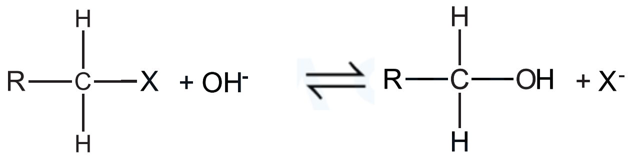
(Chloromethyl)benzene

Suggest a reason why (chloromethyl)benzene undergoes substitution via S_N1 mechanism.

[1]

• (chloromethyl)benzene favours substitution via S_N1 due to resonance stabilisation of the benzyl carbocation.

(c) Different alkyl halides would have different reactivity towards nucleophilic substitution.



$$RCH_2X + OH^- \rightleftharpoons RCH_2OH + X^-$$

where X^- is a leaving group

The difference in reactivity is dependent on the stability of the leaving group. The more stable the halide ion, the better the leaving group. The pK_a values of HX is given below.

Halide (X)	pK_a (HX)
F	+3
Cl	–7
Br	–9
I	–10

(i) Suggest the relationship between pK_a of HX and the stability of the halide ion. [1]

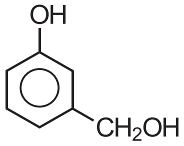
•The smaller the pK_a of HX, the more stable the halide ion.

(ii) Iodomethane and chloromethane are separately reacted with hydroxide ions. Using your answer in **(c)(i)**, explain why iodomethane reacts at a faster rate. [1]

As the pK_a of HI is the smallest, I^- is the most stable halide ion, and thus •a better leaving group than Cl^-. Thus, iodomethane is more susceptible towards nucleophilic substitution.

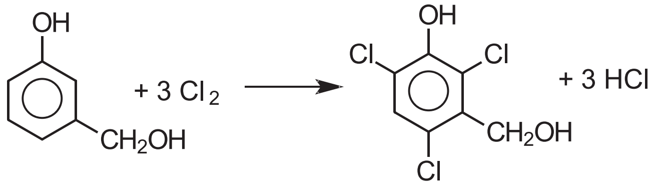
(d) Chlorinated phenols have gained an increasing use as fungicides, herbicides, insecticides, and precursors in the synthesis of other pesticides since the early 1930s.

It can be easily synthesised from its precursor **A** using aqueous chlorine.



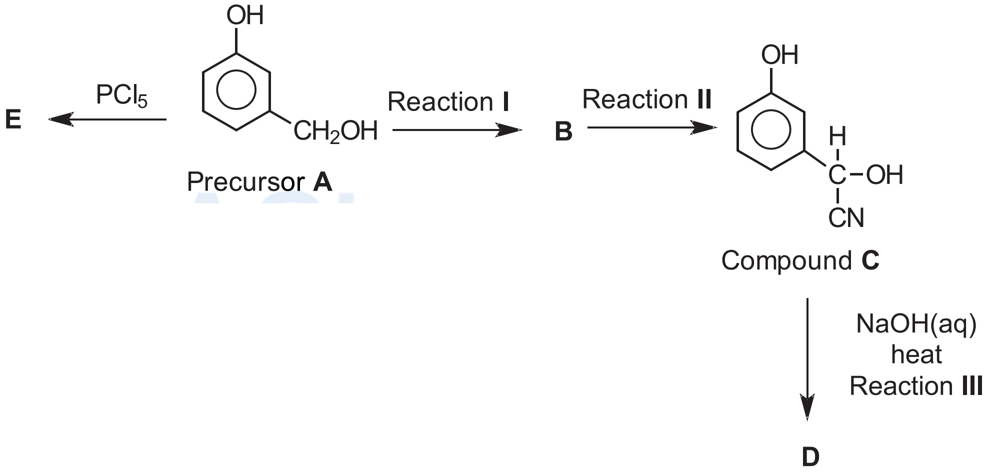
Precursor **A**

(i) Write a balanced equation for the reaction between precursor **A** and aqueous chlorine. [1]



•

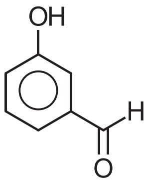
(ii) Precursor **A** undergoes a series of reactions shown in the reaction scheme below.



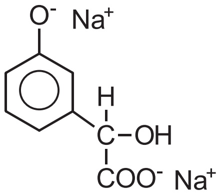
State the reagent and condition for Reaction **I** and **II**, and hence draw the structures of **B**, **D** and **E**. [5]

•Reaction I: acidified $K_2Cr_2O_7$, warm with immediate distillation
•Reaction II: HCN, in small amount of KCN, 10 – 20 °C

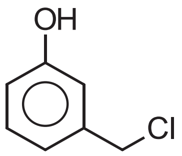
• B:



• D:



• E:



(iii) Reaction **III** can be used as a distinguishing test between compound **C** and precursor **A**. State the observation for this distinguishing test. [1]

•NH_3 gas will be evolved for compound C. No gas evolved for precursor A.

[Total: 20]

5 **(a)** Describe and explain the relative thermal stabilities of the hydrogen halides down the group. [2]

- **Thermal stability decreases down the group: HF > HCl > HBr > HI**
- **This is because the atomic radius increases down the group, resulting in decreasing degree of effective overlap of orbitals and decreasing covalent bond strength and hence bond energy of HX decreases down the group.**

(b) Potassium chlorochromate (VI), $KCrClO_3$, was made using concentrated hydrochloric acid and potassium dichromate(VI).

$$K_2Cr_2O_7 + 2HCl \rightarrow 2KCrClO_3 + H_2O$$

Chlorine gas may be evolved as a side product. It was found that chlorine gas will not be produced if dilute hydrochloric acid was used instead.

