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DUNMAN HIGH SCHOOL Preliminary Examination 2018 Year 6

H2 CHEMISTRY

Paper 1 Multiple Choice

9729/01 24 September 2018 1 hour

Additional Materials: Data Booklet **Optical Mark Sheet**

INSTRUCTIONS TO CANDIDATES

- 1 Write your **name**, **index number** and **class** on this question paper and the OTAS Mark Sheet.
- 2 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 **Optical Mark Sheet.**

- 3 Each correct answer will score one mark. A mark will not be deducted for wrong answer.
- 4 Any rough working should be done in this booklet.

- 5 The use of an approved scientific calculator is expected, where appropriate.
- 6 On the OTAS Mark Sheet, please shade the code as "Class/Index number".

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For illustration only:	I 3	3 0	1	2	3	4	5	6	7	8	9
A student from class 6C38, with index number 02, should shade "3802".	D E E	8	1	2	3	4	5	6	7	8	9
	X (1	2	3	4	5	6	7	8	9
	N U	2	1	2	3	4	5	6	7	8	9
	M B	0	1	2	3	4	5	6	7	8	9
	R	A	B	C	D	E	F	G	Н	-	

- 1 Which option contains one mole of the stated particles? $[D = {}^{2}_{1}H]$
 - **A** carbonate ions in 60 g of sodium carbonate
 - **B** neutrons in 1.8 g of heavy water, D₂O
 - **C** electrons in 0.1 mol of OH⁻ ions
 - **D** oxygen atoms in 11.35 dm³ of O_3 , under s.t.p.
- $\mathbf{2}$ NF₃ can be obtained from the reaction between ammonia and fluorine gas.

 $4NH_3 \ \textbf{+} \ 3F_2 \ \rightarrow \ NF_3 \ \textbf{+} \ 3NH_4F$

Which statement about the reaction is correct?

- **A** NH₃ undergoes disproportionation.
- **B** The oxidation number of nitrogen in NF_3 is +3.
- C NH₃ is a stronger oxidising agent than F₂.
- **D** One mole of F_2 loses two moles of electrons.
- **3** Use of the Data Booklet is relevant to this question.

Which statement regarding ${}^{26}Mg^{2+}$ and ${}^{27}Al^{3+}$ ions is true?

- 1 ${}^{26}Mg^{2+}$ has more protons than ${}^{27}Al^{3+}$.
- 2 Both ions have more neutrons than protons in their nuclei.
- 3 Both ions have outer electronic configuration 2s²2p⁶.
- 4 Both ions have the same number of neutrons.
- A 1 and 2 only

- **B** 1 and 3 only
- C
 3 and 4 only
 D
 2, 3 and 4 only

4 Two ideal gases X and Y were placed separately into two bulbs of the same volume and pressure. The density of gas X is three times that of gas Y and the molecular mass of gas X is twice that of gas Y.

What is the ratio of the temperature (in Kelvin) of gas **X** to that of gas **Y** in the two separate bulbs?

- A
 1:3
 B
 1:6

 C
 2:3
 D
 3:2
- **5** A compound has the structure shown.



What are the values of the bond angles x, y and z?

	x	У	z
Α	90°	109.5°	104.5°
В	90°	120°	180°
С	109.5°	109.5°	180°
D	109.5°	120°	104.5°

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

Which graph shows the correct trend when the melting point of the oxide of each of the elements Mg, A*l*, Si and P is plotted against its ionic radius?



7 The graph represents the change in mass that occurs when 1.0 g of powdered magnesium carbonate, MgCO₃, is heated at a temperature, T.



Which graph would be obtained by heating 1.0 g of powdered calcium carbonate, CaCO₃, at the same temperature, T?



8 X_2 , Y_2 and Z_2 are Cl_2 , Br_2 and I_2 but are not necessarily in the given order.

The table below recorded observations when these halogens are separately added to aqueous solutions containing the halide ions followed by the addition of an organic solvent, CCl_4 .

Experiment	Reactants	Observation after shaking with CCl ₄
1	X ₂ (aq) + Y ⁻ (aq)	Violet organic layer seen.
2	Y ₂ (aq) + X ⁻ (aq)	(Observations not recorded)
3	Z ₂ (aq) + X ⁻ (aq)	Orange-red organic layer seen.
4	Z ₂ (aq) + Y ⁻ (aq)	Violet organic layer seen.

Which statement could be deduced from the above experiments, given X_2 (aq) is an orange solution?

- **A** The colour of the organic layer in Experiments 2 and 4 is the same.
- **B** Identity of **Z**₂ is Br₂.
- **C** There is no redox reaction occurring in Experiment 3.
- \mathbf{D} **X**₂ is a stronger oxidising agent than **Z**₂.
- **9** For which process is the enthalpy change always negative?
 - **A** Dissolving an ionic solid in water.
 - **B** Reaction between an acid and a base.
 - **C** Forming gaseous atoms from a diatomic molecule.
 - **D** Synthesising a compound from its elements.
- 10 A rock sample was found to contain isotopes **T** and **U** which are radioactive. Initially, the ratio of the number of atoms of **T** to **U** in the rock sample is 1 : 16. The decay of isotopes **T** and **U** was found to follow first order kinetics. The half–life of **T** is 12 days while that of **U** is 3 days.

How long, in days, will it take for a rock sample to contain a molar ratio of **T** to **U** of 4 : 1?

Α	6	В	12
С	18	D	24

11 The stoichiometry of a reaction is shown by the equation below.

$$\mathbf{L}(g) + \mathbf{M}(g) \rightleftharpoons \mathbf{Q}(g) + \mathbf{R}(g) \qquad \Delta H = -20 \text{ kJ mol}^{-1}$$

Two experiments were carried out in enclosed vessels which the rate of production of **R** was measured. The results are shown in the diagram below.



Which changes in the conditions might explain the results shown?

- 1 Temperature of the vessel is higher in Experiment 2.
- 2 A smaller vessel is used in Experiment 2.
- 3 A catalyst is used in Experiment 2.

Α	1, 2 and 3	В	1 and 2 only
С	2 and 3 only	D	1 only

12 In which reaction is the first reactant **not** acting as a Bronsted-Lowry base?

- **A** <u>NH₃</u> + CH₃Cl \rightarrow CH₃NH₃⁺ + Cl⁻
- **B** OH^- + HSO₄⁻ \rightarrow H₂O + SO₄²⁻
- **C** <u>CH₃OH</u> + HC $lO_4 \rightarrow$ CH₃OH $_2^+$ + C lO_4^-
- **D** <u>HNO₃</u> + H₂SO₄ \rightarrow H₂NO₃⁺ + HSO₄⁻

8

Which statement is correct?

- 1 When calcium nitrate is added into a 1 dm³ solution containing 0.01 mol of fluoride and 0.01 mol of carbonate ions in order to separate fluoride and carbonate ions, calcium fluoride is collected as the filtrate upon filtration.
- 2 Calcium fluoride has a lower molar solubility than calcium carbonate.
- 3 Addition of sodium fluoride to a saturated solution containing calcium fluoride does not change the solubility product of calcium fluoride.

Α	1, 2 and 3 only	В	2 and 3 only
С	1 and 3 only	D	3 only

14 A concentration cell set up is shown below. The net effect of a concentration cell is the same as mixing the two solutions of different concentrations until concentration equilibrium is established.



Which statement is true?

- A The E_{cell} value decreases when small amount of NH₃ (aq) is added to the half-cell **M**.
- **B** The E_{cell} value increases when small amount of KCl (s) is added to the half-cell **N**.
- **C** The electrons flow from half-cell **N** to **M**.
- **D M** is the oxidation half-cell.
- **15** A current of 5 amperes was passed for 5 seconds through a molten salt containing X³⁺ ions. The mass of X deposited was 5 g. If M is the relative molecular mass of X and e is the electronic charge, then an expression of Avogadro Constant is given by

Α	5M 3e	В	<u>125</u> 3Me
С	<u>3e</u> 5M	D	<u>3Me</u> 125

16 The table shows the electronic configuration of three d–block elements in the Periodic Table.

Element	Electronic configuration				
X	[Ar]3d ⁷ 4s ²				
Y	[Ar]3d ⁸ 4s ²				
Z	[Ar]3d ¹⁰ 4s ¹				

Which statement is correct?

- 1 The electronic configuration of central metal ion for $[\mathbf{Y}(CN)_6]^{4-}$ is $[Ar]3d^7$.
- 2 Upon reduction from $\mathbf{Z}Cl_2(aq)$ to $[\mathbf{Z}Cl_2]^-(aq)$, a colourless solution will be formed.
- 3 The E^{\ominus} value of X^{3+}/X^{2+} is likely to be less positive than that of Z^{3+}/Z^{2+} .
- 4 **X** is likely to form an oxoanion of formula XO_4^{2-} .

Α	1, 2 and 4 only	В	2 and 3 only
С	1 and 4 only	D	3 and 4 only

17 Chloralose is a drug that is commonly used in neuroscience and veterninary medicine as an anesthetic.



chloralose

How many stereoisomers does chloralose have?

Α	16	В	32
С	64	D	128

18 2,2–dimethylpropane reacts with chlorine gas in the presence of ultraviolet light to give a mixture of products.

Which statement regarding this reaction is correct?

- A Only one mono-substituted product is formed.
- **B** Only the propagation step involves C–C*l* bond formation.
- **C** Both propagation and termination steps produce hydrogen chloride.
- **D** Only the initiation step of the mechanism involves homolytic fission.
- **19** Compound **Z** can be obtained by a two-step process involving intermediate **X**.



20 The flow chart below shows a series of reactions.



Which class of compound are P, Q and R?

	Р	Q	R
Α	halogenoalkane	primary alcohol	carboxylic acid
В	halogenoalkane	primary alcohol	aldehyde
С	primary alcohol	aldehyde	carboxylic acid
D	primary alcohol	halogenoalkane	aldehyde



11

21 Which of the following synthetic routes is correct?

22 Which row shows the given molecules arranged in order of increasing pK_a values?

	smallest p <i>K</i> a value		largest p <i>K</i> a value
A	СООН	СН3	ОН
в	NO ₂	ОН	СН ₂ ОН
с	CF ₃ CH ₂ OH	НСООН	CH₃OH
D	NO ₂	СН3	О)—он

23 Which reagent is able to distinguish between the two compounds below?

	CH₃CH(OH)CH(OH)CH ₃		HOCH ₂ CH ₂ OCOCH ₃
Α	Hot alkaline I₂(aq)	в	Hot acidified K ₂ Cr ₂ O ₇ (aq)
С	2,4-DNPH	D	Neutral aqueous FeCl ₃

24 Which products are formed when butanal reacts with Fehling's solution?

- **A** Cu_2O and $CH_3CH_2COO^-$
- **B** Cu₂O and CH₃CH₂CH₂CH₂OH
- C Cu₂O and CH₃CH₂CH₂COO⁻
- **D** CuO and CH₃CH₂CH₂COO⁻

25 Which synthetic route will give the following ester as the product?



- Which compound has the lowest pK_b value?
- $\mathbf{A} \qquad \overset{\mathbf{O}}{\overset{\mathbf{H}}{\underset{\mathbf{H}_{3}\mathbf{C}}{=}\mathbf{C}-\mathsf{NH}-\mathsf{CH}_{2}\mathsf{CH}_{3}}}$
- **B** (CH₃CH₂)₂NH

26

c $N-CH_2CH_3$

27 The diagram below shows a sequence of reactions.



How can the three reactions be classified?

	Reaction 1	Reaction 2	Reaction 3
Α	hydrolysis	substitution	acid-base
в	hydrolysis	addition	acid-base
С	acid-base	substitution	hydrolysis
D	acid-base	addition	hydrolysis

28 The molecule shown is used in the treatment of Parkinson's disease.



Which statement about the molecule is correct?

- 1 It is likely to be soluble in water due to zwitterion formation.
- 2 Two Br atoms will be incorporated when aqueous bromine is added.
- 3 One mole of molecule reacts with three moles of sodium carbonate to form a salt.

Α	1 only	В	1 and 2 only
С	1 and 3 only	D	1, 2 and 3 only

29 Nucleophilic substitution of 2–chloro–2–methylpropane follows an S_N1 mechanism.

 $(CH_3)_3CCl + OH^- \rightarrow (CH_3)_3COH + Cl^-$

 $S_N 1$ reactions take place more rapidly in polar solvents.

Which solvent should be used?

- 1 water
- 2 hexane
- 3 ethanol
- 4 tetrachloromethane
- A
 1 and 2 only
 B
 1 and 3 only
- **C** 1, 2 and 4 only **D** 1, 3 and 4 only

30 Lysine is an amino acid.



lysine

Which structure is predominant when lysine is in aqueous solution at pH 5?

$$A \qquad \begin{array}{c} H_{3} \stackrel{+}{N} CHCO_{2}H \\ (CH_{2})_{4} \\ + NH_{3} \end{array}$$

$$B \qquad \begin{array}{c} H_{2} NCHCO_{2}^{-} \\ (CH_{2})_{4} \\ + NH_{3} \end{array}$$

$$C \qquad \begin{array}{c} H_{3} \stackrel{+}{N} CHCO_{2}^{-} \\ (CH_{2})_{4} \\ + NH_{2} \end{array}$$

$$D \qquad \begin{array}{c} H_{3} \stackrel{+}{N} CHCO_{2}^{-} \\ (CH_{2})_{4} \\ + NH_{3} \end{array}$$

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2018 DHS YEAR 6 H2 CHEMISTRY (9729) Preliminary Examination Paper 1 MCQ – Answers

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
С	В	D	С	D	Α	Α	Α	В	D	С	Α	D	D	Α	В	С	Α	С	Α
Ŭ			V		~	~	~	D	D	v	~	U		~		v	~	v	

21	22	23	24	25	26	27	28	29	30
D	В	Α	С	D	В	С	Α	В	D

|--|



DUNMAN HIGH SCHOOL Preliminary Examination 2018 Year 6

H2 CHEMISTRY

Paper 2 Structured Questions

9729/02 13 September 2018 2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

INSTRUCTIONS TO CANDIDATES

- 1 Write your **name**, **index number** and **class** on this cover page.
- 2 Write in dark blue or black pen.
- 3 You may use an HB pencil for any diagrams or graphs.
- 4 Do not use staples, paper clips, glue or correction fluid.
- 5 Answer **all** questions in the spaces provided on the Question Paper.

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

You are advised to show all workings in calculations.

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

For Exam	iner's Use
Question No.	Marks
1	13
2	12
3	25
4	10
5	15
Total	75

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

- 1 Isoprene, E, is an organic compound that could be used to synthesise limonene, which is commonly used in fragrances.
 - (a) E can be synthesised from 3–methylbut–1–ene, A, in a 4–step process as follows.



(i) **B** is a major product of step **I**.

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



[3]

(b) The following reaction shows an alternative route to form intermediates for the synthesis of isoprene, **E**.



- 1. Delocalisation of unpaired electron forming •Z.
- 2. •**Z** reacts with Cl_2 to form **Z** and a radical.

The structures of Z, •G and •Z are as follows.



Use the information above to draw out the mechanism for the conversion of $\cdot G$ to **Z**. You are advised to use skeletal or structural formula for all species, so that it is clear which bonds are broken and which are formed. Indicate any unpaired electrons by a dot (\cdot). Use curly half-arrows to indicate the movement of unpaired electrons.

(iv) Describe a chemical test that could distinguish between **A** and **F**. State reagents, conditions and observations clearly in your test.

 2 (a) Fig 2.1 shows a bar chart of the third ionisation energy (3rd IE) of nine consecutive elements (J to R) in Periods 2 and 3 of the Periodic Table.



