RIVER VALLEY HIGH SCHOOL
JC 2 PRELIMINARY EXAMINATION

CANDIDATE NAME	
CLASS	2 0 J
CENTRE NUMBER	S
INDEX NUMBER	

H2 CHEMISTRY

9729/01

Paper 1 Multiple Choice

23 September 2021

1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, glue or correction fluid.
Write your name, class, centre number and index number on the Answer Sheet in the spaces provided.

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

Read the instructions on the Answer Sheet very carefully.

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

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

1 When potassium chlorate(V) $KClO_3$, is heated at its melting point, it disproportionates to potassium chlorate(VII) $KClO_4$, and potassium chloride.

What is the maximum number of moles of potassium chlorate(VII) which could be produced from 0.200 mol of potassium chlorate(V)?

A 0.200 **B** 0.150 **C** 0.100 **D** 0.0500

2 Methane was burned in an incorrectly adjusted Bunsen burner. The methane was converted into a mixture of carbon dioxide and carbon monoxide in the ratio 99:1, together with water vapour.

What will be the volume of oxygen consumed when y dm^3 of methane is burned?

A $2y - \frac{0.01y}{2}\ dm^3$

B $2y - 0.01y\ dm^3$

C $y - \frac{0.01y}{2}\ dm^3$

D $y - 0.01y\ dm^3$

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

The table shows the fifth, sixth, seventh, eighth and ninth ionisation energies of three elements in the third period.

	Ionisation energy/ kJ mol^{-1}				
	5^{th}	6^{th}	7^{th}	8^{th}	9^{th}
Element **A**	6274	21267	25431	29872	35905
Element **B**	7004	8496	27107	31719	36621
Element **D**	6542	9362	11018	33604	38600

Which statements are correct?

1 The first ionisation energy of **A** is lower than that of **B**.

2 The atom of element **A** will be isoelectronic with D^{2+}.

3 **A** and **D** forms an ionic solid AD_3.

A 1 and 3 only **B** 2 and 3 only **C** 1 only **D** 2 only

4 In which order are the electrons lost in forming Ga^{4+} ion?

	1st	2nd	3rd	4th
A	3d	4p	4s	4s
B	3d	4s	4s	4p
C	4p	4s	3d	3d
D	4p	4s	4s	3d

5 Which pair of liquids, when mixed, will give out heat?

A CH_2Cl_2 and $CH_3COCH_2CH_3$

B CH_2Cl_2 and C_6H_{12}

C CF_4 and $COCl_2$

D CCl_4 and $C_{10}H_{21}OH$

6 A 10 m^3 of oxygen gas at a pressure of 50 kPa and 30 m^3 of nitrogen gas at a pressure of 100 kPa are introduced to a 15 m^3 vessel at 300 K. The pressure in the vessel after mixing is **E** kPa.

Subsequently, the 15 m^3 vessel is heated to a temperature of **F** K and total pressure at **F** K is 350 kPa.

Given that the gases do not react at all temperatures, what are the values of **E** and **F**?

	E kPa	**F** K
A	233	401
B	233	451
C	400	263
D	400	343

7 A molecule of BCl_3 is planar, whereas a molecule of PH_3 is pyramidal.

Which statements are responsible for the difference in shapes?

1 The repulsion between chlorine atoms is greater than that between hydrogen atoms.

2 The boron atom in BCl_3 has six electrons in its valence shell, whereas the phosphorus atom in PH_3 has eight.

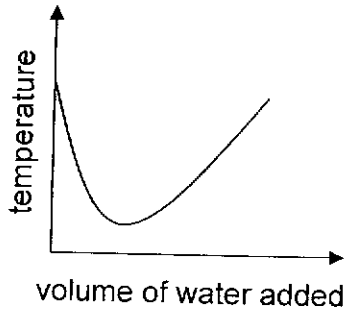
3 The atomic radius of phosphorus is greater than that of boron.