Use data from the *Data Booklet* to explain why this is so. [2]

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$ $E^\circ = +1.33$ V

$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ $E^\circ = +1.36$ V

• $E^\circ_{cell} = +1.33 - (+1.36) = -0.03$ V

Since $E^\circ_{cell} < 0$, the reaction is not spontaneous and Cl^- will not be oxidised to form chlorine gas when dilute hydrochloric acid was used.

• When concentrated hydrochloric acid is used, $[Cl^-]$ increases, the position of the above equilibrium shifts to the left by Le Chatelier's Principle and favours oxidation.

$E_{Cl2/Cl-}$ becomes less positive and E_{cell} becomes positive. Hence, the reaction is spontaneous, producing chlorine gas.

(c) **(i)** Vanadium is a transition element that exhibits variable oxidation states.

Explain why vanadium has the ability to form compounds with different oxidation states.

[1]

● Transition elements can exhibit a variety of oxidation states due to close proximity in energy of the 3d and 4s electrons. Thus both 3d and 4s electrons are available for bond formation (both ionic and covalent).

(ii) A Latimer diagram shown below summarises the standard electrode potential data of vanadium complexes in acidic medium.

$$\begin{tikzcd} VO_3^- \arrow[r, "+1.00\ V"] \arrow[rr, bend left, "x"] & VO^{2+} \arrow[r, "+0.34\ V"] & V^{3+} \end{tikzcd}$$

x, the standard electrode potential of converting VO_3^- to V^{3+}, is **not** the summation of +1.00 V and +0.34 V. It can be calculated from $\Delta G^\ominus$.

Write a half-equation for the conversion of VO_3^- to V^{3+}.

[1]

• $VO_3^- + 6H^+ + 2e^- \rightarrow V^{3+} + 3H_2O$

(iii) Calculate x, given that $\Delta G^\ominus$ for the conversion of VO_3^- to V^{3+} is -129000 J mol^{-1}.

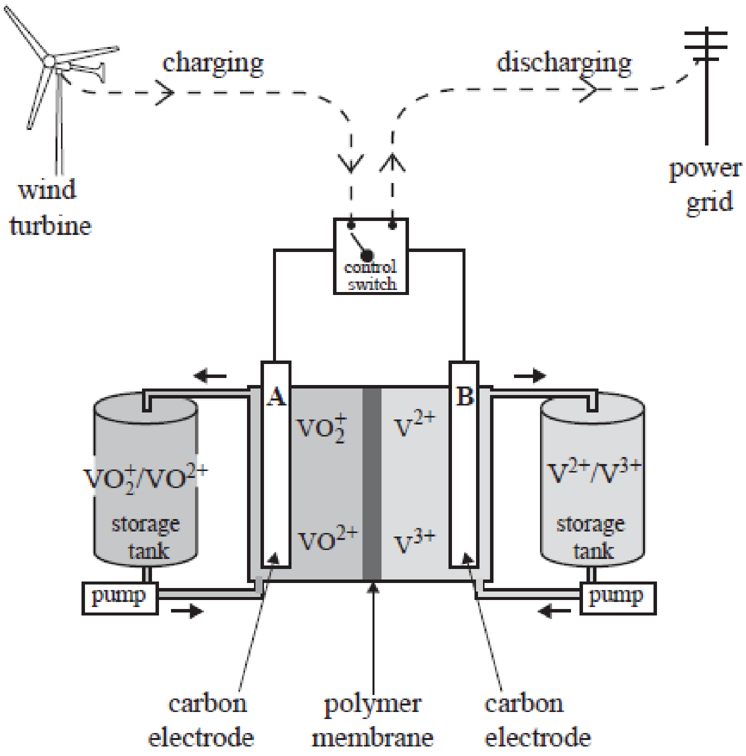
[1]

$\Delta G^\ominus = -nFE^\ominus$

• $E^\ominus = (-129 \times 10^3) / -(2 \times 96500) = +0.67$ V

(d) A vanadium redox battery is used to store electrical energy generated at a wind farm in Tasmania. The battery supplies electricity to the power grid as required through a control switch.

The diagram below shows the structure of a cell in a vanadium redox battery. The reactants are dissolved in an acidic solution, stored in large tanks and pumped through the cell. The cell is recharged using electricity generated by the wind turbines. A polymer membrane allows the movement of particular ions.



(i) State the polarity of electrode **A** when the cell is **discharging.** Explain your answer. [2]

$VO_2^+(aq) + 2H^+(aq) + e^- \rightleftharpoons VO^{2+}(aq) + H_2O(l)$ $\quad E^\ominus = +1.00$ V
$V^{3+}(aq) + e^- \rightleftharpoons V^{2+}(aq)$ $\quad E^\ominus = -0.26$ V
• When the cell is discharging, it is a galvanic cell. Since $E^\ominus$ VO_2^+/VO^{2+} is more positive than $E^\ominus$ V^{3+}/V^{2+}, VO_2^+ will undergo reduction.
• Therefore, electrode A is the cathode and is positive.

