

RIVER VALLEY HIGH SCHOOL JC 2 PRELIMINARY EXAMINATION

CANDIDATE NAME	<mark>Sug</mark>	geste	<mark>ed An</mark>	swers		
CLASS	2	0	J			
CENTRE NUMBER	S				INDEX NUMBER	

H2 CHEMISTRY

Paper 2 Structured Questions

9729/02 15 September 2021

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, index number, class and name on all the work that you hand in. Write in dark blue or black pen. You may use an HB pencil for any diagrams or graphs.

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

DO NOT WRITE IN ANY BARCODES.

Answer **all** questions in the spaces provided on the Question Paper. If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

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

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

	For Examiner's Use							
Question Number	1	2	3	4	5	6	7	
Marks	12	9	12	9	8	18	7	
significant figures			units				Total	75

This document consists of 23 printed pages and 1 blank page.

9729/02/PRELIMS/21



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1 In recent years, there has been worldwide interest in the possible extraction of "shale gas" (a form of natural gas) as an important energy source.

2

(a) One of the problems associated with using shale gas is its variable composition.

Table 1.1 shows the percentage composition of shale gas from four different sources **J**, **K**, **L** and **M**.

source	CH4	C ₂ H _x	C ₃ H _y	CO ₂	N ₂
J	80.3	8.1	2.3	1.4	7.9
к	82.1	14.0	3.5	0.1	0.3
L	88.0	0.8	0.7	10.4	0.1
м	77.5	4.0	0.9	3.3	14.3

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In the formulae above, x and y are variables.

(i) Draw the structures of three possible hydrocarbons with 3 carbon atoms.

(Any 3 of the compounds below)

- CH₃CH₂CH₃
- CH₃CH=CH₂
- CH₃C≡CH
- CH₂=C=CH₂
- Δ (cyclopropane)
- (ii) State the source of shale gas, J, K, L or M, that will likely provide the most energy when completely burned.

Explain your answer.

 ${\bf K},$ since it has the greatest % of hydrocarbons / carbon-containing compounds

(iii) Suggest a method by which carbon dioxide can be removed from shale gas.

(Any one of these 3 answers)

- reacted with lime / CaO / soda lime / Ca(OH)₂ / KOH / NaOH /
- liquefied under pressure
- dissolved in water under pressure

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RV RV (b) Fracking is the process of drilling down into the earth before a high-pressure water mixture is directed at the rock to release the shale gas inside.

Water, sand and chemicals are injected into the rock at high pressure which allows the gas to flow out to the head of the well.

Magnesium hydroxide is one of the chemicals that can be used to control pH.

(i) The equation for the formation of the gaseous hydroxide ion is shown.

$$\frac{1}{2}H_2(g) + \frac{1}{2}O_2(g) + e^- \rightarrow OH^-(g) \qquad \Delta H = \Delta H_f(OH^-(g))$$

Use the data from Table 1.2 and the *Data Booklet*, construct a Born-Haber Cycle to calculate $\Delta H_{\rm f}$ (OH⁻(g)).



Table 1.2



(c) Hydrazine, N₂H₄, can be also used as an energy source and is stored as a liquid. It reacts exothermically with oxygen to give only gaseous products.



(i) Hydrazine reacts with oxygen according to the following equation.

 $N_2H_4(I) + O_2(g) \rightarrow N_2(g) + 2H_2O(g)$

Given that the standard enthalpy change of vapourisation of hydrazine is +36.9 kJ mol⁻¹, calculate the enthalpy change of the above reaction with relevant data from the *Data Booklet*.



(ii) Explain, using Gibbs free energy change, why the reaction of hydrazine with oxygen is spontaneous at all temperatures.

 $\Delta G_{\rm r} = \Delta H_{\rm r} - T\Delta S_{\rm r}$ $\Delta S_{\rm r} \text{ is positive since there is an increase in number of gaseous}$ $\underline{\text{particles}} \text{ from 1 to 3.}$ Since both the $\Delta H_{\rm r}$ and $-T\Delta S_{\rm r}$ terms are negative, $\Delta G_{\rm r}$ is always <u>negative</u>. Hence, the reaction is spontaneous at all temperatures. [2]



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RV RV 2 (a) (i) Describe the reactions, if any, of the chlorides MgCl₂ and PCl₅ with water. Write equations for all reactions that occur, and suggest the pH of the resulting solutions. Relate the reactivity of these chlorides to their structures and bonding.