A 1 only **B** 2 only **C** 1 and 3 only **D** 2 and 3 only

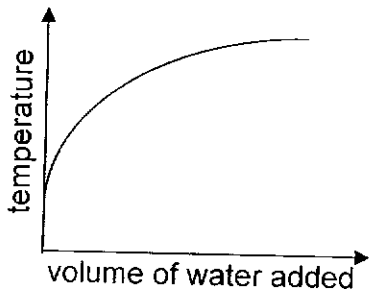
8 When water is stirred with glucose, strong hydrogen bonds are initially formed between glucose molecules and water molecules.

As more water is added, these hydrogen bonds are broken. Which of these graphs best represents the observed temperature changes?

A



C



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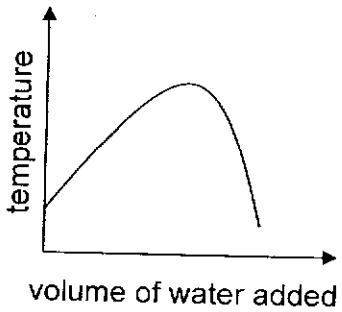

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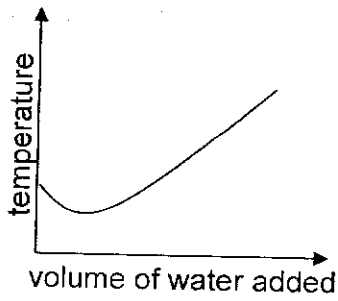


9 Highly toxic disulfur decafluoride decomposes by a free-radical process.

$$S_2F_{10}(g) \ll SF_4(g) + SF_6(g)$$

In a study of the decomposition, S_2F_{10} was placed in a 2.0 dm^3 flask and heated to 100 °C. The equilibrium $[S_2F_{10}]$ was found to be 0.5 mol dm^{-3}. More S_2F_{10} was then added and the new equilibrium $[S_2F_{10}]$ was 2.5 mol dm^{-3}.

What is the amount of S_2F_{10} reacted in terms of the equilibrium constant, K_c of the decomposition reaction when more S_2F_{10} was added?

A $(0.5K_c)^{0.5} - (2.5K_c)^{0.5}$

B $(2.5K_c)^{0.5} - (0.5K_c)^{0.5}$

C $(2K_c)^{0.5} - (10K_c)^{0.5}$

D $(10K_c)^{0.5} - (2K_c)^{0.5}$

10 Nitrogen oxide reacts with hydrogen gas as shown in the equation below.

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$$

The reaction was determined to be second order with respect to NO and first order with respect to H_2. In an experiment, 2.0 mol dm^{-3} of excess NO was used to react with H_2, the concentration of H_2 decreased to 6.25% of its original value in 24 minutes.

How many minutes will it take for the concentration of H_2 to decrease to 6.25% of its original value if the experiment was repeated using an excess of 4.0 mol dm^{-3} of NO?

A 1.5 **B** 4.5 **C** 6.0 **D** 9.0

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

Water dissociates as follows: $H_2O(l) \ll H^+(aq) + OH^-(aq)$

At 25 °C, the equilibrium value of $[H^+] = 10^{-7}$ mol dm^{-3} and $[H_2O] = \frac{1000}{18}$ mol dm^{-6}.

In which order would the numerical value of pH, pK_a and pK_w increase for this equilibrium at 25 °C?

	smallest ⟶		*largest*
A	pH	pK_a	pK_w
B	pH	pK_w	pK_a
C	pK_a	pK_w	pH
D	pK_w	pK_a	pH

12 The following reaction occurs when light is shone for a fixed period into a solution of CH_2ICH_2I and I_2 in tetrachloromethane at 100 °C.

$$CH_2ICH_2I \rightarrow CH_2{=}CH_2 + I_2$$

What conclusions about the rate of formation of iodine can be drawn from the data in the table?

experiment	relative initial concentrations		relative light intensity	relative initial rate of formation of iodine
	CH_2ICH_2I	I_2		
1	2	1	4	2
2	2	1	1	1
3	1	1	4	1
4	1	2	4	1