(ii) Write an equation for the reaction that occurs when the cell is being **recharged**. [1]

• $VO^{2+} + H_2O + V^{3+} \rightarrow VO_2^+ + V^{2+} + 2H^+$

(e) Nitrogen containing compounds such as ammonia and amines are common ligands found in transition metal complexes.

(i) Explain the relative basicities of ammonia, methylamine, dimethylamine and trimethylamine in the gaseous phase. [2]

● Basicity increases in the order of ammonia, methylamine, dimethylamine and trimethylamine.
●The greater the number of electron donating methyl group, the more available the lone pair on N for dative bonding with a proton.

(ii) Amides, such as ethanamide, are nitrogen containing compounds that do not exhibit basic properties like amines.

Explain why amides are neutral. [1]

● Amides are neutral because the lone pair of electrons on nitrogen atom in amides is in a *p* orbital, and can overlap with the π orbital of the adjacent carbonyl group. Hence, not available for donation to a proton.

(f) In 1893, Alfred Werner proposed the octahedral configuration of transition metal complexes. He was able to interpret isomeric properties using extensive studies on the octahedral cobalt complexes.

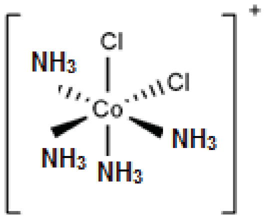
The following table gave information of two cobalt complexes **A** and **B** which are isomers of each other.

	Complex	Colour of solid	Does the complex have a dipole moment
A	$CoCl_2(NH_3)_4^+$	Violet	Yes
B	$CoCl_2(NH_3)_4^+$	Green	No

(i) Suggest structures for the cobalt complexes **A** and **B**.

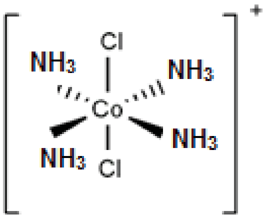
[2]

A



cis isomer

B

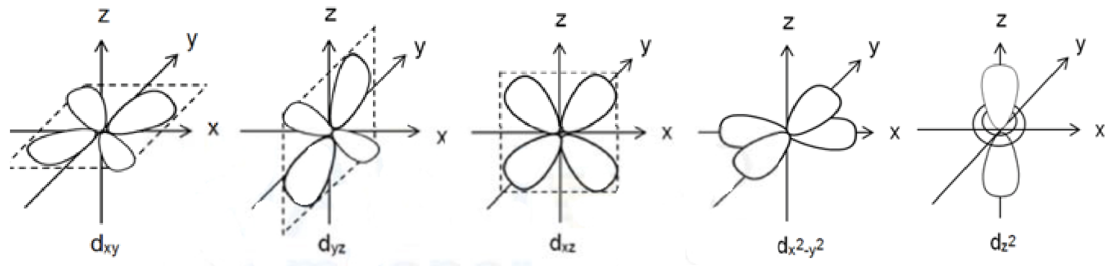


trans isomer hence no net dipole

(ii) The crystal field theory can be used to explain colour of transition metal complexes.

Describe, using the shape and orientation of the d orbitals, the splitting of degenerate d orbitals into two energy levels in octahedral complexes.

[3]

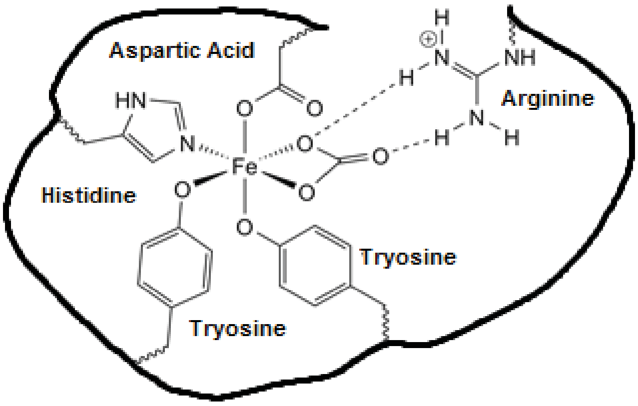


●

● d_{z^2} and $d_{x^2-y^2}$ orbitals experience stronger electronic repulsion with the negative charges as the orbital lobes are in the region of the negative charges. Due to these stronger electronic repulsion, the d_{z^2} and $d_{x^2-y^2}$ orbitals are at a higher energy level and the degenerate d orbitals split into 2 different energy levels.

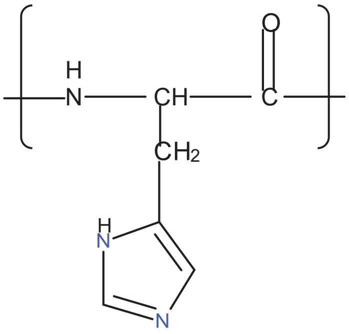
● the d_{xy}, d_{yz} and d_{xz} orbitals have lobes that project between the charges hence are at a lower energy level.

(g) R-groups on amino acids residues on protein act as ligands in biological systems. *Transferrin* is a protein in the blood that transports iron from food to the rest of the body.