MgC l_2 has a **giant ionic lattice structure** and **strong electrostatic attraction between Mg²⁺ and Cl⁻ ions**. MgC l_2 dissolves in water readily to form an acidic solution of **pH 6.5**. Both hydration of ions and partial hydrolysis of Mg²⁺(aq) occurs. Hydrolysis occurs due to the polarisation of water molecules by the Mg²⁺ ion

 $MgCl_2(s) + 6H_2O(I) \rightarrow [Mg(H_2O)_6]^{2+}(aq) + 2CF(aq)$

 $[Mg(H_2O)_6]^{2+}(aq) + H_2O(I) \ll [Mg(H_2O)_5OH]^+(aq) + H_3O^+(aq)$

 PCl_5 has a <u>simple covalent structure</u>. PCl_5 dissolves and undergoes hydrolysis in water to form an acidic solution of <u>pH 2</u>. P atom in PCl_5 has <u>energetically accessible vacant 3d orbitals to</u> form dative bonds with water molecules.

 $PCl_5(s) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 5HCl(aq)$

[3]

(ii) Carbon is in the same group as silicon. Suggest and explain if CCl_4 will react with water.

CCl₄ does not react with water as carbon does not have energetically accessible empty 3d orbitals to accept the lone pair of electrons from water molecules.

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- (b) Phosphorus exist in isotopes, mainly ³¹P, ³²P and ³³P. ³¹P is the most stable isotope.
 - (i) Define *isotopes*.

lsotopes are atoms of the same element with the same number of protons but different number of neutrons.

- [1]
- (ii) ³¹P being the most stable isotope can react with chlorine to form phosphorus chloride. Phosphorus in phosphorus chloride can exhibit variable oxidation states. Based on your knowledge in periodicity, state the two common oxidation states of phosphorus in phosphorus chloride
 - +3, +5 [1]

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(iii) Phosphorus can exist as cations or anions.

Given the angle of deflection for ${}^{31}P^+$ is 6°, calculate the angle of deflection for ${}^{33}P^{3-}$ and add labelled line to the figure below to represent the paths of beam of ${}^{33}P^{3-}$ ions, at high temperature, in an electric field.



(iv) ³²P is unstable and decays rapidly to another element. During the decay, a neutron is converted to a proton with the release of an electron, forming a charged ion.

Write an equation to show the reaction.



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9729/02/PRELIMS/02

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3 The use of the *Data Booklet* is relevant in this question.

Values of the standard reduction potentials for certain silver species are given in Table 3.1. All ionic states refer to aqueous ions but other state symbols have been omitted.

Table 3.1

Electrode reaction	E N
$Ag^{2+} + e^- \ll Ag^+$	+2.00
$Ag_2S+2e^-\ll2Ag^++S^{2-}$	-0.69

These data are relevant to (a), (b) and (c).

- (a) Copper and silver are transition elements found in Group 11 and they can be found in their metallic form in nature. Even though copper and silver are analogous to each other, i.e. both have certain similarities in their physical and chemical properties, there are some differences as well.
 - (i) It is found that Cu⁺ ions form a pink solid in a blue solution. Explain why this can occur.

Cu⁺ ions undergo <u>disproportionation</u> to form Cu²⁺ and Cu. $E_{cell} = +0.52 - (+0.15) = +0.37 V$ (spontaneous)

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(ii) On the contrary, Ag^+ ions remain stable in water but not Ag^{2+} ions.

Use the data in Table 3.1, together with data from the *Data Booklet*, to explain why this is so for both silver species. Support your answers with relevant calculations where necessary.