(b) Fig 2.2 shows another bar chart of the logarithm of all the ionisation energies, log (IE), of an element **S** against the number of electrons removed.



(i) Explain the general trend shown in Fig 2.2.

(ii) On the axes provided, draw and label the orbital which the fifth electron is removed from.



[1]

The Periodic Table shows helium placed at the top of Group 18.
(i) Suggest why the element helium could be placed at the top of Group 2.
[1
(ii) Suggest why the element helium is not placed at the top of Group 2, by comparing one physical property. Explain your answer.
[2
[Total: 12

(c)

- 3 The ions of transition elements form *complexes* by reacting with *ligands*.
 - (a) (i) State what is meant by the terms:
 - Complex
 [1]
 Ligand
 [1]
 - (ii) Two of the complexes formed by copper are Cu(H₂NCH₂CH₂NH₂)₂(OH)₂ and CuCl₄²⁻. Draw three–dimensional diagrams of their structures in the boxes below and name their shapes.

Cu(H ₂ NCH ₂ CH ₂ NH ₂) ₂ (OH) ₂	CuCl4 ^{2–}
Shape:	Shape:

[3]

(iii) State the oxidation number of Cu in $Cu(H_2NCH_2CH_2NH_2)_2(OH)_2$.

.....[1]

(iv) Platinum forms square–planar complexes, in which all four ligands lie on the same plane as the Pt atom. There are two isomeric complexes with the formula $Pt(NH_3)_2Cl_2$. Suggest the structures of the two isomers.

isomer 1	isomer 2

[3]

By comparison with a similar type of isomerism in organic chemistry, suggest the type of isomerism shown here and label the isomers above.

Гуре of isomerism:[1]

- (b) Copper forms two series of compounds, one containing copper(II) ions and the other containing copper(I) ions.
 - (i) Complete the electronic configuration of these species.

Cu: [Ar].....[1]

Cu(I): [Ar].....[1]

- (ii) Explain why the following statements are true.
 - Copper metal is a better electrical conductor than calcium metal.
 - Copper(II) salts are generally coloured.

 (c) Copper(I) oxide and copper(II) oxide can both be used in the ceramic industry to give blue, green or red tints to glasses, glazes and enamels.

The table lists the ΔH_{f}^{Θ} values for some compounds.

Compound	$\Delta H_{\rm f}^{\Theta}$ / kJ mol ⁻¹
Cu ₂ O (s)	-168.6
CuO (s)	-157.3
Cu(NO ₃) ₂ (s)	-302.9
NO ₂ (g)	+33.2

(i) Copper(II) oxide can be produced in a pure form by heating copper(II) nitrate. Use suitable $\Delta H_{\rm f}^{\Theta}$ values from the table to calculate the $\Delta H_{\rm r}^{\Theta}$ for this reaction.

$$Cu(NO_3)_2 (s) \rightarrow CuO (s) + 2NO_2 (g) + \frac{1}{2}O_2(g)$$

[1]

(ii) Copper(I) oxide can be produced from copper(II) oxide.

2CuO (s)
$$\rightleftharpoons$$
 Cu₂O (s) + $\frac{1}{2}$ O₂(g) reaction 1

Suggest whether a low or high temperature would favour the production of copper(I) oxide. Explain your reasoning with appropriate calculation.

 	 	 	 	 		••••	 	 ••••	 	 	 	 	••••		
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 	 	 	 	 ••••	••••	••••	 	 ••••	 	 	 	 	••••		
 	 	 	 	 			 	 	 	 	 	 		[2]

(iii) For reaction 1, ΔS^{\ominus} = +93.6 J K⁻¹ mol⁻¹. Use this value and your answer in (c)(ii) to calculate ΔG^{\ominus} .

[1]

(iv) Write the expression of the equilibrium constant, K_c , for reaction 1. State the units.

[2]

(v) For any reaction, ΔG^{\ominus} and the equilibrium constant, K_c , are related according to the equation,

 ΔG^{\ominus} = -2.303RT log K_{c}

Use this equation to calculate a value of K_c for reaction 1.

[1]

(d) In 1977, Kutal *et al.* conducted a detailed investigation into the photoassisted (solar energy) isomerisation of norbornadiene to quadricyclene.



In the presence of copper(I) salts as a catalyst, the isomerisation was reversible with the release of approximately 1.08 kJ of energy per gram of quadricyclene.

(i) State the type of isomerism that has occurred when norbornadiene is converted to quadricyclene.

.....[1]

(ii) Based on the above given information, suggest a possible practical use of this norbornadiene–quadricyclene interconversion system. Explain how this system can work to fulfil that practical use.



4 (a) Cyclohexene can react with Br_2 to form 1,2–dibromocyclohexane as shown below.



An experiment was carried out where the cyclohexene was titrated with the Br_2 generated by the oxidation of Br^- in the electrolytic cell:

$$2Br^- \rightarrow Br_2 + 2e^-$$

The experiment was carried out at a constant current as shown in the figure below.

The initial solution contains an unknown quantity of cyclohexene and a large amount of Br⁻ dissolved in a suitable inert solvent that does not participate in the reaction.

The figure below consists of electrolytic and galvanic cells shown on the left-hand and right-hand sides respectively.



 Br_2 generated from electrolysis, reacts with the cyclohexene. At the end–point, all the cyclohexene has reacted and the concentration of Br_2 suddenly rises, signalling the end of the reaction.

(i) State whether Br_2 is generated at the cathode or anode of the electrolytic cell.

.....[1]

(ii) The rise in the concentration of Br₂ is detected by measuring the current between the two Pt detector electrodes in the galvanic cell using the microammeter. The detector current flows by virtue of the reactions:

Detector anode: $2Br^- \rightarrow Br_2 + 2e^-$

Detector cathode: $Br_2 + 2e^- \rightarrow 2Br^-$

Suggest why there is no current detected before equivalence point is reached.

In an experiment, 2 cm³ of 0.600×10^{-3} g cm⁻³ cyclohexene is to be titrated.

(iii) Calculate the amount, in moles, of the cyclohexene used.

(iv) The experiment was carried out with a constant current of 5×10^{-3} A for the electrolytic cell. Determine the time taken for complete titration.

(b) Br atoms introduced artificially by industrial activities raise concerns of ozone destruction.

15

One method that is used to determine the concentration of ozone in the ozone layer is to pass air through alkaline potassium iodide and to measure the amount of iodine liberated.

The following reaction takes place.

$$O_3 + H_2O + 2I^- \rightarrow O_2 + I_2 + 2OH^-$$

The iodine liberated is measured using a platinum electrode immersed in alkaline potassium iodide solution against a standard silver/silver chloride reference electrode. The e.m.f. of the system, in volts, is given by the equation.

 $E = 0.32 + 0.029 \log_{10} [I_2]$, where $[I_2]$ is expressed in mol dm⁻³.

To determine ozone in the atmosphere, a light–weight balloon containing the electrochemical cell was released into the atmosphere. The data collected was then transmitted to the ground station for further processing.

A sample of air was passed through 10 cm^3 of alkaline potassium iodide. The pressure of this sample of air was found to be 0.24 atm measured at room temperature. The potential of the platinum electrode immersed into this solution against the standard silver/silver chloride electrode was 0.21 V.

(i) Calculate the concentration of iodine liberated.

(ii) Hence, calculate the volume of ozone present in this sample of air.

(c) Halogens form binary compounds with hydrogen known as hydrogen halides. State and explain how the thermal stability of hydrogen halides varies down the Group.

 5 (a) Nucleophilic addition of an alcohol to aldehydes and ketones yield hemiacetals. The reaction is slow and reversible under neutral conditions. Upon further reaction with alcohols in the presence of acids as catalyst, hemiacetals can form acetals.



The acid-catalysed acetal formation from the hemiacetal shown below, involves 4 steps.



- 1. Protonation of the hydroxyl group of the hemiacetal.
- 2. Loss of water leads to an unstable and highly reactive oxonium ion.



oxonium ion

- 3. Nucleophilic attack of alcohol, R_3OH , on the oxonium ion to give $HOR_3 OR_3$
- 4. Loss of a proton to give the acetal.

(i) Draw the mechanism as described above, showing clearly the flow of electrons.

(ii) State the purpose of removing water from the reaction mixture.

.....[1]

(b) Tamiflu is the anti-influenza drug currently being used to treat 'Bird–flu'. It can be synthesised from Shikimic acid, which occurs naturally in star anise.



Shikimic acid

Part of the synthetic route is shown below. Formation of acetals between selected -OH groups of Shikimic acid and ketones helps to control which of the -OH groups reacts to synthesise **C** from **B**.



(i) Draw the structures of **B** and **C** in the boxes provided above.
20

(ii) Explain why **B** was formed from **A** instead of Shikimic acid directly.

(c) Like Shikimic acid, methanoic acid occurs naturally in ants. It is a weak acid and dissociates according to the equation shown.

HCOOH (aq) \rightleftharpoons HCOO⁻ (aq) + H⁺ (aq) $K_a = 1.60 \times 10^{-4} \text{ mol dm}^{-3}$

(i) Explain what is meant by the term pK_a as applied to methanoic acid.

[2]	 	

A flask contains 0.0100 mol of methanoic acid dissolved in 250 cm³ of water.

(ii) Calculate the pH of this solution.

[2]

[1]

(iii) Hence, calculate the degree of dissociation, α , of methanoic acid in this solution.

(d) Salicylic acid occurs naturally in plants.



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Suggested solutions



DUNMAN HIGH SCHOOL Preliminary Examination 2018 Year 6

H2 CHEMISTRY

Paper 2 Structured Questions

9729/02

2 hours

13 September 2018

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

INSTRUCTIONS TO CANDIDATES

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For Examiner's Use		
Question No.	Marks	
1	13	
2	12	
3	25	
4	10	
5	15	
Total	75	

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

- 1 Isoprene, E, is an organic compound that could be used to synthesise limonene, which is commonly used in fragrances.
 - (a) E can be synthesised from 3–methylbut–1–ene, A, in a 4–step process as follows.



(i) **B** is a major product of step **I**.

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



(ii) Suggest the reagents and conditions for steps II and III.

step II : alcoholic NaOH heat under reflux

step III : cold alkaline KMnO₄

(iii) Predict, with reasoning, whether the mixture of products formed in step I is optically active.

[2] The reaction mixture in **B** is <u>not optically active</u>. During electrophilic addition, a <u>trigonal planar carbocation</u> is formed. *Cl⁻* has a <u>50% chance</u> each of <u>attacking the carbocation from the top or bottom of the plane</u>. Hence, resulting in a <u>racemic mixture</u> formed.

[3]

[2]



(b) The following reaction shows an alternative route to form intermediates for the synthesis of isoprene, **E**.



(i) State the reagents and conditions used to form **F** and **G** from **A**.

Limited Cl₂, uv

(ii) Predict the ratio in which **F** and **G** will be formed.

[1]

[2]

[1]

F : **G** 6 : 1

(iii) Z was one of the other products formed in the reaction in (b). It was suggested that the radical, •G, is involved in the formation of Z.

The mechanism of **•G** converting to **Z** is thought to involve 2 steps.

- 1. Delocalisation of unpaired electron forming •Z.
- 2. •**Z** reacts with Cl_2 to form **Z** and a radical.

The structures of Z, •G and •Z are as follows.



Use the information above to draw out the mechanism for the conversion of $\cdot G$ to Z. You are advised to use skeletal or structural formula for all species, so that it is clear which bonds are broken and which are formed. Indicate any unpaired electrons by a dot (•). Use curly half-arrows to indicate the movement of unpaired electrons.



(iv) Describe a chemical test that could distinguish between **A** and **F**. State reagents, conditions and observations clearly in your test.

Add 1 cm³ of **A** and **F** each into separate test tubes. Add <u>**NaOH**(aq)</u> into both test tubes and <u>**heat**</u>, <u>**followed** by</u> adding excess <u>**HNO**₃(aq)</u> then add <u>**AgNO**₃(aq)</u>.

<u>F</u> : <u>White ppt</u> of AgC/ seen <u>A</u> : <u>no white ppt</u> seen

[Total: 13]

[1]

[1]

2 (a) Fig 2.1 shows a bar chart of the third ionisation energy (3rd IE) of nine consecutive elements (J to R) in Periods 2 and 3 of the Periodic Table.

3rd IE

(i) Write an equation for the third ionisation energy of element J.

 $J^{2+}(g) \rightarrow J^{3+}(g) + e^{-1}$

(ii) Identify element N.

Mg

- (iii) Using your answers in (a)(i), (a)(ii) and the electronic configurations of the species involved, explain the following features of Fig 2.1.
 - 1. The significantly higher 3rd IE of **N** compared to **O**.

Electronic configuration: N^{2+} (1s²2s²2p⁶); O^{2+} ([Ne]3s¹)

The 3rd ionisation energy of N involves the removal of a 2p electron

The 3rd ionisation energy of **O** involves the removal of a <u>3s</u> electron

A <u>significantly larger amount of energy</u> is required to remove the <u>2p</u> electron in N^{2+} which is much more strongly held by the nucleus as it is found in an <u>inner</u> <u>quantum shell</u> compared to <u>3s</u> electron in O^{2+} .

Hence 3^{rd} ionisation energy of **N** is significantly higher than that of **O**.

2. The lower 3^{rd} IE of **Q** than **P**.

Electronic configuration: P²⁺ ([Ne]3s²); Q²⁺ ([Ne]3s²3p¹)

The 3^{rd} ionisation energy of P involves the removal of a <u>3s</u> electron The 3^{rd} ionisation energy of Q involves the removal of a <u>3p</u> electron <u>Smaller</u> amount of energy is required to remove the <u>3p</u> electron in Q^{2+} which is of <u>higher energy</u> than <u>3s</u> electron in P^{2+} . (The 3p electron also experiences increased screening effect provided by the filled 3s subshell.) Hence 3^{rd} ionisation energy of **Q** is lower than that of **P**

(b) Fig 2.2 shows another bar chart of the logarithm of all the ionisation energies, log (IE), of an element **S** against the number of electrons removed.



(i) Explain the general trend shown in Fig 2.2.

In an atom of S,

[2]

[4]

Number of protons unchanged \Rightarrow <u>nuclear charge unchanged</u> As electrons are removed from the atom, the <u>increasingly positively charged</u> <u>ion</u> holds the remaining electrons <u>more strongly</u> hence <u>more energy</u> is required to remove the remaining electrons resulting in higher I.E Thus, successive I.E shows an increasing trend.

(ii) On the axes provided, draw and label the orbital which the fifth electron is removed from.

[1]





- (c) The Periodic Table shows helium placed at the top of Group 18.
 - (i) Suggest why the element helium could be placed at the top of Group 2.

Helium has <u>2 valence electrons</u> like all other Group 2 elements.

(ii) Suggest why the element helium is not placed at the top of Group 2, by comparing **one** physical property. Explain your answer.

[2]

[1]

Helium atoms are held by <u>weak instantaneous dipole induced dipole</u> <u>interactions</u> while within group 2 elements exist <u>strong electrostatic forces</u> <u>of attraction between cations and a sea of delocalised electrons</u>.

Hence, helium has <u>low melting/boiling point</u> and it <u>exist as a gas</u> while group 2 elements has <u>high melting/boiling point and exist as a solid</u> at room temperature. Include energy

OR

Hence, <u>helium</u> is a <u>non-conductor of electricity</u> due to (<u>absence of</u> <u>mobile/delocalised electrons</u>) while <u>group 2 elements</u> are <u>good conductor</u> of <u>electricity</u> due to (<u>presence of delocalised electrons</u>).