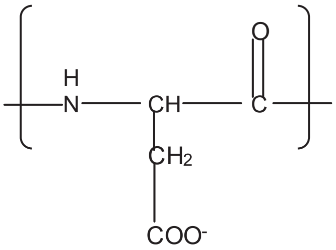


binding sites of *Transferrin*

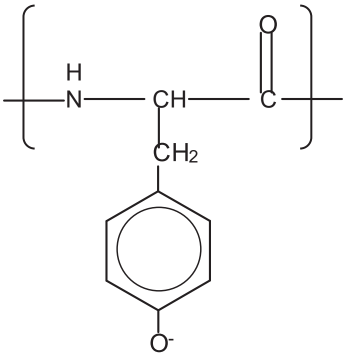
Transferrin binds to iron(III) via tryosine, histidine and aspartic acid residues as shown below.



Histidine residue
Side chain pK_a = 6.00



Aspartic acid residue
Side chain pK_a = 3.65

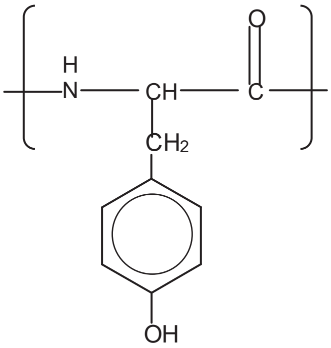


Tyrosine residue
Side chain pK_a = 10.07

The key to controlling uptake and release iron(III) is the change in pH. At pH 7.4, free transferrin binds to iron(III) to form the iron-transferrin complex. When the pH is lowered from 7.4 to 5.5, free iron(III) ions will be released from the protein binding site.

(i) Draw the structural formula of the tyrosine residue at its most stable state at pH 5.5.

[1]



- **tyrosine residue pronotated**

(ii) Suggest how the decrease in pH releases iron(III) from the protein complex. [1]

- **When pH decreases, tryrosine and histidine are protonated, it reduces the protein affinity to/ can no longer form dative bonds with Fe(III) thus releasing the free Fe(III).**

[Total: 20]

TEMASEK
JUNIOR COLLEGE

2017 JC2 PRELIMINARY EXAMINATIONS
HIGHER 2

CANDIDATE NAME									
CIVICS GROUP			/						
CENTRE NO. / INDEX NO.					/				

CHEMISTRY **9729/04**

Paper 4 Practical **28 August 2017**

2 hours 30 minutes

Candidates answer on the Question Paper.

READ THESE INSTRUCTIONS FIRST

Write your Civics Group and name on all the work you hand in.
Give details of the practical shift and laboratory where appropriate, in the boxes provided.
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.
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 14 and 15.
At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

Shift
Laboratory

For Examiner's Use	
1	/ 15
2	/ 24
3	/ 16
Total	/ 55

This document consists of 15 printed pages.

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

1 **Determination of change in oxidation number of a transition metal ion, M^{2+}**

You are to determine, by titration, the change in oxidation number of a transition metal ion, M^{2+}, when reacted with acidified potassium manganate(VII).

FA 1 is 0.0200 mol dm^{-3} potassium manganate(VII), $KMnO_4$
FA 2 is 0.0470 mol dm^{-3} transition metal salt, MSO_4
FA 3 is 1.00 mol dm^{-3} sulfuric acid, H_2SO_4

(a) Method

(i)

1. Fill the burette with **FA 1.**
2. Using a pipette, transfer 25.0 cm^3 of **FA 2** into the conical flask.
3. Using a measuring cylinder, transfer 25.0 cm^3 of **FA 3** to the same conical flask.
4. Carry out as many accurate titrations as necessary to obtain consistent results. Add **FA 1** until the contents of the conical flask turns a permanent pale pink colour.
5. Record below, in a table form, all of your burette readings and the volume of **FA 1** added in each accurate titration.

Results

Final burette reading /cm^3	**23.50**	**23.50**
Initial burette reading /cm^3	**0.00**	**0.00**
Volume of FA 1 /cm^3	**23.50**	**23.50**
	√	√

●Appropriate headings and units for accurate data where headings should match readings.
●All accurate burette readings recorded to 0.05 cm^3
●Has two uncorrected, accurate titres value within ±0.10cm^3
●●●3m – accuracy [6]

(ii) From your titrations, obtain a suitable volume of **FA 1** to be used in your calculations. Show clearly how you obtained this volume.

●**Average titre =** $\frac{23.50+23.50}{2}$

= 23.50 cm^3

25.0 cm^3 of **FA 2** required _**23.50**______________ cm^3 of **FA 1** [1]

(b) Calculations

Show your working and appropriate significant figures in the final answer to **each** step of your calculations.

(i) Calculate the amount of potassium manganate(VII) present in the volume of **FA 1** calculated in **(a)(ii)**.

●**Amount of MnO_4^-**

= $\frac{23.50}{1000} \times 0.02$

= 4.70 x 10^{-4} mol

amount of $KMnO_4$ = **4.70×10^{-4} mol** [1]

(ii) Determine the amount of **M**SO_4 in 25.0 cm^3 of **FA 2**.