Ag ²⁺ ions undergo redox* / reacts with water
E_{cell} for Ag ²⁺ [R] and water [O] = +2.00 - (+1.23) = +0.77 V
(spontaneous*)
Ag* ions cannot undergo redox* / cannot react with water
<i>E</i> cell for Ag ⁺ [R] and water [O] = $+0.80 - (+1.23) = -0.43 V$ (non-
spontaneous*)
OR
<i>E</i> cell for Ag ⁺ [O] and water [R] = $-0.83 - (+2.00) = -2.83 V$ (non-
spontaneous*)
OR E_{cell} for Ag ⁺ [O] and water [R] = -0.83 - (+2.00) = -2.83 V (non-spontaneous*)

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'Toning' of a coin is the result of a chemical reaction between the metal (b) surface of the coin and an atmospheric element.

When a silver coin is subjected to prolonged exposure to air and sulfidecontaining compounds such as hydrogen sulfide, the surface will develop a tarnish which is predominantly silver(I) sulfide, Ag₂S.

Depending on the thickness and unevenness of the tarnish layer, the coins can exhibit a range of colours, in which a coin with rainbow toning or unusual toning patterns are unique and has significantly high value to coin collectors.



Example of natural toning on a silver dollar coin

(i) Construct a balanced equation for the formation of silver(I) sulfide on the silver coin via exposure in air and hydrogen sulfide.

$$O_2 \ + 2H_2S + 4Ag \ \rightarrow 2H_2O \ + 2Ag_2S$$

(ii) Calculate the E_{cell} for this reaction.

$$E_{cell} = E_{(O_2/H_2O)} - E_{(Ag_2S/Ag)}$$

= +1.23 - (-0.69)
= +1.92 V

Nowadays, silver coins can be toned artificially via electrolysis. An example (C) of the setup is given below:



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8,8° silver coin

9

The electrolyte is prepared by adding sodium hydroxide and sulfur in hot water to form a concentrated aqueous solution of sodium sulfide. The silver coin is clamped with a crocodile clip and submerged in the electrolyte. The reaction begins when the free crocodile clip end comes in contact with the electrolyte.

(i) Effervescence can be seen at the free crocodile clip end. Identify the gas evolved and explain why the gas is produced.

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Gas is <u>H</u><sub>2</sub>. (2H<sub>2</sub>O + 2e<sup>-</sup> \rightarrow H<sub>2</sub> + 2OH<sup>-</sup>)
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H₂O is preferentially reduced, <u>as $E(H_2O/H_2)$ </u> (= -0.83 V) <u>is more</u> positive than $E(Na^+/Na)$ (= -2.71 V).

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(ii) Given that a current of 50 mA passes through the circuit in the setup above, calculate the time taken, in seconds, for 1.50×10^{-4} g of silver(I) sulfide to be deposited on the coin.

Amount of silver sulfide deposited = 1.50×10^{-4} g of Ag₂S

 $= 6.051 \times 10^{-7} \text{ mol of Ag}_2\text{S}$

Amount of electrons required = 1.210×10^{-6} mol of e

 $Q = It = nF = 1.210 \times 10^{-6}(96500) = 0.11678C = 0.1168 C$

t = 0.1168 / 0.05 = 2.336 s → <u>2.34 s</u>

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(d) Table 3.2 shows the numerical values of lattice energies for the silver halides. These have been determined from experimental data or theoretically calculated.

Silver halide	Experimental value / kJ mol ⁻¹	Theoretical value / kJ mol ⁻¹
AgF	-953	-920
AgC <i>l</i>	-908	-833
AgBr	-900	-815

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AgI -883 -77	}
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(i) By quoting appropriate data from the *Data Booklet*, explain why the theoretical lattice energy values of the silver halides decrease from AgF to AgI.

The <u>ionic radii of F⁻, Cl⁻, Br⁻ and I⁻ are 0.136 nm, 0.181 nm,</u> 0.195 nm and 0.216 nm respectively. As $|_{LE}| \propto \frac{q_+q_-}{r_+ + r_-}$ and the <u>ionic radii</u> of the halide ions <u>increases from F⁻ to I⁻</u>, the values of the theoretical lattice energies of the silver halides decrease from AgF to AgI.

(ii) Silver fluoride and silver iodide have the same crystal structure. There is close agreement between the experimental and theoretical values of lattice energy for AgF but not for AgI.

Suggest a reason for this.

<u>**I**</u>⁻ is a large anion and is polarised by Ag⁺ ion which results in the ionic bond in AgI having <u>some covalent character</u>, causing the experimental value to deviate from the theoretical value of lattice energy.