1 proportional to $\sqrt{\text{light intensity}}$

2 independent of initial concentration of I_2

3 proportional to initial concentration of CH_2ICH_2I

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

13 Which equations represent a Brønsted-Lowry acid-base reaction?

1 $C_6H_6 + Br^+ \rightarrow [C_6H_6Br]^+$

2 $CH_3CH_2NH_3^+ + NH_3 \rightarrow CH_3CH_2NH_2 + NH_4^+$

3 $CH_3CH_2^+ + Br^- \rightarrow CH_3CH_2Br$

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

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

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

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

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

	First to precipitate	⟶	Last to precipitate
A	$BaSO_4$	$BaCO_3$	$Ba(IO_3)_2$
B	$Ba(IO_3)_2$	$BaCO_3$	$BaSO_4$
C	$BaSO_4$	$Ba(IO_3)_2$	$BaCO_3$
D	$BaCO_3$	$Ba(IO_3)_2$	$BaSO_4$

15 Which factors determine the total amount of oxygen produced at the anode during the electrolysis of aqueous sodium fluoride?

	mass of electrode	current	time
A	✓	✓	X
B	✓	X	X
C	X	✓	✓
D	X	X	✓

16 **W**, **X**, **Y** and **Z** are four consecutive elements in Period 3 but not necessarily in the order presented.

- Chloride of **W** dissolves in water and turns moist blue litmus red.
- **X** is a good conductor of electricity.
- **Y** has the highest melting point.
- **Z** has the largest ionic radius.

Which of the following is the correct sequence of the four elements in order of increasing atomic number?

A **X**, **Y**, **W**, **Z**

B **Y**, **W**, **X**, **Z**

C **X**, **W**, **Y**, **Z**

D **Z**, **Y**, **W**, **X**

17 In the construction of heart pacemakers, it is possible to use a small magnesium electrode which creates an electrical cell with the inhaled oxygen. The relevant half-equations are as follows:

$$Mg^{2+} + 2e^- \ll Mg \qquad E = -2.38\ V$$

$$\tfrac{1}{2}O_2 + 2H^+ + 2e^- \ll H_2O \qquad E = +1.23\ V$$

Under standard conditions, the cell e.m.f. would be +3.61 V. However, when placed in the human body, a potential of +3.25 V is observed.

What is the best explanation for this lower e.m.f.?

A The low concentration of Mg^{2+} ions surrounding the magnesium electrode.

B The body fluid surrounding the electrodes has a pH of 7.5.

C The high concentration of O_2 surrounding the electrodes.

D The size of the magnesium electrode.

18 The high reactivity of fluorine is largely due to the low energy of the F–F bond.

Which statement does **not** account for the weak F–F bond?

A The F–F bond is weak because of the repulsion between the non-bonding electrons.

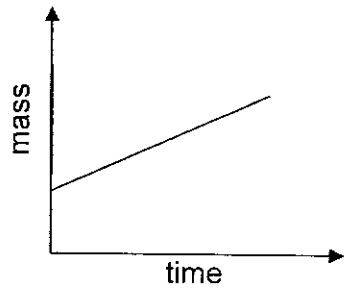
B The F–F bond is weak because of the short bond length.

C The F–F bond is weak because of the small number of electrons in fluorine atom.

D The F–F bond is weak because of the small size of fluorine atom.

19 Electrolysis of aqueous copper(II) sulfate was carried out using copper electrodes and a steady current. Which graph shows the change in mass of the cathode with time?

A



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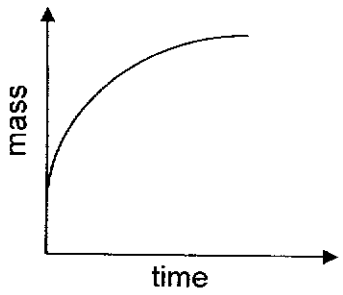

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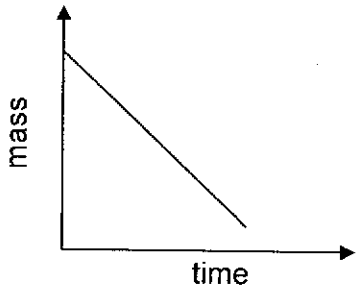