●Amount of MSO_4 in 25.0 cm^3 of FA 2
$= 0.0470 \times \frac{25}{1000}$
$= 1.175 \times 10^{-3}$ mol
$= 1.18 \times 10^{-3}$ mol (3sf)

amount of **M**SO_4 in 25.0 cm^3 = **1.18×10^{-3} mol** [1]

(iii) Use your answer to **(b)(i)** and **(b)(ii)** to calculate the number of moles of **M**SO_4 that react with 1 mole of $KMnO_4$

●Number of moles of MSO4 reacting with 1 mole of $KMnO_4$

$= \frac{1.175\times10^{-3}}{4.7\times10^{-4}} = 2.50$ mol

amount of **M**SO_4 = **2.50 mol** [1]

(iv) Two possible equations for the reaction of acidified $KMnO_4$ with **M**SO_4 are shown below:

Equation 1: $2KMnO_4 + 10MSO_4 + 8H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5M_2(SO_4)_3 + 8H_2O$
Equation 2: $2KMnO_4 + 5MSO_4 + 8H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5M(SO_4)_2 + 8H_2O$

State and explain which of the above two equations is consistent with your answer in **(b)(iii)**.

●Equation 2 as ratio of $KMnO_4$: MSO_4 is 2:5 OR 1:2.5
Hence it is 2.5 mol of MSO_4 reacting with 1 mol of $KMnO_4$

[1]

(v) Use your answer in **(b)(iv)** to state the oxidation number of the transition metal **M** in the product of the reaction.

●Oxidation state of M in product is +4

Workings: **M**$(SO_4)_2 \rightarrow x+2(-2) = 0 \rightarrow x= +4$

[1]

(c) **(i)** A student suggested that using a burette to measure 25.0 cm^3 of **FA 2** would give a more accurate result than using a pipette. The percentage error of a 25.0 cm^3 pipette is 0.24%.

Calculate the percentage error of using a burette and deduce if the above claim by the student is correct.

Using the burette to measure 25.0 cm^3 of FA 2 involve 2 readings, thus the max error would be 2x (±0.05) = ±0.10

●%error would be $\frac{0.10}{25} \times 100\% = 0.400\%$

●Since %error using burette > %error using pipette (0.24%). The claim is incorrect as it is less accurate to use a burette to measure the 25.0 cm^3 of FA2.

[2]

(ii) Another student decided to use a 25.0 cm^3 pipette instead of a measuring cylinder to measure the volume of **FA 3** in **Step 3**.

State and explain whether this alteration will improve the accuracy of the experimental results.

●No this alteration will not improve the accuracy of the experiment as the acid was used in excess.

[1]

[Total: 15]

2 Determination of the enthalpy change of neutralisation, ΔH$_n$

You are to determine the enthalpy change for the neutralisation reaction given below.

$$HA(aq) + NaOH(aq) \rightarrow NaA(aq) + H_2O(l)$$

FA 4 is 1.80 mol dm^{-3} HA
FA 5 is aqueous sodium hydroxide, NaOH

(a) **Method**

Read through the instructions carefully and prepare a table below for your results before starting any practical work.

1. Support the styrofoam cup in the 250 cm^3 beaker.
2. Rinse and fill the burette with **FA 4**.
3. Use the measuring cylinder to transfer 25 cm^3 of **FA 5** into the styrofoam cup.
4. Place the thermometer in the styrofoam cup and record the temperature of the solution. Tilt the cup if necessary to ensure the thermometer bulb is fully immersed.
5. Run 5.00 cm^3 of **FA 4** into the cup. Stir, and record the new temperature of the solution and the volume of **FA 4** added.
6. Run a second 5.00 cm^3 of **FA 4** into the cup. Stir and record the new temperature and the total volume of **FA 4** added.
7. Continue adding **FA 4** in 5.00 cm^3 portions. Stir and record each new temperature and total volume of **FA 4** until a total of 45.00 cm^3 has been added.

Results

Total Vol. FA 4 /cm^3	**Temp./^{0}C**
0.00	27.5
5.00	31.0
10.00	34.0
15.00	36.5
20.00	38.0
25.00	39.0
30.00	38.0
35.00	37.0
40.00	36.5
45.00	36.0

•Table with initial temp of solution and 9 sets of results with appropriate headers
•Record every volume to 2dp and temperature recorded to 1dp.