[Total: 12]

- **3** The ions of transition elements form *complexes* by reacting with *ligands*.
 - (a) (i) State what is meant by the terms:

Complex

Ligand

[2]

A complex is formed when a **metal ion or atom** forms dative covalent or **coordinate bonds** with **surrounding ion or molecules**.

A ligand is a neutral molecule or an anion containing at least one atom with a lone pair of electrons that can be donated into low lying vacant orbital of metal atom/ion to form a coordinate bond.

(ii) Two of the complexes formed by copper are Cu(H₂NCH₂CH₂NH₂)₂(OH)₂ and CuCl₄²⁻. Draw three–dimensional diagrams of their structures in the boxes below and name their shapes.

Cu(H ₂ NCH ₂ CH ₂ NH ₂) ₂ (OH) ₂	CuCl ₄ ^{2–}	
Shapa	Shano:	
	onape.	[3]

 $Cu(H_2NCH_2CH_2NH_2)_2(OH)_2$



CuC*l*4^{2–} Shape: tetrahedral or square planar



(iii) State the oxidation number of Cu in $Cu(H_2NCH_2CH_2NH_2)_2(OH)_2$.

+2

[1]

(iv) Platinum forms square–planar complexes, in which all four ligands lie on the same plane as the Pt atom. There are two isomeric complexes with the formula $Pt(NH_3)_2Cl_2$. Suggest the structures of the two isomers.



By comparison with a similar type of isomerism in organic chemistry, suggest the type of isomerism shown here and label the isomers above.

Type of isomerism: Cis-trans isomerism

[4]

- (b) Copper forms two series of compounds, one containing copper(II) ions and the other containing copper(I) ions.
 - (i) Complete the electronic configuration of these species.
 - Cu [Ar].....
 - Cu(I) [Ar].....
 - Cu [Ar] 3d¹⁰ 4s¹ Cu(I) [Ar] 3d¹⁰
 - (ii) Explain why the following statements are true.

Copper metal is a better electrical conductor than calcium metal.

Copper(II) salts are generally coloured.

[3]

[1]

[2]

Copper metal are better electrical conductor because both **4s and 3d valence** electrons are available for delocalisation. This increases the number of mobile charge carriers which in turn increases the conductivity of copper metal.

In the presence of ligands, the **degenerate d orbitals are split into two groups of orbital with different energies**. When white light shines on the complex, a d electron **undergoes d-d transition and is promoted to a higher energy partially filled or empty d orbital**. During the transition, the **d electron absorbs a quantum/photon of light of certain wavelength** from the visible region of the electromagnetic spectrum. The **colour observed is the colour of transmitted light** which is a mixture of remaining wavelengths that have not been absorbed. This colour is the complementary colour of the absorbed light.

(c) Copper(I) oxide and copper(II) oxide can both be used in the ceramic industry to give blue, green or red tints to glasses, glazes and enamels.

Compound	∆ <i>H</i> _f ⊖ / kJ mol⁻¹
Cu ₂ O (s)	-168.6
CuO (s)	-157.3
Cu(NO ₃) ₂ (s)	-302.9
NO ₂ (g)	+33.2

The table lists the $\Delta H_{\rm f}^{\Theta}$ values for some compounds.

(i) Copper(II) oxide can be produced in a pure form by heating copper(II) nitrate. Use suitable ΔH_{f}^{Θ} values from the table to calculate the ΔH_{r}^{Θ} for this reaction.

$$Cu(NO_3)_2(s) \rightarrow CuO(s) + 2NO_2(g) + \frac{1}{2}O_2(g)$$

$$\Delta H^{\ominus}_{r} = -157.3 + 2(33.2) + 0 - (-302.9)$$

= +212 kJ mol⁻¹

(ii) Copper(I) oxide can be produced from copper(II) oxide.

2CuO (s)
$$\rightleftharpoons$$
 Cu₂O (s) + $\frac{1}{2}$ O₂(g) reaction 1

Suggest whether a low or high temperature would favour the production of copper(I) oxide. Explain your reasoning with appropriate calculation.

 $\Delta H^{\ominus}_{r} = -168.6 - 2(-157.3)$ = +146 kJ mol⁻¹

Since the production of copper(I) oxide from copper(II) oxide is an **endothermic process**, it will be favoured by **high temperature** as predicted by **Le Chatelier's Principle**. The equilibrium will **shift to the right** to counter the high temperature.

(iii) For reaction 1, ΔS^{\ominus} = +93.6 J K⁻¹ mol⁻¹. Use this value and your answer in (c)(ii) to calculate ΔG^{\ominus} .

 $\Delta G^{\ominus} = 146 - (298)(0.0936)$ = +118.1 kJ mol⁻¹ = +118 kJ mol⁻¹

(iv) Write the expression of the equilibrium constant, K_c , for reaction 1. State the units.

 $K_{\rm c} = [O_2]^{1/2}$ Units: mol¹/₂ dm⁻³/₂

(v) For any reaction, ΔG^{\ominus} and the equilibrium constant, K_c , are related according to the equation,

$$\Delta G^{\ominus} = -2.303 \text{RT} \log K_{c}$$

Use this equation to calculate a value of K_c for reaction 1.

$$\log K_{\rm c} = \frac{-118.1 \times 10^3}{(2.303)(8.31)(298)} = -20.71$$
$$K_{\rm c} = 1.95 \times 10^{-21}$$

[2]

[1]

[2]

[1]

(d) In 1977, Kutal *et al.* conducted a detailed investigation into the photoassisted (solar energy) isomerisation of norbornadiene to quadricyclene.



In the presence of copper(I) salts as a catalyst, the isomerisation was reversible with the release of approximately 1.08 kJ of energy per gram of quadricyclene.

(i) State the type of isomerism that has occurred when norbornadiene is converted to quadricyclene.

Functional group isomerism

(ii) Based on the above given information, suggest a possible practical use of this norbornadiene–quadricyclene interconversion system. Explain how this system can work to fulfil that practical use.

[2]

[1]

This system can potentially work as a solar energy storage system. Norbornadiene is first irradiated with solar energy and converted to quadricyclene. Energy can be released when quadricyclene is reacted with copper(I) salts. This means that solar energy can be stored in the covalent bonds of quadricyclene.

[Total: 25]

4 (a) Cyclohexene can react with Br_2 to form 1,2–dibromocyclohexane as shown below.



An experiment was carried out where the cyclohexene was titrated with the Br₂ generated by the oxidation of Br⁻ in the electrolytic cell:

$$2Br^- \rightarrow Br_2 + 2e^-$$

The experiment was carried out at a constant current as shown in the figure below.

The initial solution contains an unknown quantity of cyclohexene and a large amount of Br⁻ dissolved in a suitable inert solvent that does not participate in the reaction.

The figure below consists of electrolytic and galvanic cells shown on the left-hand and right-hand sides respectively.



Br₂ generated from electrolysis, reacts with the cyclohexene. At the end–point, all the cyclohexene has reacted and the concentration of Br₂ suddenly rises, signalling the end of the reaction.

(i) State whether Br₂ is generated at the cathode or anode of the electrolytic cell.

Anode

[1]

(ii) The rise in the concentration of Br₂ is detected by measuring the current between the two Pt detector electrodes in the galvanic cell using the microammeter. The detector current flows by virtue of the reactions:

Detector anode: $2Br^- \rightarrow Br_2 + 2e^-$

Detector cathode: $Br_2 + 2e^- \rightarrow 2Br^-$

Suggest why there is no current detected before equivalence point is reached. [1]

Both Br₂ and Br⁻ must be present for the detector half–reactions to occur.

Prior to the equivalence point, there is Br^- but <u>no Br_2 is present for reduction</u> <u>at the detector cathode</u> as any Br_2 formed would have reacted with cyclohexene.

In an experiment, 2 cm^3 of 0.600 x $10^{-3} \text{ g cm}^{-3}$ cyclohexene is to be titrated.

(iii) Calculate the amount, in moles, of the cyclohexene used.

[1]

mass of cyclohexene = $2 \times 0.600 \times 10^{-3}$ = 1.20×10^{-3} g

number of moles of cyclohexene = $\frac{1.20 \times 10^{-3}}{82.0}$ = **1.46 x 10^{-5 mol**

(iv) The experiment was carried out with a constant current of 5 x 10^{-3} A for the electrolytic cell. Determine the time taken for complete titration.

[2]

$$2e^{-} \equiv Br_2 \equiv \bigcirc$$

number of moles of $e^- = 1.4634 \times 10^{-5} \times 2$ = 2.9268 x 10⁻⁵ mol

time taken =
$$\frac{nF}{I}$$

= $\frac{2.9268 \times 10^{-5} \times 96500}{5 \times 10^{-3}}$
= **595 s**

(b) Br atoms introduced artificially by industrial activities raise concerns of ozone destruction.

One method that is used to determine the concentration of ozone in the ozone layer is to pass air through alkaline potassium iodide and to measure the amount of iodine liberated. The following reaction takes place.

$$O_3 + H_2O + 2I^- \rightarrow O_2 + I_2 + 2OH^-$$

The iodine liberated is measured using a platinum electrode immersed in alkaline potassium iodide solution against a standard silver/silver chloride reference electrode. The e.m.f. of the system, in volts, is given by the equation.

 $E = 0.32 + 0.029 \log_{10} [I_2]$, where $[I_2]$ is expressed in mol dm⁻³.

To determine ozone in the atmosphere, a light–weight balloon containing the electrochemical cell was released into the atmosphere. The data collected was then transmitted to the ground station for further processing.

A sample of air was passed through 10 cm^3 of alkaline potassium iodide. The pressure of this sample of air was found to be 0.24 atm measured at room temperature. The potential of the platinum electrode immersed into this solution against the standard silver/silver chloride electrode was 0.21 V.

(i) Calculate the concentration of iodine liberated.

[1]

 $0.21 = 0.32 + 0.029 \log_{10} [I_2]$ $[I_2] = 1.61 \times 10^{-4} \text{ mol dm}^{-3}$

(ii) Hence, calculate the volume of ozone present in this sample of air.

[2]

number of moles of $O_3 = 1.6103 \times 10^{-4} \times \frac{10}{1000}$ = 1.6103 x 10⁻⁶ mol

pV = nRT $V = \frac{nRT}{p}$ $= \frac{(1.6103 \times 10^{-6})(8.31)(293)}{0.24 \times 101325}$ $= 1.61 \times 10^{-7} \text{ m}^{3}$

(c) Halogens form binary compounds with hydrogen known as hydrogen halides. State and explain how the thermal stability of hydrogen halides varies down the Group.

[2]

Thermal stability of hydrogen halides <u>decreases</u> down the group.

Down the group,

<u>bond energy decreases</u> [BE (H–F) > BE (H–C*l*) > BE (H–Br) > BE (H–I)], <u>covalent bond strength</u> also <u>decreases</u> [H–F > H–C*l* > H–Br > H–I]. Hence, thermal stability <u>decreases</u> [H–F > H–C*l* > H–Br > H–I].

[Total: 10]

5 (a) Nucleophilic addition of an alcohol to aldehydes and ketones yield hemiacetals. The reaction is slow and reversible under neutral conditions. Upon further reaction with alcohols in the presence of acids as catalyst, hemiacetals can form acetals.



The acid-catalysed acetal formation from the hemiacetal shown below, involves 4 steps.



- 1. Protonation of the hydroxyl group of the hemiacetal.
- 2. Loss of water leads to an unstable and highly reactive oxonium ion.



oxonium ion

- 3. Nucleophilic attack of alcohol, R_3OH , on the oxonium ion to give $H_{-C}^{OR} OR_3$
- 4. Loss of a proton to give the acetal.
- (i) Draw the mechanism as described above, showing clearly the flow of electrons.

[4]

Step 1:



14

Step 2:



Step 3:



Step 4:



(ii) State the purpose of removing water from the reaction mixture.

[1]

By Le Chatelier's Principle, removal of water shifts the position of equilibrium to the right, hence **increasing the yield**.

OR

Water is a competing nucleophile to the alcohol, hence other **<u>side products</u> <u>may be formed</u>**.

(b) Tamiflu is the anti-influenza drug currently being used to treat 'Bird–flu'. It can be synthesised from Shikimic acid, which occurs naturally in star anise.



Shikimic acid

Part of the synthetic route is shown below. Formation of acetals between selected -OH groups of Shikimic acid and ketones helps to control which of the -OH groups reacts to synthesise **C** from **B**.





[2]



(ii) Explain why **B** was formed from **A** instead of Shikimic acid directly.

[1]

A (acid chloride) is more reactive than Shikimic acid.

Using **A** will give a better yield as the reaction is irreversible compared to reversible reaction when Shikimic acid is used. The reaction also requires milder conditions (doing–away with heating and use of catalyst).

(c) Like Shikimic acid, methanoic acid occurs naturally in ants. It is a weak acid and dissociates according to the equation shown.

HCOOH (aq) \rightleftharpoons HCOO⁻ (aq) + H⁺ (aq) $K_a = 1.60 \times 10^{-4} \text{ mol dm}^{-3}$

(i) Explain what is meant by the term pK_a as applied to methanoic acid.

[2]

[2]

 $pK_a = -lg K_a$

$$K_a = \frac{[HCOO^-][H^+]}{[HCOOH]}$$

A flask contains 0.0100 mol of methanoic acid dissolved in 250 cm³ of water.

(ii) Calculate the pH of this solution.

 $[HCOOH] = \frac{0.0100}{0.250}$ = 0.0400 mol dm⁻³ $[H^+] = √(0.0400)(1.60 \times 10^{-4})$ = 2.5298 x 10⁻³ mol dm⁻³ pH = -lg (2.5298 x 10⁻³) = **2.60**

(iii) Hence, calculate the degree of dissociation, α , of methanoic acid in this solution.

[1]

$$\alpha = \frac{[H^*]}{[HCOOH]}$$
$$= \frac{[2.5298 \times 10^{-3}]}{[0.0400]}$$
$$= 0.0632$$

(d) Salicylic acid occurs naturally in plants.



Explain why salicylic acid is more acidic than its isomer.

[2]

The conjugate base formed from the dissociation of salicylic acid is stabilised by hydrogen bonds between the -OH and $-COO^{-}$ groups.

The conjugate base formed from the dissociation of the isomer **cannot form such a bond as the –OH and –COO⁻ groups are too far apart**.

Hence the conjugate base formed from the dissociation of salicylic acid is **<u>stabilised</u> <u>to a greater extent</u>** compared to that of the isomer. The position of the dissociation equilibrium lies more to the right and salicylic acid is a stronger acid than the isomer.

[Total: 15]

|--|



DUNMAN HIGH SCHOOL Preliminary Examination 2018 Year 6

H2 CHEMISTRY

Paper 3 Free Response

9729/03 18 September 2018 2 hours

Candidates answer on separate paper.

Additional Materials: Data Booklet Writing Paper Cover Sheet Graph Paper

INSTRUCTIONS TO CANDIDATES

- 1 Write your **name**, **index number** and **class** on this cover page and on the Cover Sheet provided.
- 2 Write your answers on the separate writing papers provided.
- 3 Write in dark blue or black pen.
- 4 You may use an HB pencil for any diagrams or graphs.
- 5 Start each question on a fresh sheet of paper.

*[Marks will be deducted if you fail to do so.]

- 6 At the end of the examination, fasten all your work securely together with the Cover Sheet on top.
- 7 Do not use staples, paper clips, glue or correction fluid.

Section A

8 Answer all questions

Section B

9 Answer **one** question.

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

You are advised to show all workings in calculations.

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

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

Section A

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

1 The Williamson ether synthesis is an organic reaction, forming an ether from a halogenoalkane and alcohol in the presence of sodium. This reaction was developed by Alexander Williamson in 1850 and still remains the simplest and most popular method of preparing ethers till today.