F⁻ ion is a small ion and is not easily polarised, hence AgF is essentially ionic (no covalent character).

[Total: 12]

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- 4 Amines are a class of compounds widely used in the agricultural industry. Ethylamine, $CH_3CH_2NH_2$ (p K_b = 3.3), is widely used in the production of herbicides.
 - (a) 25.0 cm³ of 0.888 mol dm⁻³ aqueous ethylamine was placed in a conical flask. 33.90 cm³ of sulfuric acid was required to completely neutralise the ethylamine.
 - (i) Calculate the initial pH of aqueous ethylamine in the conical flask.

CH₃CH₂NH₂(aq) + H₂O(l) \rightleftharpoons CH₃CH₂NH₃⁺(aq) + OH⁻(aq) K_b = 10^{`3.3} = 5.012 × 10^{`4} mol dm^{`3} $= \frac{x^2}{0.888}$ x = [OH⁻] = <u>0.02110</u> mol dm^{`3}

9729/02/PRELIMS/02



pH = 14.0 ` (`lg 0.02110) = <u>12.3</u>

(ii) Calculate the concentration of the dilute sulfuric acid used in the experiment.

Amt of ethylamine = $0.025 \times 0.888 = 0.0222$ mol = amt of H⁺ Amount of H₂SO₄ = $\frac{0.0222}{2}$ = 0.0111 mol [H₂SO₄] = $\frac{0.0111}{33.90 \times 10^{-3}}$ = 0.327 mol dm³ (Accept: 0.311 mol dm³)

(b) (i) A universal indicator solution was used in the experiment. The colours corresponding to the pH of the solution in the conical flask are as shown in Fig. 4.1.

Using appropriate calculations, state the colour of the solution mixture at equivalence point.



At equivalence point, only the ethylammonium salt is present: $CH_3CH_2NH_3^+(aq) + H_2O(l) \rightleftharpoons CH_3CH_2NH_2(aq) + H_3O^+(aq)$ $[CH_3CH_2NH_3^+] = \frac{0.0222}{(25+33.9)\times 10^{-3}} = 0.377 \text{ mol dm}^{\cdot 3}$ $x^2 = (10^{\cdot(14-3.3)})(0.377)$ $x = 2.74 \times 10^{\cdot 6}$ pH = 5.56Accept: <u>yellow / yellow green / lime green</u>

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(ii) Chemist Holmes performed the experiment using another indicator from Table 4.1. State and explain which indicator is the most suitable choice.

Indicator	Colour	Colour in	pH range over
	in acid	alkali	which the colour
			change occurs
Alizarin yellow	Yellow	Orange	10.1–13.0
Chlorophenol red	Yellow	Violet	4.8–6.7
Methyl orange	Red	Yellow	3.1–4.4
Phenolphthalein	Colourless	Pink	8.2-10.0

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<u>Chlorophenol red</u>. The <u>working pH range of chlorophenol red lies</u> within the sharp pH change near the equivalence point.

(c) Calculate the pH of the solution mixture when 50.00 cm³ of sulfuric acid has been added.

$$[H^+] = \frac{(0.05 - 0.0339) \times 0.327 \times 2}{0.075} = 0.140 \text{ mol dm}^3$$
$$pH = \underline{0.853}$$

(d) Using relevant information above and your answers from (a)(i), (b)(i) and (c), sketch the shape of the pH curve of the titration between aqueous ethylamine and sulfuric acid.



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RV RV (a) Hydroxychloroquine (HCQ) is a drug used in the treatment of arthritis and malaria. During the initial months of the Covid-19 pandemic, it was also touted as a drug for the prevention and treatment of Covid-19 which drove up the demand for HCQ. Subsequent drug trials indicated low efficacy of the drug in reducing mortality in patients. In June 2020, the U.S. Food and Drug Administration revoked its emergency authorisation of HCQ in the treatment of Covid-19.

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State the oxidation number of carbon labelled 1 in HCQ.



(b) The large-scale production of HCQ requires a key precursor **C** to be produced and its synthetic route is shown below.