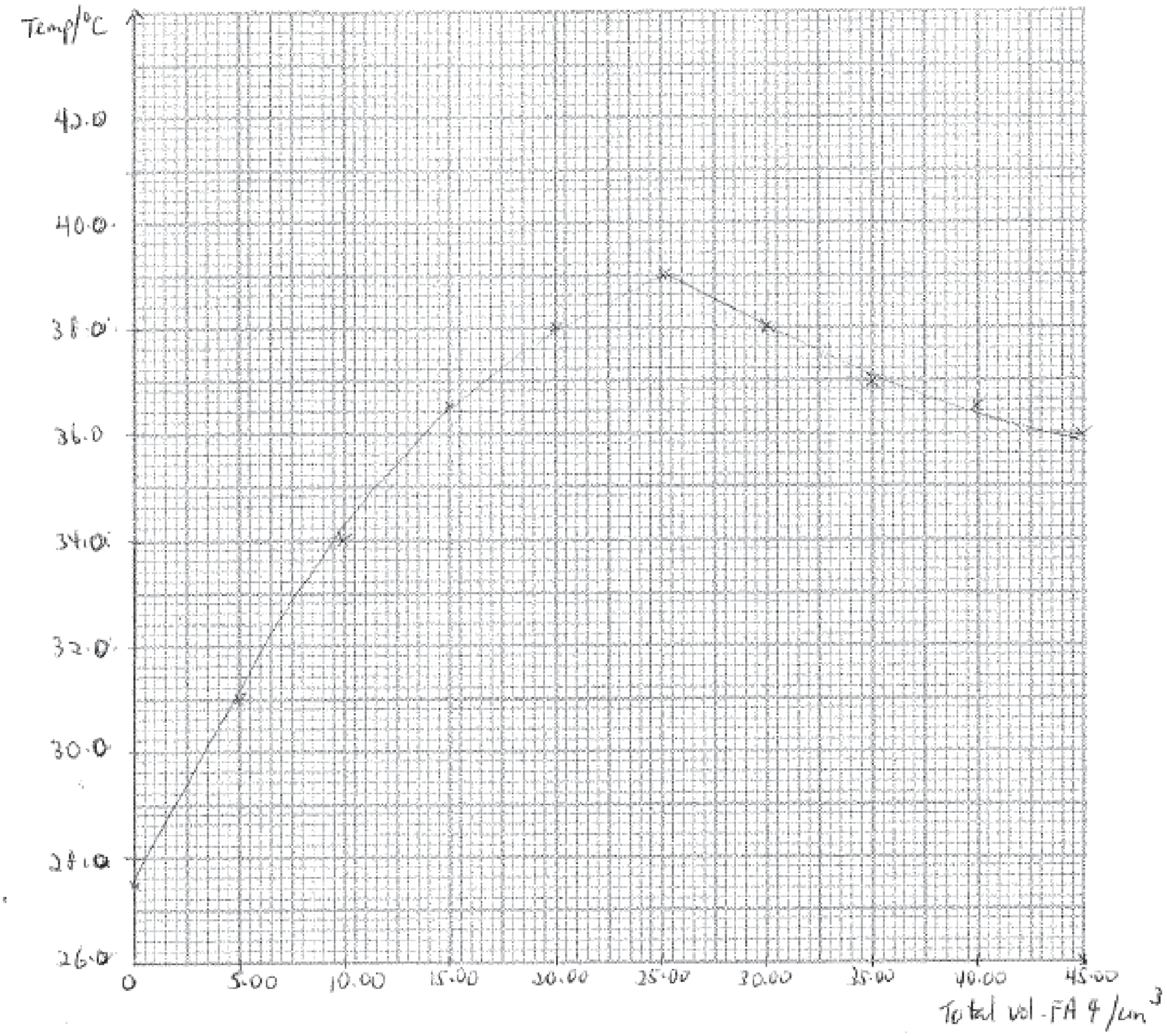
[2]

(b) **(i)** Plot a graph of temperature (*y*-axis) against total volume of **FA 4** added (*x*-axis) on the grid below. The temperature axis should allow you to include a point at least 2 °C greater than the maximum temperature recorded.

Draw two best-fit lines connecting all the plotted points with

- an increasing trend
- a decreasing trend.

Answer:



●Appropriate labels of the axis and appropriate scale of the graph

● All points accurately plotted (within ½ small square)

● Two lines of best fit drawn

[3]

(ii) Extrapolate the two lines until they cross.
The intersection gives the maximum temperature, T_{max}, at equivalence point.
Use your graph to determine the following and show clearly on your graph how you obtained these answers.

- Maximum temperature at the equivalence point, $T_{max,}$
- Maximum temperature change at the equivalence point, $\Delta T_{max.}$
- Total volume of **FA 4** added at the equivalence point, $V_{eq.}$

T_{max} = **39.0 ^{0}C**

ΔT_{max} = **11.5 ^{0}C**

$V_{eq.}$ = **25.25 cm^3**

[3]

(c) Explain the shapes of your graph lines before the equivalence point and after the equivalence point.

(i) Before the equivalence point

●Each 5 cm^3 addition of HA causes the temperature of the mixture to rise as the reaction between HA and NaOH is exothermic.

●Each rise in temperature is smaller than before because the same amount of heat is produced but the volume of mixture is larger. Thus the heat is distributed over an increasing volume of mixture.

**mark according to the students' graph – with ECF (1st mark for both (i) and (ii))*

[2]

(ii) After equivalence point

●NaOH has reacted completely and hence no more heat is produced. The temperature of the mixture falls with each 5 cm^3 addition of HA (at a lower temperature/room temperature).

[If students' answer is a downward-sloping curve]:
Each temperature fall is smaller than before as there is a smaller extent of cooling since the temperature of the mixture is now closer to temperature of the NaOH solution.

[1]

(d) **Calculations**

Show your working and appropriate significant figures in the final answer to **each** step of your calculations.

(i) Calculate the number of moles of HA present in the volume of **FA 4** recorded in **(b)**.

Amt of HA = 25.25/1000 x 1.80 mol
= 0.0455 mol

Amount of HA = **0.0455 mol**

(ii) Using your answers in **(b)**, calculate the heat energy produced when **FA 4** neutralised 25 cm^3 of sodium hydroxide.
(Assume that **4.2 J** of heat energy changes the temperature of 1.0 cm^3 of solution by 1 °C.)

Heat evolved = (25 + 25.25) x 4.2 x 11.5 J
= 2427 J

Heat energy produced = **2427 J**

(iii) Calculate the enthalpy change of neutralisation, in kJ mol^{-1}, for the reaction below.

$$HA(aq) + NaOH(aq) \rightarrow NaA(aq) + H_2O(l)$$

Enthalpy change of neutralisation = – 2427/(0.0455 x 1000) kJ mol^{-1}
= – 53.3 kJ mol^{-1}

Enthalpy change = **– 53.3 kJ mol^{-1}**

[6]

(e) Apart from using a thermometer calibrated to a greater level of precision, suggest one other improvement that could be made to the **method** carried out in **(a)**.