The following equation shows the formation of dimethyl ether, a common aerosol propellant.

$$CH_3Cl + CH_3OH \xrightarrow{Na} CH_3OCH_3 + HCl$$

 CH_3OH

(a) (i) State the purpose of sodium used in the Williamson ether synthesis.

[1]

(ii) Hence, name the mechanism of the reaction.

[1]

- (iii) Suggest suitable reagent(s) to synthesise each of the following ethers.
 - CH₃CH₂OCH₂CH₃



[2]

(b) Dimethyl ether is known as a symmetrical ether whereas *tert*-butyl ethyl ether, CH₃CH₂OC(CH₃)₃ is an example of an unsymmetrical ether. To prepare *tert*-butyl ethyl ether via the Williamson ether synthesis, there are two possible combinations of reagents, as shown in the table below.

Combination	Reagents
Α	CH ₃ CH ₂ Br and (CH ₃) ₃ COH
В	(CH ₃) ₃ CBr and CH ₃ CH ₂ OH

Identify the combination of reagents that might favour the mechanism identified in **(a)(ii)** and justify your choice, with reasoning.

[2]

(c) Since the middle of 1990s, dimethyl ether (DME) has been identified as a reliable diesel alternative for cars. The table below compares the physical and chemical properties of DME and diesel fuel.

Property	Unit	DME	Diesel Fuel
Carbon content	mass %	52.2	86
Hydrogen content	mass %	1 – 3	14
Oxygen content	mass %	34.8	0
Liquid density	kg m⁻³	667	831
*Auto-ignition temperature	К	508	523
^Stoichiometric air/fuel mass ratio	-	9.6	14.6
Normal boiling point	К	248.1	450 - 643
Enthalpy of vaporisation	kJ kg ^{−1}	467.1	300
Energy released at burning	MJ kg⁻¹	27.6	42.5

*Auto-ignition temperature is the temperature at which a fuel will ignite spontaneously without an external ignition source.

^Stoichiometric air/fuel mass ratio is the mass ratio of air to fuel that completely burns the fuel with no excess air.

With reference to the table, suggest one advantage and one disadvantage of using DME as compared to the conventional diesel fuel.

[2]

- (d) Scientists have recently discovered a new way of synthesising DME by reacting carbon dioxide directly with hydrogen in the presence of Cu-Zn/Al₂O₃ catalyst.
 - (i) Write the balanced equation for the synthesis of DME from carbon dioxide and hydrogen.

[1]

(ii) State the type of catalysis that Cu-Zn/Al₂O₃ performs and explain briefly how it promotes the synthesis of DME.

[3]

(iii) DME can also be synthesised from carbon dioxide via a two-step reaction in the laboratory.

CO₂(g) + 3H₂(g) → CH₃OH(I) + H₂O(I)
$$\Delta H$$
 = −13.1 kJ mol⁻¹
2CH₃OH(I) → CH₃OCH₃(I) + H₂O(I) ΔH = −459.1 kJ mol⁻¹

Using the thermochemical equations given and any relevant data in part (c), draw an energy cycle to determine the enthalpy change of reaction for the synthesis of DME from carbon dioxide and hydrogen at room temperature and pressure.

[5]

- (e) Both dimethyl ether and dimethyl amine have similar hybridisation around the heteroatoms, O and N, respectively.
 - (i) State the type of hybridisation of the O and N atoms in dimethyl ether and dimethyl amine respectively.

[1]

- (ii) Dimethyl ether has a solubility of 7.1 g per litre of water but dimethyl amine has a solubility of 3.54 kg per litre of water instead. Using suitable equation(s), explain briefly the difference in the solubilities between the two compounds.
 [3]
- (iii) A 0.1 mol dm⁻³ solution of dimethyl amine containing an unknown concentration of dimethylamine hydrochloride has a pH of 10.57. Given that the numerical value of K_b of dimethyl amine is 7.4 × 10⁻⁴, determine the concentration of dimethylamine hydrochloride in the solution.

[3]

(iv) Explain why trimethyl amine has a higher pK_b than dimethyl amine.

[1]

[Total: 25]

- 2 (a) Carbon undergoes combustion in oxygen to form two common oxides, CO and CO₂. These oxides are also formed when solid magnesium oxalate, MgC₂O₄, is heated strongly.
 - (i) Explain why magnesium oxalate decomposes at a lower temperature than barium oxalate, BaC₂O₄.

(ii) ZnC₂O₄ undergoes a similar reaction when heated strongly, even though zinc is not a Group 2 element.

Write an equation, with state symbols, to represent the thermal decomposition of solid zinc oxalate.

[1]

(iii) Draw the dot–and–cross diagram of $C_2O_4^{2-}$.

State the shape and bond angle around the carbon atoms of the ion.

[3]

(b) Zinc can also be used in the manufacturing of rechargeable batteries. Zinc–cerium battery is a type of rechargeable battery using a two–electrolyte system. The overall equation for the discharging process is given below.

$$Zn + 2Ce^{4+} \rightarrow Zn^{2+} + 2Ce^{3+}$$

(i) Given that the typical cell voltage for the cell is 2.2 V, calculate the standard electrode potential of the Ce⁴⁺/Ce³⁺ half–cell, using relevant data from the *Data Booklet*.

[1]

(ii) Using relevant data from the *Data Booklet*, deduce if the Ce⁴⁺/Ce³⁺ half–cell can be replaced with Br₂/Br⁻ half–cell.

[1]

5

(c) Nickel–metal hydride (Ni–MH) batteries are the most common rechargeable batteries used for devices that require large amounts of energy. Most Ni–MH batteries use an alloy containing mainly lanthanum and nickel.

In one such battery, one of the electrodes is $LaNi_5H_6$ and the other is NiO(OH). The electrolyte is aqueous KOH. During the discharging process, an electrochemical reaction takes place to produce $LaNi_5(s)$ and $Ni(OH)_2(s)$, and releases electrical energy.

(i) Construct a half–equation for the reaction that take place at each electrode during discharging.

[2]

(ii) During recharging, an electrical potential is applied across the electrodes to reverse the electrochemical reaction.

Using your answer in (c)(i), write the overall equation for the reaction that occurs during recharging.

[1]

(iii) Overcharging the Ni–MH battery may result in the electrolyte being discharged at the electrodes to form gaseous products. A safety vent is thus incorporated in the battery to release the excess pressure.

With reference to the *Data Booklet*, suggest a relevant half–equation, with state symbols, for the reaction occurring at one of the electrodes of the Ni–MH battery.

[1]

[Total: 12]

3 (a) Compounds **X** and **Y** are dichloroalkanes and constitutional isomers of each other. The structure of **Y** is as shown below.



Some additional information is provided about X:

- It is not chiral.
- It also contains a benzene ring.
- The two chlorine atoms are not bonded to the same carbon atom.

A series of chemical experiments were also conducted on Compound ${\bf X}$ to further confirm its identity.

Experiment I:

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



Experiment II:

0.25 mol of **X** and **Y** were treated separately with boiling aqueous sodium hydroxide. The products from each compound were then acidified with nitric acid and then treated with silver nitrate solution. The results obtained are shown below.

	Observation upon adding AgNO ₃	Mass of precipitate / g
X	formation of white precipitate	35.85
Y	formation of white precipitate	71.70

- 8
- (i) Deduce the rate equation based on the information given in Experiment I.

[3]

(ii) Using your answer in (a)(i) and the information given in Experiment II, deduce, with reasoning, a possible structure of X.

[2]

(iii) Draw the mechanism for the reaction of **X** with aqueous sodium hydroxide. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons.

[3]

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

Solvent	Туре	Relative rates of r	eaction with OH⁻
Solvent	туре	1º RX in S _N 2	3º RX in S _N 1
CH₃OH	Protic	1	4
H ₂ O	Protic	7	150 000
CH₃COOH	Protic	1	1
CH ₃ COCH ₃	Aprotic	5000	-

(i) Suggest, using **only** structure and bonding, the difference between *protic* and *aprotic* solvents, in terms of solvent-solvent interactions.

[1]

(ii) Suggest an explanation for the effect of solvent on the relative rate of $S_N 2$ reactions.

[2]

- (iii) Explain, with an aid of a diagram, how water increases the rate of S_N1 reaction. [2]
- (iv) Would the rate of S_N1 reaction be faster or slower if hexane was used in place of ethanoic acid?

[1]

(c) Silver forms a series of halides of general formula AgX. The chloride, bromide and iodide of silver are sparingly soluble in water at room temperature.

Data about the solubilities in water and the solubility products of the chloride, bromide and iodide of silver at 298 K are given below.

Salt	Solubility / mol dm ⁻³	Solubility product / mol ² dm ⁻⁶
AgC <i>l</i>	1.4 x 10 ^{−5}	2.0 x 10 ⁻¹⁰
AgBr	7.1 x 10 ⁻⁷	5.0 x 10 ⁻¹³
AgI	8.9 x 10 ^{−9}	to be calculated

(i) Write an expression for the solubility product, K_{sp} of silver iodide.

[1]

(ii) From the data above, calculate a value for K_{sp} of silver iodide.

[1]

(iii) Using your answer in (c)(ii), calculate the solubility of AgI in 0.0125 mol dm⁻³ AgNO₃.

[2]

(iv) When silver nitrate is added to solution containing chloride ions, a white precipitate is observed. The white precipitate dissolves when aqueous ammonia was added. Upon adding of aqueous sodium bromide to the resultant mixture, a cream precipitate is obtained.

With the aid of suitable equations, explain the chemistry of the reactions occurring.

[3]

(v) When a precipitate is formed, ΔG_{ppt}^{Θ} is given by the following equation.

$$\Delta G_{\text{ppt}}^{\ominus}$$
 = 2.303 RT log₁₀ K_{sp}

For silver fluoride, its K_{sp} value is 1.006 at 298 K.

Use the equation given above to deduce if silver fluoride is soluble in water at 298 K. Explain your answer.

[2]

[Total: 23]

10

Section B

Answer **one** question from this section.

4 Levocarnitine is a quaternary ammonium compound involved in metabolism in most mammals.



(a) A kinetic study on the reaction between levocarnitine and bromamine-T, in the presence of $RuCl_3$, was carried out in aqueous hydrochloric acid.

The following equilibrium exists for $RuCl_3$ in aqueous hydrochloric acid.

$$[\operatorname{Ru}Cl_5(\operatorname{H}_2\operatorname{O})]^{2-} + Cl^- \rightleftharpoons [\operatorname{Ru}Cl_6]^{3-} + \operatorname{H}_2\operatorname{O}$$

Explain why $[RuCl_6]^{3-}$ is likely to be the reactive species instead of $[RuCl_5(H_2O)]^{2-}$ in this study.

[1]

(b) The mechanism for the reaction between levocarnitine and bromamine-T was proposed as follows.





complex X +
$$V_{+}$$
 V_{+} V_{+} V_{-} V_{-}

(i) Use the Lewis theory of acids and bases to identify and explain the role of bromamine-T in step 1.

11

[1]

(ii) The species in the equations shown have various roles. They can be reactants, products, catalysts or intermediates.

Suggest, with a reason in each case, the roles of the species A, B and C.

[3]

- (iii) State the type of reaction that levocarnitine had undergone with bromamine-T. Explain your answer in terms of changes in oxidation number. [2]
- (c) A series of experiments were carried out at different temperatures under pseudo-first order conditions with respect to bromamine-T.

The value of the observed rate constant, k', for the catalysed reaction was determined at each temperature and the results are summarised in the table below.

k'	temperature, T
/ 10 ⁴ s ⁻¹	/ K
1.82	293
3.00	303
4.62	313
7.30	323

The activation energy, E_a , and the pre-exponential factor, A, which is a constant, for the reaction can be determined from the equation.

$$k' = Ae^{\frac{-E_a}{RT}}$$

R is the molar gas constant.

T is the reaction temperature in Kelvin.

- k is the observed rate constant at a chosen temperature.
 - (i) Calculate the values of ln k and $\frac{1}{T}$ for each of the experiments above.

[2]

(ii) Hence plot a graph of ln *k* against $\frac{1}{T}$ and determine E_a from the gradient of the best-fit line which is $\frac{-E_a}{R}$.

[4]

(iii) How would you expect the activation energy and rate of the reaction to be different if the reaction was uncatalysed? Explain your answer with the aid of a Boltzmann distribution curve.

[3]

(d) Tosyl chlorides (TsC*l*) are often used to convert alcohols (ROH) into alkyl tosylates (ROTs) as shown below.



This conversion allows alcohols to undergo nucleophilic substitution reactions by converting the poor leaving group (OH) into a good leaving group (OTs). An example of this application is given below.



(i) The tosylate group is a better leaving group than the alcohol group due the greater stability of the TsO⁻ ion formed compared to OH⁻.

Suggest an explanation for the stability of the TsO⁻ ion.



(ii) The conversion of alcohols into alkyl tosylates using tosyl chlorides is selective in nature.

Consider the following examples involving diols and suggest a factor that affects the selectivity of the conversion. Explain your answer.



(iii) Predict the product of the following conversion.



[Total: 20]

[1]

5 (a) Thermogravimetric analysis (TGA) is a technique where the mass of a sample in a controlled atmosphere is recorded as a function of temperature as the temperature of the sample is increased.

A sample of lithium pentaborate pentahydrate (LiB $_5O_8.5H_2O$) was subject to TGA and the graph obtained is shown below.



Suggest an explanation, supported with relevant calculations, for the loss in mass (Δm) of LiB₅O₈.5H₂O observed in the graph.

$$[M_r (LiB_5O_8.5H_2O) = 278.9]$$

- (b) The sample of $LiB_5O_8.5H_2O$ used in (a) was synthesised as a system of Li_2O , B_2O_3 and H_2O in the laboratory.
 - (i) Deduce the molar ratio of Li_2O : B_2O_3 : H_2O in a pure sample of $LiB_5O_8.5H_2O$. [1]
 - (ii) Aqueous sodium hydroxide can be used to react with B_2O_3 to determine its actual amount in the sample.

Given that B_2O_3 and Al_2O_3 have similar reactions with aqueous sodium hydroxide under appropriate conditions, write a balanced equation for the reaction between B_2O_3 and aqueous sodium hydroxide.

[1]

[2]

- (c) Li_2O can be produced from the thermal decomposition of lithium peroxide, Li_2O_2 .
 - (i) State and explain how the lattice energies of Li_2O and Li_2O_2 would differ.

[2]

(ii) Lithium peroxide reacts with carbon dioxide according to the equation shown below.

$$2Li_2O_2(s) + 2CO_2(g) \rightarrow 2Li_2CO_3(s) + O_2(g)$$

State the change in oxidation number of oxygen as Li_2O_2 is converted into the products.

[2]

(iii) Calculate the highest temperature reached when the 2.50 g of lithium carbonate was dissolved in 30 cm³ of water at room temperature. The standard enthalpy change of solution of lithium carbonate is -18.2 kJ mol⁻¹.

[2]

(iv) Calculate the pH of the resulting solution formed in (c)(iii) given that the K_b of carbonate ion is 1.995×10^{-4} mol dm⁻³.

[3]
(d) Phenylsulfonyl (PhSO₂) and acetate (CH₃COO) groups on adjacent carbons in a starting material can be lost to form an alkene via Julia olefination.

An example of Julia olefination is as follows.



(i) Suggest the type of reaction occurring in the final step of Julia olefination.