- (i) Suggest reasons why the synthesis of **C** should not be carried out under
 - acidic conditions
 - very alkaline conditions

Under acidic conditions

Under acidic conditions, the amine functional group on **B** will be **protonated** and its lone pair of electrons will not be available for donation. The N atom in **B** will **not be able to act as a nucleophile**.



Under very alkaline conditions, the alcohol functional group on B will be <u>deprotonated/lose its proton</u>. The alkoxide ion formed can also <u>act as a nucleophile</u> to attack **A**. There will be side products formed/**C** will not be formed/yield of **C** will be low.

OR

OH acts as a competing nucleophile to attack A

(ii) Explain why it is necessary to use a limited amount of **A** in the synthesis to have a larger yield of **C**.

Using an excess of **A** will allow **C** to undergo <u>further nucleophilic</u> <u>substitution</u>, resulting in the formation of the quaternary ammonium salt which will lower the yield of **C**.

(c) Patients with severe Covid-19 symptoms often need breathing support. This is because infected lungs are less effective at absorbing oxygen into the bloodstream.

In our bodies, haemoglobin can bind up to four molecules of oxygen.

$$Hb(aq) + 4O_2(aq) \ll Hb(O_2)_4(aq)$$

(i) Write an expression for K_c in this reaction, stating its units.

$$\kappa_{c} = \frac{[Hb(O_{2})_{4}]}{[Hb][O_{2}]^{4}}$$
 Units: mol⁻⁴ dm¹²

(ii) Experiments have shown that when $[O_2] = 8.10 \times 10^{56}$ mol dm³, the concentration of Hb and Hb(O₂)₄ are equal.

Use this information to calculate a value for K_c .

$$K_{\rm c} = \frac{[{\rm Hb}({\rm O}_2)_4]}{[{\rm Hb}][8.1 \times 10^{-6}]^4} = \underline{2.32 \times 10^{20}} \, {\rm mol}^{-4} \, {\rm dm}^{12}$$

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RV RV (iii) All Singapore households are recently issued with an oximeter to monitor their blood oxygen saturation levels. Individuals whose blood oxygen levels are 94.0% and below should see a doctor immediately.

Use your value of K_c to calculate the [O₂] necessary for 94% of the Hb to be converted to Hb(O₂)₄.

 $K_{c} = \frac{[Hb(O_{2})_{4}]}{[Hb][O_{2}]^{4}}$ 94% conversion means that ratio of Hb(O_{2})_{4}:Hb is 94:6 2.32 × 10²⁰ = $\frac{94}{6[O_{2}]^{4}}$ [O₂] = <u>**1.61 × 10**⁵ mol dm³</u> State what the *K*_c value indicates about the position of equilibrium.

A very large *K*_c value that is greater than 1 suggests that the **equilibrium position lies very much to the right**.

[Total: 8]

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9729/02/PRELIMS/02



6 (Chloromethyl)cyclohexane undergoes nucleophilic substitution reaction with ethanol in the ethanol/ water mixture. This reaction is known as the solvolysis of (chloromethyl)cyclohexane. Isomer **A** is produced rather than isomer **B**.



(a) Suggest and explain why ethanol reacts predominantly instead of water.

The <u>electron-donating ethyl group increases the availability of lone pair</u> of electrons on O in ethanol, making it a stronger nucleophile than water.

The kinetics of the solvolysis of 0.0150 mol dm⁻³ chloromethylcyclohexane in 15% ethanol/water mixture is studied using conductivity measurements. The measurements were recorded at 5 seconds interval and given in the units of microsiemens per centimetre (μ S cm⁻¹). The conductivity is directly proportional to the amount of isomer **A** present in the sample.





Fig. 6.1

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- (b) In terms of structure and bonding, explain why
 - the conductivity is zero initially
 - the conductivity increases

(Chloromethyl)cyclohexane, ethanol, water (and ether/isomer **A**) have <u>simple covalent structures</u>, <u>without charge carriers</u>, hence the conductivity of the system is zero.

HC*l*, which has a <u>simple covalent structure</u>, <u>dissociates in water</u> completely to give <u>H⁺ and C*l*⁻ ions</u>, which can act as <u>charge carriers</u>. Hence, as the reaction progresses/ HC*l* is formed, the conductivity of the solution increases.

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(c) (i) Show how the initial rate of reaction for this experiment could be determined using Fig. 2.1.