Use burette / pipette for FA 4 / instead of measuring cylinder.

or Use smaller volumes close to max T

or windshield *(but not lid because it's a titration)*

[1]

Planning

The enthalpy change of solution of solid NaOH can be calculated using the enthalpy change of neutralisation of aqueous NaOH with aqueous HC*l*, ΔH_1 and the enthalpy change of reaction of solid NaOH with aqueous HC*l*, ΔH_2.

(f) Given that the enthalpy change of neutralisation of aqueous NaOH with aqueous HC*l* is –57.0 kJ mol^{-1}, construct an energy cycle and show how it can be used to determine the enthalpy change of solution of NaOH.

$$\begin{tikzcd}
\mathrm{HCl(aq)} + \mathrm{NaOH(s)} \arrow[rr, "\Delta H_{sol}"] \arrow[dr, "\Delta H_2"'] & & \mathrm{HCl(aq)} + \mathrm{NaOH(aq)} \arrow[dl, "\Delta H_1 = -57\ \mathrm{kJmol^{-1}}"] \\
& \mathrm{NaCl(aq)} + \mathrm{H_2O(l)} &
\end{tikzcd}$$

Using Hess' Law,

$\Delta H_{sol} = \Delta H_2 - \Delta H_1$

[1]

(g) You are to plan an experiment to determine the enthalpy change of reaction of solid NaOH with aqueous HC*l*, ΔH_2. You are provided with the following reagents and the usual laboratory apparatus.

Reagents : 50 cm^3 1 mol dm^{-3} HC*l* solution
sodium hydroxide solid

Your plan should include

- calculation to show the appropriate mass of solid sodium hydroxide to be used.
- a sequence of numbered steps, the details of the experimental procedure including the measurements to be taken and tabulation of measurements and results.
- calculation of the enthalpy change of reaction of solid NaOH with HC*l* (aq).

(Assume that **4.2 J** of heat energy changes the temperature of 1.0 cm^3 of solution by 1 °C.)

[Ar Na: 23.0, H:1.0; O:16.0]

Pre-calculation

Using 30 cm^3 of 1 mol dm^{-3} HCl solution to react completely with solid NaOH.

Amt of HCl used = 30/1000 x 1 mol = 3.00 x 10^{-2} mol

NaOH is the limiting reagent.

Let amount of NaOH used be 1.00 x 10^{-2} mol

Mass of solid NaOH = 1.00 x 10^{-2} x 40 g
= 0.400 g

Procedure

1. Using a measuring cylinder, place 30 cm^3 of 1 mol dm^{-3} HCl into the styrofoam cup.
2. Measure and record the initial temperature of the HCl solution.
3. Using the electronic weighing balance, weigh accurately about 0.4 g solid NaOH in a clean and dry weighing bottle.
4. Add the solid NaOH into the cup. Stir and record the highest temperature reached.
5. Reweigh the weighing bottle.

Results

Mass of empty dry weighing bottle/g	M
Mass of weighing bottle and solid NaOH/g	M_1
Mass of weighing bottle and residual NaOH/g	M_2
Mass of NaOH added/g	$M_1 – M_2$

Initial Temp/^{0}C	T_1
Highest Temp/^{0}C	T_2
Temperature rise/^{0}C	$T_2 – T_1$

Calculation

Heat evolved = mcΔT

= $(30 \times 4.2 \times T_2 – T_1)$ J

Amt of NaOH used = $(M_1 – M_2)$ / 40 mol

$\Delta H_2 = –(40)(30 \times 4.2 \times T_2 – T_1) / 1000(M_1 – M_2)$ kJ mol^{-1}

[5]

[Total:24]

3 You are provided with the solid **FA 6** and solution **FA 7**.

You are to perform the tests below and record your observations in the spaces provided. Your answers should include

- details of colour changes and precipitates formed;
- the names of any gases evolved **and** details of the test used to identify each one.

You should indicate clearly at what stage in a test a change occurs.

If it appears that no reaction has taken place this should be clearly recorded.

Rinse and reuse test-tubes where possible.

Marks are **not** given for chemical equations.

No additional or confirmatory tests for ions present should be attempted.

Candidates are reminded that definite deductions may be made from tests where there appears to be no reaction.

(a) **FA 6** contains one cation and one anion.

	Test	*Observation*
(i)	To half a spatula-full of **FA 6** in a test-tube add excess dilute sulfuric acid. Keep the solution for test **(iii)** and **(iv)**.	• **effervescence observed** • **colourless, odourless and acidic gas evolved which gives a white ppt with $Ca(OH)_2$** • **gas is CO_2** **green solid dissolved to give blue solution**
(ii)	Place a spatula-full of **FA 6** in a test-tube and heat strongly.	• **green solid turn black on heating** • **colourless, odourless and acidic gas evolved which gives a white ppt with $Ca(OH)_2$** **gas is CO_2**
(iii)	To 1 cm depth of the solution from **(i)** in a test-tube, add a few drops of aqueous sodium hydroxide Then add excess aqueous sodium hydroxide.	• **pale blue ppt formed** • **insoluble in excess NaOH**
(iv)	To 1 cm depth of the solution from **(i)** in a test-tube, add a few drops of aqueous ammonia. Then add excess aqueous ammonia.	• **blue ppt formed** • **soluble in excess NH_3 giving dark blue solution**

The cation present in **FA 6** is Cu^{2+}

The anion present in **FA 6** is CO_3^{2-}

FA 7 contains one cation and two anions.