[1]

Consider the reaction scheme below involving Julia olefination.

$$\mathbf{A} \xrightarrow{1. \text{ base}} \mathbf{B} \xrightarrow{\text{Na / Hg}} \mathbf{C} \xrightarrow{\text{KMnO}_4 / \text{H}^+} \mathbf{D} + \mathbf{E}$$

$$\underbrace{2. C_6 H_5 \text{CHO}}_{3. (\text{CH}_3 \text{CO})_2 \text{O}} \mathbf{B} \xrightarrow{\text{Na / Hg}} (C_{14} H_{16}) \xrightarrow{\text{KMnO}_4 / \text{H}^+} \mathbf{D} + \mathbf{E}$$

$$\underbrace{1. \text{ base}}_{\text{heat}} (C_7 H_6 O_2) \xrightarrow{\text{C}} (C_7 H_{10} O_6)$$

- (ii) Compound D effervesces with sodium carbonate. Suggest the structure of D. [1]
- (iii) Compound **E** is non-cyclic and has six carbons in the longest continuous carbon chain. It also does **not** contain any chiral carbon.

One mole of **E** reacts with three moles of thionyl chloride $(SOCl_2)$ to liberate acidic gas.

Identify the functional group present in **E** and suggest its structure.

[2]

(iv) Hence suggest the structures of compounds A to C.

[3]

[Total: 20]

Suggested solutions



DUNMAN HIGH SCHOOL Preliminary Examination 2018 Year 6

H2 CHEMISTRY

Paper 3 Free Response

9729/03

2 hours

18 September 2018

Candidates answer on separate paper.

Additional Materials: Data Booklet Writing Paper Cover Sheet Graph Paper

INSTRUCTIONS TO CANDIDATES

- 1 Write your **name**, **index number** and **class** on this cover page and on the Cover Sheet provided.
- 2 Write your answers on the separate writing papers provided.
- 3 Write in dark blue or black pen.
- 4 You may use an HB pencil for any diagrams or graphs.
- 5 Start each question on a fresh sheet of paper.

*[Marks will be deducted if you fail to do so.]

- 6 At the end of the examination, fasten all your work securely together with the Cover Sheet on top.
- 7 Do not use staples, paper clips, glue or correction fluid.

Section A

8 Answer **all** questions

Section B

9 Answer one question.

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

You are advised to show all workings in calculations.

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

Section A

Answer all questions.

1 The Williamson ether synthesis is an organic reaction, forming an ether from a halogenoalkane and alcohol in the presence of sodium. This reaction was developed by Alexander Williamson in 1850 and still remains the simplest and most popular method of preparing ethers till today.

The following equation shows the formation of dimethyl ether, a common aerosol propellant.

$$CH_3Cl + CH_3OH \xrightarrow{Na} CH_3OCH_3 + HCl$$

 CH_3OH

(a) (i) State the purpose of sodium used in the Williamson ether synthesis.

[1]

Sodium reacts with CH₃OH to form a stronger nucleophile, CH₃O⁻

(ii) Hence, name the mechanism of the reaction.

[1]

S_N2 / bimolecular nucleophilic substitution

(iii) Suggest suitable reagent(s) to synthesise each of the following ethers.



- Cl OH (in the presence of Na)
- (b) Dimethyl ether is known as a symmetrical ether whereas *tert*-butyl ethyl ether, CH₃CH₂OC(CH₃)₃ is an example of an unsymmetrical ether. To prepare *tert*-butyl ethyl ether via the Williamson ether synthesis, there are two possible combinations of reagents, as shown in the table below.

Combination Reagents	
Α	CH ₃ CH ₂ Br and (CH ₃) ₃ COH
В	(CH ₃) ₃ CBr and CH ₃ CH ₂ OH

Identify the combination of reagents that might favour the mechanism identified in **(a)(ii)** and justify your choice, with reasoning.

[2]

Combination A

 CH_3CH_2Br is a **primary alkyl halide**, and hence it will be **less sterically hindered** for the nucleophile / alkoxide ion to **attack from the back** of the halogen as compared to $(CH_3)_3CBr$, a tertiary alkyl halide.

(c) Since the middle of 1990s, dimethyl ether (DME) has been identified as a reliable diesel alternative for cars. The table below compares the physical and chemical properties of DME and diesel fuel.

Property	Unit	DME	Diesel Fuel
Carbon content	mass %	52.2	86
Hydrogen content	mass %	1 – 3	14
Oxygen content	mass %	34.8	0
Liquid density	kg m⁻³	667	831
*Auto-ignition temperature	K	508	523
^Stoichiometric air/fuel mass ratio	-	9.6	14.6
Normal boiling point	K	248.1	450 - 643
Enthalpy of vaporisation	kJ kg⁻¹	467.1	300
Energy released at burning	MJ kg ^{−1}	27.6	42.5

*Auto-ignition temperature is the temperature at which a fuel will ignite spontaneously without an external ignition source.

^Stoichiometric air/fuel mass ratio is the mass ratio of air to fuel that completely burns the fuel with no excess air.

With reference to the table, suggest one advantage and one disadvantage of using DME as compared to the conventional diesel fuel.

Advantage: DME has <u>lower carbon content</u> than diesel fuel, and thus contribute to <u>lower carbon dioxide emission</u> when the same mass is burnt.

Disadvantage: DME releases <u>less energy at burning</u> than diesel fuel, and thus is a <u>less efficient fuel</u> for the same mass used.

- (d) Scientists have recently discovered a new way of synthesising DME by reacting carbon dioxide directly with hydrogen in the presence of Cu-Zn/Al₂O₃ catalyst.
 - (i) Write the balanced equation for the synthesis of DME from carbon dioxide and hydrogen.

[1]

[2]

$2CO_2 + 6H_2 \rightarrow CH_3OCH_3 + 3H_2O$

(ii) State the type of catalysis that Cu-Zn/Al₂O₃ performs and explain briefly how it promotes the synthesis of DME.

[3]

Heterogeneous catalysis

Both H_2 and CO_2 reactants are gases. The solid catalyst provides a surface for the **gaseous molecules to be** *adsorbed* to the surface, **thus increasing the concentration of the reactants / bringing the molecules closer together** and **weakening the bonds of the reactants molecules**, resulting in a lower E_a .

- 4
- (iii) DME can also be synthesised from carbon dioxide via a two-step reaction in the laboratory.

CO₂(g) + 3H₂(g) → CH₃OH(l) + H₂O(l)
$$\Delta H = -13.1 \text{ kJ mol}^{-1}$$

2CH₃OH(l) → CH₃OCH₃(l) + H₂O(l) $\Delta H = -459.1 \text{ kJ mol}^{-1}$

Using the thermochemical equations given and any relevant data in part (c), draw an energy cycle to determine the enthalpy change of reaction for the synthesis of DME from carbon dioxide and hydrogen at room temperature and pressure.

[5]



- (e) Both dimethyl ether and dimethyl amine have similar hybridisation around the heteroatoms, O and N, respectively.
 - (i) State the type of hybridisation of the O and N atoms in dimethyl ether and dimethyl amine respectively.

[1]

sp³

(ii) Dimethyl ether has a solubility of 7.1 g per litre of water but dimethyl amine has a solubility of 3.54 kg per litre of water instead. Using suitable equation(s), explain briefly the difference in the solubilities between the two compounds.

[3]

DME can form <u>hydrogen bonds with water molecules</u> whereas dimethyl amine is a weak base and can partially dissociate in water in to form ions which can form <u>ion-dipole interactions with water molecules</u>, hence dimethyl amine has a higher solubility in water.

 $(CH_3)_2NH + H_2O \rightleftharpoons (CH_3)_2NH_2^+ + OH^-$

(iii) A 0.1 mol dm⁻³ solution of dimethyl amine containing an unknown concentration of dimethylamine hydrochloride has a pH of 10.57. Given that the numerical value of K_b of dimethyl amine is 7.4 × 10⁻⁴, determine the concentration of dimethylamine hydrochloride in the solution.

[3]

A buffer system is set up.

 $(CH_3)_2NH + H_2O \rightleftharpoons (CH_3)_2NH_2^+ + OH^- K_b = 7.4 \times 10^{-4} \text{ mol dm}^{-3}$

 $\begin{array}{l} pH = 10.57 \\ pOH = 14 - 10.57 = 3.43 \\ [OH^-] = 10^{-3.43} \ mol \ dm^{-3} \end{array}$

$$K_{b} = \frac{[(CH_{3})_{2}NH_{2}^{+}][OH^{-}]}{[(CH_{3})_{2}NH]}$$

7.4 x 10⁻⁴ =
$$\frac{[(CH_3)_2 NH_2^+][10^{-3.43}]}{0.1}$$

$$[(CH_3)_2NH_2^+] = \frac{7.4 \times 10^{-3} \times 0.1}{10^{-3.43}}$$
$$= 0.199 \text{ mol dm}^{-3}$$

OR

$$pOH = pK_{b} + \log_{10} \left(\frac{[(CH_{3})_{2}NH_{2}^{*}]}{[(CH_{3})_{2}NH]} \right)$$

14 - 10.57 = -log_{10}(7.4 × 10⁻⁴) + log_{10} \left(\frac{[(CH_{3})_{2}NH_{2}^{*}]}{0.1} \right)

 $[(CH_3)_2NH_2^+] = 0.199 \text{ mol } dm^{-3}$

(iv) Explain why trimethyl amine has a higher pK_b than dimethyl amine.

The <u>lone pair of electrons on N in trimethyl amine is less available for</u> <u>donation</u> as it is <u>more sterically hindered with one more $-CH_3$ group</u> than dimethyl amine, hence decreasing its basicity.

[Total: 25]

[1]

2 (a) Carbon undergoes combustion in oxygen to form two common oxides, CO and CO₂. These oxides are also formed when solid magnesium oxalate, MgC₂O₄, is heated strongly.

6

(i) Explain why magnesium oxalate decomposes at a lower temperature than barium oxalate, BaC₂O₄.

[2]

 Mg^{2^+} has a <u>smaller ionic radius and a higher charge density</u> than Ba^{2^+} . Therefore, Mg^{2^+} has a greater polarising power than Ba^{2^+} . Mg^{2^+} distorts the electron cloud of $C_2O_4^{2^-}$ anion / weakens the bonds in the $C_2O_4^{2^-}$ anion to a greater extent. Hence MgC_2O_4 is less thermally stable.

(ii) ZnC₂O₄ undergoes a similar reaction when heated strongly, even though zinc is not a Group 2 element.

Write an equation, with state symbols, to represent the thermal decomposition of solid zinc oxalate.

[1]

 $ZnC_2O_4(s) \rightarrow ZnO(s) + CO_2(g) + CO(g)$

(iii) Draw the dot–and–cross diagram of $C_2O_4^{2-}$.

State the shape and bond angle around the carbon atoms of the ion.

[3]



Shape: Trigonal Planar about each C atom Bond Angle: 120°

(b) Zinc can also be used in the manufacturing of rechargeable batteries. Zinc-cerium battery is a type of rechargeable battery using a two-electrolyte system. The overall equation for the discharging process is given below.

$$Zn + 2Ce^{4+} \rightarrow Zn^{2+} + 2Ce^{3+}$$

(i) Given that the typical cell voltage for the cell is 2.2 V, calculate the standard electrode potential of the Ce⁴⁺/Ce³⁺ half–cell, using relevant data from the *Data Booklet*.

[1]

From the Data Booklet, $E^{\odot}(Zn^{2+}/Zn) = -0.76 \text{ V}$

 $E^{\ominus}_{cell} = E^{\ominus}_{cathode} - E^{\ominus}_{anode}$ 2.2 = $E^{\ominus}(Ce^{4+}/Ce^{3+}) - (-0.76)$ $E^{\ominus}(Ce^{4+}/Ce^{3+}) = +1.44 V$ (ii) Using relevant data from the *Data Booklet*, deduce if the Ce⁴⁺/Ce³⁺ half–cell can be replaced with Br₂/Br⁻ half–cell.

[1]

From the Data Booklet, $E^{\ominus}(Br_2/Br^-) = +1.07 \text{ V}$ $E^{\ominus}_{\text{cell}} = +1.07 - (-0.76)$ = +1.83 V > 0 (feasible)

Since it is feasible for the battery to discharge electricity, the Ce^{4+}/Ce^{3+} half–cell can be replaced with Br_2/Br^- half–cell.

(c) Nickel–metal hydride (Ni–MH) batteries are the most common rechargeable batteries used for devices that require large amounts of energy. Most Ni–MH batteries use an alloy containing mainly lanthanum and nickel.

In one such battery, one of the electrodes is LaNi₅H₆ and the other is NiO(OH). The electrolyte is aqueous KOH. During the discharging process, an electrochemical reaction takes place to produce LaNi₅(s) and Ni(OH)₂(s), and releases electrical energy.

(i) Construct a half–equation for the reaction that take place at each electrode during discharging.

[2]

Anode: LaNi₅H₆(s) + 6OH⁻(aq) \rightarrow LaNi₅(s) + 6H₂O(I) + 6e⁻

Cathode: NiO(OH)(s) + H₂O(I) + $e^- \rightarrow Ni(OH)_2(s) + OH^-(aq)$

(ii) During recharging, an electrical potential is applied across the electrodes to reverse the electrochemical reaction.

Using your answer in (c)(i), write the overall equation for the reaction that occurs during recharging.

[1]

 $LaNi_{5}(s) + 6Ni(OH)_{2}(s) \rightarrow LaNi_{5}H_{6}(s) + 6NiO(OH)(s)$

(iii) Overcharging the Ni–MH battery may result in the electrolyte being discharged at the electrodes to form gaseous products. A safety vent is thus incorporated in the battery to release the excess pressure.

With reference to the *Data Booklet*, suggest a relevant half–equation, with state symbols, for the reaction occurring at one of the electrodes of the Ni–MH battery.

[1]

Anode: $4OH^{-}(aq) \rightarrow O_2(g) + 2H_2O(I) + 4e^{-}$ OR Cathode: $2H_2O(I) + 2e^{-} \rightarrow H_2(g) + 2OH^{-}(aq)$

[Total: 12]

3 (a) Compounds **X** and **Y** are dichloroalkanes and constitutional isomers of each other. The structure of **Y** is as shown below.



Compound Y

Some additional information is provided about X:

- It is not chiral.
- It also contains a benzene ring.
- The two chlorine atoms are not bonded to the same carbon atom.

A series of chemical experiments were also conducted on Compound ${\bf X}$ to further confirm its identity.

Experiment I:

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



Experiment II:

0.25 mol of **X** and **Y** were treated separately with boiling aqueous sodium hydroxide. The products from each compound were then acidified with nitric acid and then treated with silver nitrate solution. The results obtained are shown below.

	Observation upon adding AgNO ₃	Mass of precipitate / g
Χ	formation of white precipitate	35.85
Y	formation of white precipitate	71.70

9

(i) Deduce the rate equation based on the information given in Experiment I.

[3]

Using $[OH^-] = 3.0 \text{ mol } dm^{-3} \text{ graph}$, t_{1/2} is constant at 30 min, order of reaction with respect to X is 1. OR Using $[OH^-] = 1.5 \text{ mol } dm^{-3} \text{ graph}$, t_{1/2} is constant at 60 min, order of reaction with respect to X is 1.

Using initial rate method, Initial rate for graph where $[OH^-] = 1.5 \text{ mol } dm^{-3}$ = 0.2/110 = 0.001818 mol dm⁻³ min⁻¹ Initial rate for graph where $[OH^-] = 3.0 \text{ mol } dm^{-3}$ = 0.2/52 = 0.003846 mol dm⁻³ min⁻¹

As $[OH^-]$ increases 2 times, initial rate also increases 2 times Hence, order of reaction with respect to OH^- is 1.

Rate = k [X] [OH⁻]

(ii) Using your answer in (a)(i) and the information given in Experiment II, deduce, with reasoning, a possible structure of X.

[2]

From (a)(i), X undergoes $S_N 2$ mechanism \Rightarrow X is a primary chloroalkane.