[Assume that the rate of change of conductivity is equivalent to the rate of reaction.]

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(ii) Deduce the order of reaction with respect to (chloromethyl)cyclohexane. Explaining your reasoning.

Graphwork to show 2 t_{1/2} values

The <u>conductivity is (directly) proportional to the</u> [(chloromethyl)cyclohexane]. Since the <u> $t_{1/2}$ is approximately</u> constant at 102.5 s, the reaction is <u>first order</u> with respect to [(chloromethyl)cyclohexane].

(iii) The ethanol/ water mixture was changed from 15.0% to 30.0% and a new experiment carried out at the same temperature. When a similar graph was plotted, the gradient at each point remained the same.

Deduce the order of reaction with respect to ethanol. Explain your reasoning.

Since the initial <u>rate did not change</u>, the rate of reaction is <u>independent of [ethanol]</u>, the reaction is <u>zero order</u> with respect to ethanol.

(iv) Suggest the rate equation for the reaction that would result from the proposed mechanism.

Rate = k[(chloromethyl)cyclohexane]

(v) The concentration of the organic solution can be calculated using this simplified equation:

Conductivity = 7000[(chloromethyl)cyclohexane]

Calculate the value of the initial rate in mol $dm^{-3} s^{-1}$, hence determine the rate constant and its units, using your equation from (c)(iv).

Initial rate =
$$\frac{1.447}{7000}$$
 = 2.067 × 10⁻⁴ mol dm⁻³ s⁻¹
Rate constant = $\frac{2.067 \times 10^{-4}}{0.015}$ = 0.01378 = 0.0138 s⁻¹ [3]

(vi) The solvolysis reaction proceeds via two intermediates.

One intermediate is formed first, and it will then go on to form its isomer, which is more stable. In this process, a hydrogen shift occurs where the hydrogen atom moves from one atom to the adjacent atom. An example is shown below.

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Draw the mechanism for the solvolysis of (chloromethyl)cyclohexane to form the major product. The mechanism follows the following steps:

- Bond breaking occurs to form an carbocation intermediate
- Hydrogen shift occurs to produce a more stable intermediate
- Ethanol attacks the intermediate
- Deprotonation occurs to produce the major product

Show all charges, relevant lone pairs and the movement of electron pairs by using curly arrows.



- (d) Different halogenoalkanes have different reactivity towards nucleophilic substitution.
 - (i) Explain why (bromomethyl)cyclohexane reacts at a faster rate than (chloromethyl)cyclohexane.

C`Br has a lower bond energy than C`Cl

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(ii) The difference in reactivity is also dependent on the stability of the leaving group. The more stable the halide ion, the better the leaving group and the faster the rate of reaction. The pK_a values of HX is given below.

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Halide (X⁻)	р <i>К</i> а (НХ)
F⁻	+3
C <i>l</i> −	-7
Br⁻	-9
I-	-10

Considering pK_a of HX and the stability of the halide ion, suggest a reason for the faster rate of reaction for (bromomethyl)cyclohexane.

HBr has a <u>lower</u> pK_a , so Br⁻ is a <u>more stable anion</u> than Cl^- , the activation energy is lower and the reaction is faster. [1]

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RV RV 7 (a) Compounds D and E can be used to synthesise Ranolazine in several steps.

21



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Structure of F:

9729/02/PRELIMS/02

[Turn over



(ii) Suggest reagents and conditions for each of the steps 1 and 2, and reagent **G**.

22



(b) (i) State the hybridisation of the unsaturated carbon in CH₃CN.

sp

- [1]
- (ii) Hence, suggest the difference in bond length between the C–C bond acetonitrile (CH₃CN) and ethane (CH₃CH₃).

Acetonitrile consists sp³ C – sp C bond , while ethane contains sp³
<u>C – sp³ C bond</u> . An sp-hybridised orbital has a greater s-character
than an sp ³ -hybridised orbital and smaller in size/ electron in it is
<u>closer to the nucleus</u> . Hence, the $sp^3 C - sp C$ bond in CH ₃ CN is
<u>shorter</u> than the sp ³ C – sp ³ C bond in ethane.

[Total: 7]

[2]

RV

RV

RV

RV RV