	Test	*Observations*
(v)	To 1 cm depth of **FA 7** in a test-tube, add a few drops of aqueous sodium hydroxide. Then add excess aqueous sodium hydroxide. Warm the mixture.	• no ppt formed • no gas (NH_3) evolved
(vi)	To 1 cm depth of **FA 7** in a test-tube, add a few drops of aqueous ammonia Then add excess aqueous ammonia.	• no ppt formed
(vii)	To 1 cm depth of **FA 7** in a test-tube, add aqueous silver nitrate, followed by aqueous ammonia.	• yellow ppt formed insoluble in excess NH_3
(viii)	To half a spatula-full of **FA 6** in a test-tube, add 3 cm depth of **FA 7**.	• effervescence observed • colourless, odourless and acidic gas evolved which gives a white ppt with $Ca(OH)_2$ • gas is CO_2 • brown solution formed • white/greyish white ppt formed
	Then add 1 cm depth of aqueous sodium thiosulfate.	• brown solution decolourise

One anion present in **FA 7** is I^-

With reference to tests **(v)**, **(vi)** and **(viii)**, suggest the identity of the cation present in **FA 7**.

H^+

The second anion is suspected to be the sulfate ion.

(ix) Suggest a test to verify the presence of sulfate ion in **FA 7**. Carry out the test and record your results in the space below.

Test	*Observations*
• To 1 cm depth of **FA 7** in a test-tube, add aqueous barium nitrate, followed by aqueous nitric acid.	• **white ppt formed insoluble in excess nitric acid.**

[11]

(b) **FA 8** is a solution that contains the Cr^{3+}, Mg^{2+} and Cl^{-} ions.

Plan a sequence of steps by which the three ions could be separated so that each ion is present in a separate precipitate. For each of the steps, you are to specifiy the location of the ions.

You may assume that the usual bench reagents and apparatus are available for use.

1. **Add excess NaOH(aq). Carry out filtration to separate the insoluble ppt from the solution**
   Residue: Mg^{2+} as $Mg(OH)_2$
   Filtrate: Cr^{3+} as $[Cr(OH)_6]^{3-}$, Cl^-

2. **Add sufficient HNO_3 to regenerate the ppt which is soluble in excess NaOH. Carry out filtration to separate the insoluble ppt from the solution**
   Residue: Cr^{3+} as $Cr(OH)_3$
   Filtrate: Cl^-

3. **Add excess acidified $AgNO_3$. Carry out filtration to separate the insoluble ppt (AgCl) from the solution**

[5]
[Total: 16]

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

anion	*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)	SO_2 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) Colours 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

Apparatus List

1. In addition to the fittings ordinarily contained in a chemical laboratory, the apparatus, and materials specified below will be necessary.

2. Pipette fillers (or equivalent safety devices), safety goggles and disposable plastic gloves should be used where necessary.

3. *For each candidate*

For each candidate
2 x burettes (50 cm^3);
1 x pipette (25.0 cm^3);
1 x pipette filler (students bring their own);
1 x retort stands and burette clamps;
1 x 25 cm^3 measuring cylinder;
2 x funnels (for filling burette);
2 x 250 cm^3 conical flasks;
1 x 250 cm^3 beaker
1 x white tile;
1 x thermometer with range -10 °C to +110 °C, graduated to 1 °C;
1 x Styrofoam cup
5 plastic dropping pipettes;
9 test-tubes (students bring their own);
1 x test-tube rack;
1 x test-tube holder;
1 x delivery-tube
1 x small spatula
1 x wash bottle containing deionised water;
1 x Bunsen burner;
1 x lighter (per bench)
wooden splinters
red and blue litmus paper
filter paper strips
paper towels

Additional pipette filler, test-tubes and dropping pipettes should be available.

Chemicals Required

Question 1-3:

Label	**Per candidate**	**Identity**	**Notes (preparation)**
FA 1	120 cm^3	0.02 mol dm^{-3} potassium managanate (VII)	
FA 2	100 cm^3	0.940 mol dm^{-3} ammonium iron (II) sulfate	Dissolve 7.36g of $(NH_4)_2SO_4.FeSO_4.6H_2O$ in 200 cm^3 of solution made with 20% 1.0 mol dm^{-3} H_2SO_4 and 80% water mixture.
FA 3	100 cm^3	1.0 mol dm^{-3} sulfuric acid	
FA 4	100 cm^3	1.8 mol dm^{-3} HCl	
FA 5	70 cm^3	2.00 mol dm^{-3} NaOH	
FA 6	Solid	Solid basic copper (II) carbonate	About 4 spatula (spoonful) per candidate
FA 7	20 cm^3	HI (aq)	Freshly prepared (per shift) 1:1 portion of (1) 0.25 $moldm^{-3}$ of KI (41.5g/dm^3) (2) 0.5 $moldm^{-3}$ of H_2SO_4 (aq)