From expt II, 0.25 mol of X forms 0.25 mol of AgCl \Rightarrow There is only one Cl atom in the alkyl side chain OR there is only one Clatom bonded to the benzene ring



(iii) Draw the mechanism for the reaction of **X** with aqueous sodium hydroxide. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons.

[3]



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

Solvent	Tupo	Relative rates of reaction with OH ⁻		
Solveni	туре	1º RX in	3º RX in	
		S _N 2	S _N 1	
CH₃OH	Protic	1	4	
H ₂ O	Protic	7	150 000	
CH₃COOH	Protic	1	1	
CH ₃ COCH ₃	Aprotic	5000	_	

(i) Suggest, using **only** structure and bonding, the difference between *protic* and *aprotic* solvents, in terms of solvent-solvent interactions.

[1]

Protic solvent refers to molecules with **H** atoms that can be used to form hydrogen bonds. Aprotic solvents can only form permanent dipole-permanent dipole interactions between molecules/ have no H atoms that can form hydrogen bonds.

(ii) Suggest an explanation for the effect of solvent on the relative rate of $S_{\rm N}2$ reactions.

[2]

For S_N2 reactions, protic solvents like water can form **hydrogen bond with OH**⁻ and hence, slowing down the rate of reaction. Aprotic solvents like CH₃COCH₃, do not form hydrogen bond and hence **the lone pair of electron on OH**⁻ **is more available to attack the electron deficient C on 1**° **RX**.

(iii) Explain, with an aid of a diagram, how water increases the rate of $S_N 1$ reaction.

[2]



The ion dipole interaction stabilised the carbocation.

(iv) Would the rate of $S_N 1$ reaction be faster or slower if hexane was used in place of ethanoic acid?

[1]

Slower.

(c) Silver forms a series of halides of general formula AgX. The chloride, bromide and iodide of silver are sparingly soluble in water at room temperature.

Data about the solubilities in water and the solubility products of the chloride, bromide and iodide of silver at 298 K are given below.

Salt	Solubility / mol dm ⁻³	Solubility product / mol ² dm ⁻⁶
AgCl	1.4 x 10 ⁻⁵	2.0 x 10 ⁻¹⁰
AgBr	7.1 x 10 ^{−7}	5.0 x 10 ⁻¹³
AgI	8.9 x 10 ⁻⁹	to be calculated

(i) Write an expression for the solubility product, K_{sp} of silver iodide.

[1]

*K*_{sp} = [Ag⁺] [I[−]]

(ii) From the data above, calculate a value for K_{sp} of silver iodide.

[1]

$$\begin{split} [Ag^+] &= [I^-] \\ \mathcal{K}_{sp} &= (8.9 \times 10^{-9})^2 \\ &= \frac{7.92 \times 10^{-17} \text{ mol}^2 \text{ dm}^{-6}}{} \end{split}$$

(iii) Using your answer in (c)(ii), calculate the solubility of AgI in 0.0125 mol dm⁻³ AgNO₃.

[2]

Let solubility of AgI in 0.0125 mol dm⁻³ AgNO₃ be x mol dm⁻³.

 $AgI(s) \rightleftharpoons Ag^{+}(aq) + I^{-}(aq)$

 $K_{sp} = [Ag^+][I^-] = (0.0125 + x) (x) = 7.92 \times 10^{-17}$

It can be assumed that $x \le 0.0125$ such that $(0.0125 + x) \approx 0.0125$

 $(0.0125)(x) = 7.92 \times 10^{-17}$

12

 $x = 6.34 \times 10^{-15} \,\mathrm{mol} \,\mathrm{dm}^{-3}$

Solubility of AgI in 0.0125 mol dm⁻³ AgNO₃ = 6.34×10^{-15} mol dm⁻³

(iv) When silver nitrate is added to solution containing chloride ions, a white precipitate is observed. The white precipitate dissolves when aqueous ammonia was added. Upon adding of aqueous sodium bromide to the resultant mixture, a cream precipitate is obtained.

With the aid of suitable equations, explain the chemistry of the reactions occurring.

[3]

 $Ag^{+}(aq) + Cl^{-}(aq) \rightarrow AgCl(s)$ White ppt is formed due to the formation of insoluble AgCl.

 $AgCl + 2NH_3 \rightarrow [Ag(NH_3)_2]^+ + Cl^-$ White ppt dissolves due to the formation of a complex ion.

Ag⁺(aq) + Br[−](aq) → AgBr(s) Cream ppt is obtained when NaBr is added to the resultant mixture because K_{sp} of AgBr < K_{sp} of AgC*l* so ionic product still exceeds K_{sp} of AgBr

(v) When a precipitate is formed, $\Delta G_{\text{opt}}^{\Theta}$ is given by the following equation.

$$\Delta G_{\rm ppt}^{\Theta}$$
 = 2.303 RT log₁₀ K_{sp}

For silver fluoride, its K_{sp} value is 1.006 at 298 K.

Use the equation given above to deduce if silver fluoride is soluble in water at 298 K. Explain your answer.

[2]

 $\Delta G_{ppt}^{\Theta} = 2.303 \text{ RT} \log_{10} K_{sp}$ = 2.303(8.31)(298)(log_{10} 1.006) = **+14.8 J mol^{-1}**

Since $\Delta G_{ppt}^{\Theta} > 0$, precipitation will not occur. Therefore, AgF is soluble in water at 298 K.

[Total: 23]

Section B

Answer one question from this section.

4 Levocarnitine is a quaternary ammonium compound involved in metabolism in most mammals.



(a) A kinetic study on the reaction between levocarnitine and bromamine-T, in the presence of RuC*l*₃, was carried out in aqueous hydrochloric acid.

The following equilibrium exists for RuCl₃ in aqueous hydrochloric acid.

$$[\operatorname{Ru}Cl_5(\operatorname{H}_2\operatorname{O})]^{2-} + Cl^- \rightleftharpoons [\operatorname{Ru}Cl_6]^{3-} + \operatorname{H}_2\operatorname{O}$$

Explain why $[RuCl_6]^{3-}$ is likely to be the reactive species instead of $[RuCl_5(H_2O)]^{2-}$ in this study.

[1]

By Le Chatelier's Principle, the presence of <u>chloride ions from aqueous HCl</u> will shift the <u>position of equilibrium to the right</u>, favouring the formation of $[RuCl_6]^{3-}$.

(b) The mechanism for the reaction between levocarnitine and bromamine-T was proposed as follows.



- 14
- (i) Use the Lewis theory of acids and bases to identify and explain the role of bromamine-T in step 1.

[1]

Bromamine-T acts as a <u>Lewis base</u> in step 1 as it <u>donates its lone pair of</u> <u>electrons</u> on N atom to H^+ .

(ii) The species in the equations shown have various roles. They can be reactants, products, catalysts or intermediates.

Suggest, with a reason in each case, the roles of the species **A**, **B** and **C**.

[3]

A is an intermediate as it was formed in step 1 and then reacted in step 2.

B is a catalyst as it reacted in step 2 and was regenerated in step 4.

C is a product as it was formed in step 4 and not reacted in other steps.

(iii) State the type of reaction that levocarnitine had undergone with bromamine-T. Explain your answer in terms of changes in oxidation number. [2]

Oxidation

The oxidation number of <u>carbon</u> (bonded to -OH group) <u>increased from 0 in</u> <u>levocarnitine</u> to <u>+2 in species C</u>.



(c) A series of experiments were carried out at different temperatures under pseudo-first order conditions with respect to bromamine-T.

The value of the observed rate constant, k', for the catalysed reaction was determined at each temperature and the results are summarised in the table below.

k'	temperature, T
/ 10 ⁴ s ^{−1}	/ K
1.82	293
3.00	303
4.62	313
7.30	323

The activation energy, E_a , and the pre-exponential factor, A, which is a constant, for the reaction can be determined from the equation.

$$k' = Ae^{\frac{-E_a}{RT}}$$

R is the molar gas constant.

T is the reaction temperature in Kelvin.

k is the observed rate constant at a chosen temperature.

<i>k'</i> / 10 ⁴ s ⁻¹	In <i>k'</i>	temperature, T / K	¹ / K ^{−1}
1.82	9.81	293	0.00341
3.00	10.3	303	0.00330
4.62	10.7	313	0.00319
7.30	11.2	323	0.00310

(i) Calculate the values of ln k and $\frac{1}{T}$ for each of the experiments above.

15

[2]

(ii) Hence plot a graph of ln *k* against $\frac{1}{T}$ and determine E_a from the gradient of the best-fit line which is $\frac{-E_a}{R}$.



Gradient = $\frac{-E_a}{R}$ = -4380.1 K Hence E_a = 36399 J mol⁻¹ = <u>36.4 kJ mol⁻¹</u>

(iii) How would you expect the activation energy and rate of the reaction to be different if the reaction was uncatalysed? Explain your answer with the aid of a Boltzmann distribution curve.

[3]



The activation energy will be <u>higher</u> and the rate of reaction <u>slower</u> if the reaction was uncatalysed.

When a catalyst is used,

- reaction takes place via an <u>alternative pathway</u> that requires a <u>lower</u> <u>activation energy</u>
- there are <u>more reactant particles with energy ≥ *E*_a and <u>frequency of</u> <u>effective collisions increases</u></u>
- rate of reaction increases, since the <u>rate of reaction is proportional to the</u> <u>frequency</u> of effective collisions.
- (d) Tosyl chlorides (TsC*l*) are often used to convert alcohols (ROH) into alkyl tosylates (ROTs) as shown below.

ROH
$$\xrightarrow{\text{TsC}l}$$
 ROTs pyridine

This conversion allows alcohols to undergo nucleophilic substitution reactions by converting the poor leaving group (OH) into a good leaving group (OTs). An example of this application is given below.



(i) The tosylate group is a better leaving group than the alcohol group due the greater stability of the TsO⁻ ion formed compared to OH⁻.

Suggest an explanation for the stability of the TsO⁻ ion.

$$TsO^{-} = --- \left(\bigcirc \right) = 0$$

[1]

TsO⁻ is **resonance stabilised** as the **negative charge on oxygen is delocalised into the adjacent S=O bond**.

(ii) The conversion of alcohols into alkyl tosylates using tosyl chlorides is selective in nature.

Consider the following examples involving diols and suggest a factor that affects the selectivity of the conversion. Explain your answer.



Degree of substitution of alcohol OR degree of **steric hindrance around alcohol** group.

Tosyl group is a **bulky group** so TsC*l* can **approach the less hindered/ less substituted alcohol more easily**.

(iii) Predict the product of the following conversion.



[Total: 20]

5 (a) Thermogravimetric analysis (TGA) is a technique where the mass of a sample in a controlled atmosphere is recorded as a function of temperature as the temperature of the sample is increased.

A sample of lithium pentaborate pentahydrate ($LiB_5O_8.5H_2O$) was subject to TGA and the graph obtained is shown below.



Suggest an explanation, supported with relevant calculations, for the loss in mass (Δm) of LiB₅O₈.5H₂O observed in the graph.

 $[M_{\rm r} ({\rm LiB}_5{\rm O}_8.5{\rm H}_2{\rm O}) = 278.9]$

The mass loss is likely due to the loss of the five water molecules in LiB₅O₈.5H₂O.

% mass loss = $\frac{5 \times 18}{278.9} \times 100 = 32.3$ % which agrees well with the value obtained from the graph (≈ 32.5 %).

- (b) The sample of $LiB_5O_8.5H_2O$ used in (a) was synthesised as a system of Li_2O , B_2O_3 and H_2O in the laboratory.
 - (i) Deduce the molar ratio of $Li_2O : B_2O_3 : H_2O$ in a pure sample of $LiB_5O_8.5H_2O$. [1]

Since $LiB_5O_8.5H_2O = \frac{1}{2}Li_2O = \frac{5}{2}B_2O_3 = 5H_2O$,

molar ratio of $Li_2O : B_2O_3 : H_2O = 1 : 5 : 10$

(ii) Aqueous sodium hydroxide can be used to react with B₂O₃ to determine its actual amount in the sample.

Given that B_2O_3 and Al_2O_3 have similar reactions with aqueous sodium hydroxide under appropriate conditions, write a balanced equation for the reaction between B_2O_3 and aqueous sodium hydroxide.

 $\underline{B_2O_3 + 2NaOH + 3H_2O \rightarrow 2Na[B(OH)_4]}$

[1]

[2]

(c) Li_2O can be produced from the thermal decomposition of lithium peroxide, Li_2O_2 .

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(i) State and explain how the lattice energies of Li₂O and Li₂O₂ would differ.

[2]

 $\Delta H_{\text{latt}}^{\ominus}(\text{Li}_2\text{O})$ will be **more exothermic** than that of $\Delta H_{\text{latt}}^{\ominus}(\text{Li}_2\text{O}_2)$

For ionic compounds, $I\Delta H_{latt} I \propto \left| \frac{q_+q_-}{r_++r_-} \right|$

<u>cationic charge (q+) and radius (r+)</u> are the <u>same</u> for both compounds. <u>anionic charge (q_)</u> is the <u>same</u> for both compounds. <u>Anionic radius (r_): $O^{2-} < O_2^{2-}$ </u>

(ii) Lithium peroxide reacts with carbon dioxide according to the equation shown below.

$$2\text{Li}_2\text{O}_2(s) + 2\text{CO}_2(g) \rightarrow 2\text{Li}_2\text{CO}_3(s) + \text{O}_2(g)$$

State the change in oxidation number of oxygen as Li_2O_2 is converted into the products.

[2]

The oxidation number of O increases from -1 in Li₂O₂ to 0 in O₂.

The oxidation number of O decreases from -1 in Li₂O₂ to -2 in Li₂CO₃.

(iii) Calculate the highest temperature reached when the 2.50 g of lithium carbonate was dissolved in 30 cm³ of water at room temperature. The standard enthalpy change of solution of lithium carbonate is -18.2 kJ mol⁻¹.

[2]

Moles of Li₂CO₃ = 2.50 / ($6.9 \times 2 + 12 + 16 \times 3$) = 0.033875 mol q = $18.2 \times 10^3 \times 0.033875 = 616.53 \text{ J}$

 $\Delta T = q / mc = 616.53 / (30 \times 4.18) = 4.9165 °C/K$ Highest temperature = 20 + 4.9165 = <u>24.9 °C</u> OR <u>298 K</u>

(iv) Calculate the pH of the resulting solution formed in (c)(iii) given that the K_b of carbonate ion is 1.995×10^{-4} mol dm⁻³.

[3]

$$[CO_3^{2-}] = \frac{0.033875}{0.030} = 1.129 \text{ mol } dm^{-3}$$
$$[OH^{-}] = \sqrt{(K_b \times [CO_3^{2-}])}$$
$$= \sqrt{(1.995 \times 10^{-4} \times 1.129)}$$
$$= 0.01501 \text{ mol } dm^{-3}$$

(d) Phenylsulfonyl (PhSO₂) and acetate (CH₃COO) groups on adjacent carbons in a starting material can be lost to form an alkene via Julia olefination.

An example of Julia olefination is as follows.



(i) Suggest the type of reaction occurring in the final step of Julia olefination.

[1]

Elimination

Consider the reaction scheme below involving Julia olefination.



(ii) Compound D effervesces with sodium carbonate. Suggest the structure of D. [1]



(iii) Compound **E** is non-cyclic and has six carbons in the longest continuous carbon chain. It also does **not** contain any chiral carbon.

One mole of **E** reacts with three moles of thionyl chloride $(SOCl_2)$ to liberate acidic gas.

Identify the functional group present in **E** and suggest its structure.

[2]

Functional group: carboxylic acid



(iv) Hence suggest the structures of compounds A to C.







В





В

[Total: 20]

OR

Name:	Index Number:		Class:	
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DUNMAN HIGH SCHOOL Preliminary Examinations 2018 Year 6

H2 CHEMISTRY

Paper 4 Practical

9729/04 28 August 2018 2 hour 30 minutes

INSTRUCTIONS TO CANDIDATES

- 1 Write your name, index number and class on this cover page.
- 2 Give details of the practical shift and laboratory where appropriate, in the boxes provided.
- 3 Write in dark blue or black pen.
- 4 You may use an HB pencil for any diagrams or graphs.
- 5 Do not use staples, paper clips, glue or correction fluid.
- 6 You are to start with Question 1 FIRST.
- 7 Protective eye goggles and gloves must be worn at ALL TIMES.

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 17 and 18.

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

Shift	
Laboratory	

For Examiner's Use		
Question No.	Question No. Marks	
1	14	
2	13	
3	28	
Total	55	

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

1 Investigation of reaction kinetics between triacetin and lipase

Lipase is an enzyme that breaks down, hydrolyses, the lipids present in animal fats and vegetable oils. It does so by hydrolysing ester bonds. A general reaction scheme for this process is shown below; the size of the R group and its level of saturation will depend on the lipid used.

CH2OCOR				CH₂OH		
CHOCOR	+	3H ₂ O	>	с́нон	+	3RCOOH
 CH ₂ OCOR				I CH₂OH		
				glycerol		fatty acid

Olive oil is often used as a substrate in testing for lipase, with the oleic acid released being titrated with sodium hydroxide solution. Oleic acid, $C_{17}H_{33}COOH$, is a mono–unsaturated fatty acid.

In this experiment, glycerol triethanoate (triacetin) is used as the substrate. Lipase breaks this substrate down into glycerol and ethanoic acid as shown below.



The ethanoic acid produced lowers the pH of the solution. This change can be detected by using a suitable acid–base indicator, bromocresol purple which changes from purple at high pH value to yellow at lower pH value. Sodium carbonate is added to the triacetin to ensure that the pH is high enough at the start of the experiment. Only after the sodium carbonate has all reacted with the liberated ethanoic acid will the ethanoic acid concentration rise and the pH value decreases. The reaction time is measured from the initial point of mixing the solutions until the end–point of the indicator is reached.

The following reagents are provided for this experiment.

- **FA1** is triacetin
- **FA 2** is 0.5% sodium carbonate solution
- **FA 3** is 8% lipase solution
- **FA 4** is bromocresol purple solution

Procedure

- 1. To a test-tube, add 2 drops of **FA 2** followed by 1 drop of **FA 4**.
- 2. Using a dropper, add 5 drops of **FA 1** to the test tube.
- 3. Using a 250 cm³ beaker, collect 200 cm³ of warm water from the dispenser.
- 4. **Swirl the bottle** containing **FA 3** before using a syringe to transfer 0.20 cm³ of **FA 3** into the test tube. Start the stopwatch immediately and place the test tube into the warm water bath.
- 5. **Shake the test tube continuously**. This is necessary to ensure that **FA 1** and **FA 3** are continually mixed.
- 6. Record the reaction time, *t* (in seconds) when the mixture turns yellow. This will be a gradual process.
- 7. Repeat steps 1 6 for four other test tubes, using different volumes of **FA 3** as shown in the table below.

Test Tube	Volume of FA 3 / cm ³
1	0.20
2	0.40
3	0.60
4	0.80
5	1.00

8. Calculate the value of reaction rate, $\frac{1}{t}$, for each experiment.

(a) Results:

(i)



(ii) Plot the reaction rate, $\frac{1}{t}$, against the volume of **FA 3** used.

4

(iii) By considering the graph in (a)(ii), deduce the order of reaction with respect to lipase, FA 3. Explain your deduction.



(iv) The weighted reaction time can be obtained by multiplying the appropriate conversion factor to the reaction time, *t* (in seconds).

Test Tube	Conversion factor	Weighted reaction time / s
1	0.20	
2	0.40	
3	0.60	
4	0.80	
5	1.00	

Based on your deduction in (a)(iii), sketch the expected graph of weighted reaction time, in seconds, against the volume of FA 3 used. Explain your sketch.



(b) Explain how the volumes of FA 1, FA 2 and FA 3 should change in the procedure in order to investigate the relationship between substrate concentration and the rate of reaction. You are **not** required to give exact figures.

7

2 Planning

An ideal gas is a theoretical idea – a gas in which there are no attractive forces between the molecules, and in which the molecules take up no space. The ideal gas law is usually stated as pV = nRT, where

- *p* is the pressure
- V is the volume
- *n* is the number of moles
- T is the temperature in K

of the gas, and

• *R* is the ideal gas constant.

The value of R is determined experimentally by measuring the other variables in the equation, and solving mathematically to get the value of the constant. R is the same for all gases – provided the gas has ideal behaviour.

In this experiment you will determine the ideal gas constant using H_2 gas. The H_2 will be generated using the reaction between magnesium and hydrochloric acid.

 $Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$

You may assume you are provided with:

- a two-necked round bottom flask,
- a rubber tubing,
- a water tub,
- 0.1 mol dm⁻³ hydrochloric acid,
- thermometer,
- barometer (instrument used to measure pressure),
- one piece of magnesium ribbon strip of about 0.06 g,
- apparatus normally found in a school laboratory
- (a) Your plan should contain the following:
 - the procedure that you would follow and the measurements that you would take
 - a tabulation of the experimental data to be collected
 - the reactants and conditions that you would use
 - the mass of magnesium that you would use and the volume of hydrochloric acid that you would measure. Assume that the molar volume of gas under experimental conditions is 24.0 dm³ mol⁻¹.

[A_r: Mg, 24.3]

.....[7] (b) State two basic assumptions of an ideal gas.

- (c) Real gases do not obey the ideal gas law exactly. Sketch a **fully labelled** graph representing the deviation from ideality for one mole of each of the following gases.
 - ideal gas
 - H₂ gas
 - CH₄ gas



[4]

[Total: 13]

3 Investigation of chemical reactions of electrolytes

You are provided with the following. **FA 5** is sodium chloride solution **FA 6** and **FA 9** are aqueous electrolytes, each containing one cation and one anion.

(a) Electrolysis of FA 5

1. Set up the apparatus and circuit as shown in Fig. 3.1.



Fig 3.1

- 2. Transfer about 200 cm³ of **FA 5** into the glass beaker.
- 3. Ensure that the graphite (anode) is partially submerged in **FA 5** by adjusting the height of the clamp.
- 4. Immerse one end of the graphite (cathode) in **FA 5** for a few minutes and record your observations in Table 3.1. You do **not** need to collect and test any gases evolved.

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Table	3.1
-------	-----

electrolyte	observations at the electrodes
54.5	anode:
FA 5	cathode:

[1]

5. Perform the tests described in Table 3.2, and record your observations in the table.

Table 3.2

	tests	observations
1.	Add one drop of Universal Indicator solution to FA 5 near the cathode .	
2.	Place a piece of moist blue litmus paper near the anode . Observe until no further change is seen.	

[2]

6. Remove both electrodes from **FA 5** and rinse them thoroughly with deionised water.

Consider your observations in Table 3.2.

(i) Explain, with the aid of an equation, the observations made in test 1 in Table 3.2.

.....[2]

(ii) With reference to the data below, suggest an explanation for your observations in test 2 in Table 3.2, in terms of *E* values.

electrode reaction	E [⇔] / V
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23



(b) (i) Qualitative analysis of FA 6

FA 7 is a solution of potassium sodium tartrate tetrahydrate in sodium hydroxide. **FA 8** is an organic compound with only one functional group.

Perform the tests described in Table 3.3, and record your observations in the table. You do **not** need to test and identify any gases evolved. If there is no observable change, write **no observable change**.

Table	3.3
-------	-----

	tests	observations
1.	To 1 cm depth of FA 6 in a test-tube, add aqueous ammonia dropwise, with shaking, until no further change is seen.	
2.	To 1 cm depth of FA 6 in a test-tube, add an equal volume of FA 7 .	
	Add 1 cm depth of FA 8 and shake the mixture thoroughly.	
	Warm the mixture in a water bath. Observe the mixture until no further changes are seen.	
<u>.</u>		[4]

13

Identify the cation present in FA 6 and the functional group present in FA 8.

Functional group present in **FA 8**:[1]

(ii) Electrolysis of FA 6

- 1. Repeat steps 1 to 3 of the procedure in 3(a) using FA 6.
- 2. Immerse one end of the graphite (cathode) in **FA 6** for a few minutes until it is coated with a **thin layer of solid** and record your observations in Table 3.4. You do **not** need to identify any gases evolved.
- 3. Remove the graphite (cathode) from **FA 6** and rinse it with deionised water.
- 4. Retain the graphite (cathode) for further tests in (b)(iii).

Table 3.4

electrolyte	observations at the electrodes
	anode:
FA 6	cathode:

[1]

(iii) Investigation of some chemical reactions involving the solid deposited

Perform the tests described in Table 3.5, and record your observations in the table. Test and identify any gases evolved. If there is no observable change, write **no observable change**.

Tab	e	3.	5
-----	---	----	---

	tests	observations
1.	Put the graphite (cathode) from (b)(ii) in a boiling tube.	
	Carry out the following steps in the fume hood.	
	Cautiously add 2 cm depth of concentrated hydrochloric acid to the boiling tube and shake the mixture thoroughly to dissolve, as much as possible, the solid coated on the electrode.	
	Add an equal volume of FA 6 to the boiling tube.	
Deca	ant the solution into another boiling t	ube and retain it for tests 2 and 3.
2.	Put about 2 cm depth of the solution from test 1 into a test-tube.	
	Add an equal volume of potassium iodide and shake the mixture thoroughly.	
	Filter the mixture.	
3.	Put about 2 cm depth of the solution from test 1 into a test-tube.	
	Add 1 cm depth of deionised water to the test-tube.	
	Then add a small piece of aluminium foil and shake the mixture thoroughly. Observe the mixture until no further changes are seen.	
3.	Add an equal volume of potassium iodide and shake the mixture thoroughly. Filter the mixture. Put about 2 cm depth of the solution from test 1 into a test-tube. Add 1 cm depth of deionised water to the test-tube. Then add a small piece of aluminium foil and shake the mixture thoroughly. Observe the mixture until no further changes are seen.	
- (c) Consider your observations in Table 3.5.
 - (i) Explain the colour changes you observed in test 1 in Table 3.5, in terms of the ions present in the solutions.

(ii) State the role of potassium iodide in test 2 in Table 3.5. Explain your answer in terms of oxidation state changes.

.....[1]

(d) Identification of ions present in FA 9

(i) Perform the tests described in Table 3.6, and record your observations in the table. Test and identify any gases evolved. If there is no observable change, write **no observable change**.

Table	3.6
-------	-----

	tests	observations
1.	Test the FA 9 solution using Universal Indicator paper.	
2.	To 2 cm depth of FA 9 in a test-tube, add barium nitrate dropwise, with shaking, until no further change is seen.	

(ii) Suggest the identity of **FA 9**. Describe one chemical test using a reagent from the Qualitative Analysis Notes provided to confirm the identity of the **cation** in **FA 9**.

Identity of FA 9 :[1]
Chemical test:
[1]
[Total: 28]

Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of aqueous cations

action	reaction with		
calion	NaOH(aq)	NH₃(aq)	
aluminium, Al ³⁺ (aq)	white ppt. soluble in excess	white ppt. insoluble in excess	
ammonium, NH₄⁺ (aq)	ammonia produced on heating	_	
barium, Ba ²⁺ (aq)	no ppt. (if reagents are pure)	no ppt.	
calcium, Ca²⁺(aq)	white. ppt. with high [Ca²+(aq)]	no ppt.	
chromium(III), Cr³⁺(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, Mg²⁺(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess	
manganese(II), Mn²⁺(aq)	off-white ppt., rapidly turning brown on contact with air insoluble in excess	off-white ppt., rapidly turning brown on contact with air insoluble in excess	
zinc, Zn ²⁺ (aq)	white ppt. soluble in excess	white ppt. soluble in excess	

(b) Reactions of anions

ion	reaction
carbonate, CO ₃ ²-	CO ₂ liberated by dilute acids
chloride, C <i>l</i> [–] (aq)	gives white ppt. with Ag⁺(aq) (soluble in NH₃(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, NO₃⁻ (aq)	NH_3 liberated on heating with OH ⁻ (aq) and A <i>l</i> foil
nitrite, NO₂⁻ (aq)	NH ₃ liberated on heating with OH ⁻ (aq) and A <i>l</i> foil; NO liberated by dilute acids (colourless NO \rightarrow (pale) brown NO ₂ in air)
sulfate, SO₄ ^{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, NH₃	turns damp red litmus paper blue	
carbon dioxide, CO ₂	gives a white ppt. with limewater (ppt. dissolves with excess CO ₂)	
chlorine, Cl ₂	bleaches damp litmus paper	
hydrogen, H ₂	"pops" with a lighted splint	
oxygen, O ₂	relights a glowing splint	
sulfur dioxide, SO ₂	turns aqueous acidified potassium manganate(VII) from purple to colourless	

(d) Colour of halogens

halogen	colour of element	colour in aqueous solution	colour in hexane
chlorine, Cl ₂	greenish yellow gas	pale yellow	pale yellow
bromine, Br ₂	reddish brown gas / liquid	orange	orange-red
iodine, I ₂	black solid / purple gas	brown	purple

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Suggested solutions



DUNMAN HIGH SCHOOL Preliminary Examinations 2018 Year 6

H2 CHEMISTRY

Paper 4 Practical

9729/04 28 August 2018 2 hour 30 minutes

INSTRUCTIONS TO CANDIDATES

- 1 Write your name, index number and class on this cover page.
- 2 Give details of the practical shift and laboratory where appropriate, in the boxes provided.
- 3 Write in dark blue or black pen.
- 4 You may use an HB pencil for any diagrams or graphs.
- 5 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 17 and 18.

Shift Laboratory

For Examiner's Use		
Question No.	Marks	
1	14	
2	13	
3	28	
Total	55	

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

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

1 Investigation of reaction kinetics between triacetin and lipase

Lipase is an enzyme that breaks down, hydrolyses, the lipids present in animal fats and vegetable oils. It does so by hydrolysing ester bonds. A general reaction scheme for this process is shown below; the size of the R group and its level of saturation will depend on the lipid used.

CH2OCOR				CH ₂ OH		
CHOCOR	+	3H ₂ O	>	снон	+	3RCOOH
I CH ₂ OCOR				I CH₂OH		
				glycerol		fatty acid

Olive oil is often used as a substrate in testing for lipase, with the oleic acid released being titrated with sodium hydroxide solution. Oleic acid, $C_{17}H_{33}COOH$, is a mono–unsaturated fatty acid.

In this experiment, glycerol triethanoate (triacetin) is used as the substrate. Lipase breaks this substrate down into glycerol and ethanoic acid as shown below.



The ethanoic acid produced lowers the pH of the solution. This change can be detected by using a suitable acid–base indicator, bromocresol purple which changes from purple at high pH value to yellow at lower pH value. Sodium carbonate is added to the triacetin to ensure that the pH is high enough at the start of the experiment. Only after the sodium carbonate has all reacted with the liberated ethanoic acid will the ethanoic acid concentration rise and the pH value decreases. The reaction time is measured from the initial point of mixing the solutions until the end–point of the indicator is reached.

The following reagents are provided for this experiment.

- **FA1** is triacetin
- **FA 2** is 0.5% sodium carbonate solution
- **FA 3** is 8% lipase solution
- **FA 4** is Bromocresol purple solution

Procedure

- 1. To a test-tube, add 2 drops of **FA 2** followed by 1 drop of **FA 4**.
- 2. Using a dropper, add 5 drops of **FA 1** to the test tube.
- 3. Using a 250 cm³ beaker, collect 200 cm³ of warm water from the dispenser.
- 4. **Swirl the bottle** containing **FA 3** before using a syringe to transfer 0.20 cm³ of **FA 3** into the test tube. Start the stopwatch immediately and place the test tube into the warm water bath.
- 5. Shake the test tube continuously. This is necessary to ensure that FA 1 and FA 3 are continually mixed.
- 6. Record the reaction time, *t* (in seconds) when the mixture turns yellow. This will be a gradual process.
- 7. Repeat steps 1 6 for four other test tubes, using different volumes of **FA 3** as shown in the table below.

Test Tube	Volume of FA 3 / cm ³
1	0.20
2	0.40
3	0.60
4	0.80
5	1.00

8. Calculate the value of reaction rate, $\frac{1}{t}$, for each experiment.

(a) Results:

(i)

Test Tube	Reaction time 't' / s	1/t / s ⁻¹
1	166	0.00602
2	139	0.00719
3	117	0.00854
4	89	0.0112
5	72	0.0138

[4]

- 1/t vs vol of FA 3 used 1/t / s⁻¹ 0.016 0.014 0.012 0.01 0.008 0.006 0.004 0.002 0 0 0.2 0.4 0.6 0.8 1 1.2 Vol of FA 3 used / cm³
- (ii) Plot the reaction rate, $\frac{1}{t}$, against the volume of **FA 3** used.

[3]

(iii) By considering the graph in (a)(ii), deduce the order of reaction with respect to lipase, FA 3. Explain your deduction.

[3]

A best fit <u>linear graph</u> was obtained. This suggest that the relative rate as represented by 1/t <u>increases proportionately</u> with increasing volume of lipase used. The increasing volume of lipase used can be treated as increasing concentration since volume of all other reagents are maintained the same. Hence, the <u>order of reaction with respect to lipase is 1</u>.

(iv) The weighted reaction time can be obtained by multiplying the appropriate conversion factor to the reaction time, *t* (in seconds).

Test Tube	Conversion factor	Weighted reaction time / s
1	0.20	
2	0.40	
3	0.60	
4	0.80	
5	1.00	

Based on your deduction in (a)(iii), sketch the expected graph of weighted reaction time, in seconds, against the volume of FA 3 used. Explain your sketch.

[2]



Since the **weighted factor is the same magnitude as the volume of FA3 used** and that **order of reaction with respect to FA3 is one**, a straight line with zero gradient is expected.

(b) Explain how the volumes of FA 1, FA 2 and FA 3 should change in the procedure in order to investigate the relationship between substrate concentration and the rate of reaction. You are **not** required to give exact figures.

[2]

The volume of FA 1 (triacetin) must change with each experiment eg it should increase from test tube 1 to 5 while the volume of FA 3 (lipase) should be kept constant for all 5 test tubes. The volume of FA 2 (sodium carbonate) solution should be kept constant for all 5 test tubes. Any changes in rate of reaction could then be attributed to the change in substrate concentration.

[Total: 14]

2 Planning

An ideal gas is a theoretical idea – a gas in which there are no attractive forces between the molecules, and in which the molecules take up no space. The ideal gas law is usually stated as pV = nRT, where

- *p* is the pressure
- V is the volume
- *n* is the number of moles
- T is the temperature in K

of the gas, and

• *R* is the ideal gas constant.

The value of R is determined experimentally by measuring the other variables in the equation, and solving mathematically to get the value of the constant. R is the same for all gases – provided the gas has ideal behaviour.

In this experiment you will determine the ideal gas constant using H_2 gas. The H_2 will be generated using the reaction between magnesium and hydrochloric acid.

 $Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$

You may assume you are provided with:

- a two-necked round bottom flask,
- a rubber tubing,
- a water tub,
- 0.1 mol dm⁻³ hydrochloric acid,
- thermometer,
- barometer (instrument used to measure pressure),
- one piece of magnesium ribbon strip of about 0.06 g,
- apparatus normally found in a school laboratory
- (a) Your plan should contain the following:
 - the procedure that you would follow and the measurements that you would take
 - a tabulation of the experimental data to be collected
 - the reactants and conditions that you would use
 - the mass of magnesium that you would use and the volume of hydrochloric acid that you would measure. Assume that the molar volume of gas under experimental conditions is 24.0 dm³ mol⁻¹.
 [A_r: Mg, 24.3]

[7]

Pre-Calculations:

If 0.06 g of Mg was used, No. of moles of HC*l* required = $\frac{0.06}{24.3} \times 2 = 4.938 \times 10^{-3}$ mol Volume of HC*l* required = 49.38 cm³ (volume of HC*l* used must be greater than 49.4 cm³) Volume of H₂ evolved = 2.469 × 10⁻³ × 24000 = 59.3 cm³ (assuming r.t.p.)

Maximum mass of Mg allowed to evolve 50 cm³ of H₂: No. of moles of Mg = $\frac{0.05}{24}$ = 2.083 × 10⁻³ mol Mass of Mg = 2.083 × 10⁻³ × 24.3 = 0.0506 g Minimum volume of HC*l* required = $\frac{2.083 \times 10^3 \times 2}{0.1}$ = 0.0417 dm³ = 41.7 cm³

Procedure:



1) Cut the magnesium strip to three roughly equal pieces. Using a weighing balance, weigh each piece of magnesium strip in a weighing bottle. Each strip should weigh about 0.02 g.

2) Place one piece of cut magnesium strip into the two-necked round bottom flask.

3) Secure the two-necked round bottom flask with a retort stand.

4) Using a 50 cm³ measuring cylinder, **measure out 25 cm³ of 0.1 mol dm⁻³ hydrochloric acid**. Transfer the 25 cm³ of 0.1 mol dm⁻³ hydrochloric acid to a dropping funnel.

5) Connect the dropping funnel to one of the necks of the two-necked round bottom flask.

6) Fill the water tub with tap water.

7) Submerge the mouth of an inverted 50.00 cm³ burette (filled with water) in the water tub and secure the burette with a second retort stand. Adjust the water level in the burette until it is between 48.00 cm³ and 50.00 cm³. Note and record the initial reading of the burette.

8) **Connect one end of a rubber tubing** (with stopper) to the other neck of the two-necked round bottom flask and place the other end inside the inverted burette.

9) Measure and record the **ambient temperature using the thermometer**.

10) Measure and record the pressure of the room using the barometer.

11) Open the tap of the dropping funnel fully and gently swirl the two-necked round bottom flask. Close the tap immediately when all the hydrochloric acid is added.

12) Note the final reading of the burette when all effervescence has ceased.

13) Repeat Steps 2 to 12 with the other two pieces of magnesium.

Tabulation of data:

Experiment	Mass of empty weighing bottle /g	Mass of weighing bottle and Mg strip /g	Mass of Mg strip used / g	Final burette reading / cm ³	Initial burette reading / cm ³	Volume of H ₂ produced / cm ³	Temperature / °C	Barometer reading / kPa
1								
2								
3								

(b) State two basic assumptions of an ideal gas.

[2]

[4]

The gas particles have **negligible volume compared to the volume of the container**. There are **no intermolecular forces of attraction** between gas particles.

The collisions which occur between gas particles and with walls of the container are **perfectly elastic**.

The gas particles are in **constant random motion**.

- (c) Real gases do not obey the ideal gas law exactly. Sketch a **fully labelled** graph representing the deviation from ideality. Your sketch should include:
 - ideal gas
 - H₂ gas
 - CH₄ gas



[Total: 13]

3 Investigation of chemical reactions of electrolytes

You are provided with the following. **FA 5** is sodium chloride solution. **FA 6** and **FA 9** are aqueous electrolytes, each containing one cation and one anion.

(a) Electrolysis of FA 5

1. Set up the apparatus and circuit as shown in Fig. 3.1.



Fig 3.1

- 2. Transfer about 200 cm³ of **FA 5** into the glass beaker.
- 3. Ensure that the graphite (anode) is partially submerged in **FA 5** by adjusting the height of the clamp.
- 4. Immerse one end of the graphite (cathode) in **FA 5** for a few minutes and record your observations in Table 3.1. You do **not** need to collect and test any gases evolved.

Table 3.	1
----------	---

electrolyte	observations at the electrodes		
	anode: <u>effervescence / bubbles</u> of greenish yellow, pungent gas observed		
FA 5	cathode: vigorous <u>effervescence /</u> more <u>bubbles</u> of colourless, odourless gas observed		

[1]

5. Perform the tests described in Table 3.2, and record your observations in the table.

Table 3.2

	tests	observations		
1.	Add one drop of Universal Indicator solution to FA 5 near the cathode .	<u>Green</u> Universal Indicator solution turned <u>purple/violet</u> .		
2.	Place a piece of moist blue litmus paper near the anode . Observe until no further change is seen.	<u>Gas evolved</u> turned moist blue litmus paper red and then <u>bleached</u> it.		

[2]

6. Remove both electrodes from **FA 5** and rinse them thoroughly with deionised water.

Consider your observations in Table 3.2.

(i) Explain, with the aid of an equation, the observations made in test 1 in Table 3.2.

[2]

$\underline{2H_2O+2e^-} \rightarrow H_2 + 2OH^-$

<u>Water is preferentially reduced</u> at the cathode, producing hydrogen gas and <u>hydroxide ions</u> which make the solution near the cathode <u>basic</u>.

(ii) With reference to the data below, suggest an explanation for your observations in test 2 in Table 3.2, in terms of *E* values.

electrode reaction	E [⊕] / V
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23

The observations from test 2 of Table 3.2 suggest that <u>chlorine gas is produced at</u> <u>the anode</u>.

Thus **FA 5** could be concentrated sodium chloride solution with a <u>high concentration</u> of chloride ions (> 1 mol dm⁻³) so that by <u>Le Chatelier's Principle, the position of</u> the Cl₂ + 2e⁻ \rightleftharpoons 2C*I*⁻ equilibrium will shift to the left to favour the backward oxidation reaction.

Then <u> $E(CI_2/CF)$ becomes less positive than $E^{-\Theta}(O_2/H_2O) = +1.23 V$ and chloride ion is preferentially oxidised at the anode.</u>

[3]

(b) (i) Qualitative analysis of FA 6

FA 7 is a solution of potassium sodium tartrate tetrahydrate in sodium hydroxide. **FA 8** is an organic compound with only one functional group.

Perform the tests described in Table 3.3, and record your observations in the table. You do **not** need to test and identify any gases evolved. If there is no observable change, write **no observable change**.

Table	3.3
-------	-----

	tests	observations
1.	To 1 cm depth of FA 6 in a test-tube, add aqueous ammonia dropwise, with shaking, until no further change is seen.	Blue ppt formed, soluble in excess aqueous ammonia to give dark blue solution.
2.	To 1 cm depth of FA 6 in a test-tube, add an equal volume of FA 7 .	Blue ppt formed, soluble in excess FA 7 to give dark blue solution.
	Add 1 cm depth of FA 8 and shake the mixture thoroughly.	Dark blue solution turned lighter blue (due to dilution).
	Warm the mixture in a water bath. Observe the mixture until no further changes are seen.	Effervescence of gas Blue solution turned purple and then colourless. Brick-red / red-brown precipitate formed.
		[4]

Identify the cation present in FA 6 and the functional group present in FA 8.

[2]

FA 6: <u>Cu²⁺(aq)</u> FA 8: (aliphatic) Aldehyde

(ii) Electrolysis of FA 6

- 1. Repeat steps 1 to 3 of the procedure in 3(a) using FA 6.
- 2. Immerse one end of the graphite (cathode) in **FA 6** for a few minutes until it is coated with a **thin layer of solid** and record your observations in Table 3.4. You do **not** need to identify any gases evolved.
- 3. Remove the graphite (cathode) from **FA 6** and rinse it with deionised water.
- 4. Retain the graphite (cathode) for further tests in (b)(iii).

electrolyte	observations at the electrodes
FAC	anode: <u>bubbles</u> of colourless, odourless gas observed
FA 6	cathode: <u>pink/red-brown solid</u> deposited

[1]

(iii) Investigation of some chemical reactions involving the solid deposited

Perform the tests described in Table 3.5, and record your observations in the table. Test and identify any gases evolved. If there is no observable change, write **no observable change**.

	tests	observations
1.	Put the graphite (cathode) from (b)(ii) in a boiling tube.	
	Carry out the following steps in the fume hood.	
	Cautiously add 2 cm depth of concentrated hydrochloric acid to the boiling tube and shake the mixture thoroughly to dissolve, as much as possible, the solid coated on the electrode.	Pink/red-brown solid dissolved to give yellow solution.
	Add an equal volume of FA 6 to the boiling tube.	Yellow solution turned green.
Dec	ant the solution into another boiling t	ube and retain it for tests 2 and 3.
2.	Put about 2 cm depth of the solution from test 1 into a test-tube.	
	Add an equal volume of potassium iodide and shake the mixture thoroughly.	Green solution turned brown/orange. White/cream precipitate formed.
	Filter the mixture.	Brown/orange solution as filtrate and White/cream solid as residue.
3.	Put about 2 cm depth of the solution from test 1 into a test-tube.	

Table 3.5

Add 1 cm depth of deionised water to the test-tube.	Green solution turned pale blue/pale green.
Then add a small piece of aluminium foil and shake the mixture thoroughly. Observe the mixture until no further changes are seen.	Effervescence of a colourless, odourless gas that extinguished a lighted splint with a 'pop' sound. The gas is hydrogen.
	Aluminium foil dissolved and red- brown solid formed on its surface.
	Pale blue/ pale green solution decolourised.

[6]

- (c) Consider your observations in Table 3.5.
 - (i) Explain the colour changes you observed in test 1 in Table 3.5, in terms of the ions present in the solutions.

Copper deposited on the electrode dissolved in concentrated HCl to form [CuC l_4]²⁻ ions which gave the yellow solution.

FA 6 is blue due to the presence of $[Cu(H_2O)_6]^{2+}$ ions in the solution.

On adding **FA 6** to the yellow solution, <u>a mixture of $[Cu(H_2O)_6]^{2+}$ and $[CuCl_4]^{2-}$ ions gave a green solution.</u>

- [2]
- (ii) State the role of potassium iodide in test 2 in Table 3.5. Explain your answer in terms of oxidation state changes.

Potassium iodide is a <u>reducing agent</u> in test 2. The <u>oxidation number of iodine</u> <u>increased from -1 in I⁻ to 0 in I₂</u> while the oxidation number of copper deceased from +2 in Cu²⁺ to +1 in Cu⁺.

[1]

(d) Identification of ions present in FA 9

(i) Perform the tests described in Table 3.6, and record your observations in the table. Test and identify any gases evolved. If there is no observable change, write **no observable change**.

Table	3.6
-------	-----

	tests	observations
1.	Test the FA 9 solution using Universal Indicator paper.	Green UI paper turned dark brown and solution is <u>pH 1</u>
2.	To 2 cm depth of FA 9 in a test-tube, add barium nitrate dropwise, with shaking, until no further change is seen.	white ppt formed

[2]

(ii) Suggest the identity of **FA 9**. Describe one chemical test using a reagent from the Qualitative Analysis Notes provided to confirm the identity of the **cation** in **FA 9**.

[2]

FA 9 is dilute sulfuric acid.

Add <u>CO₃²⁻(aq)</u> ions to **FA 9** and <u>CO₂ will be liberated, forming white ppt with</u> <u>Ca(OH)₂(aq)</u>, if H⁺ is present.

[Total: 29]