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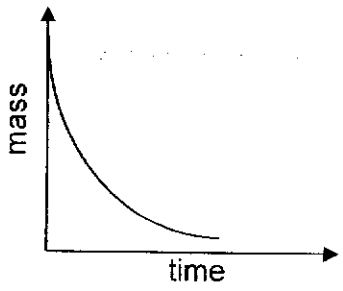
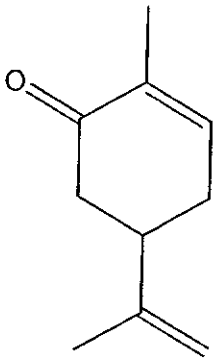


20 Carvone is the main ingredient of the flavouring agent oil of spearmint.



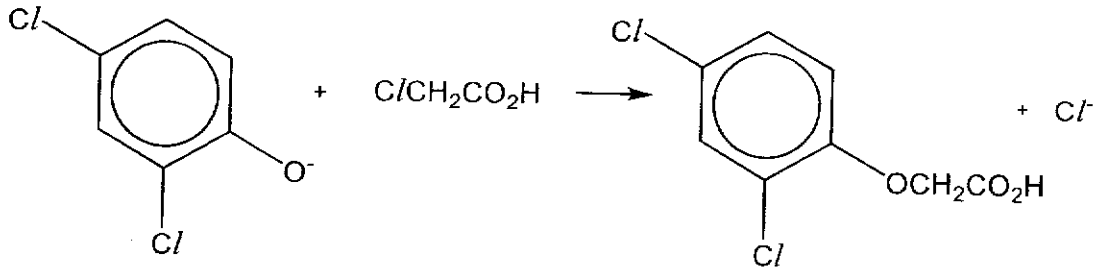
carvone

It can be reduced and hydrogenated to form **M**.

How many chiral centres do the molecules of carvone and **M** have?

	carvone	**M**
A	0	2
B	0	3
C	1	2
D	1	3

21 The weed killer (2,4-D) can be synthesised in the laboratory by the following reaction.



2,4-D

What is the mechanism of this reaction?

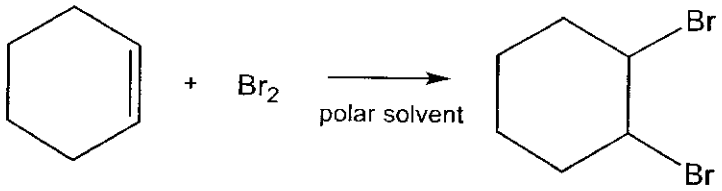
A condensation

B electrophilic substitution

C nucleophilic addition

D nucleophilic substitution

22 The equation represents an organic reaction.



Which statement about this reaction is **incorrect**?

A A nucleophile is involved in this reaction.

B A planar product is formed in the reaction.

C Bromine acts as an electrophile.

D The reaction can take place in the dark or in the presence of light.

23 Which method is the best in separating benzene from a mixture of benzene and an amine?

A extracting the benzene with hexane

B nitrating the benzene with a nitrating mixture

C shaking the mixture with dilute aqueous acid

D shaking the mixture with dilute aqueous alkali

24 A small peptide **N** is hydrolysed according to the following reaction.

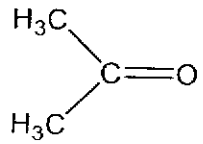
N $\rightarrow 2NH_2CH_2CO_2H + NH_2CH(CH_3)CO_2H + 2NH_2CH(CH_2OH)CO_2H$

(M_r = 75) (M_r = 89) (M_r = 105)

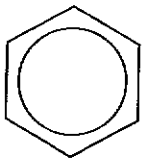
What is the M_r of **N**?

A 359 **B** 377 **C** 431 **D** 449

25 By considering the mechanism of the following reactions, which reaction does a carbon atom change from being sp^2 hybridised to being sp^3 hybridised?

1  + CN^-

2 $CH_3CH_2C\ell + OH^-$

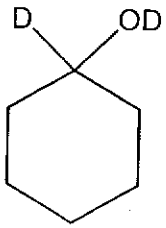
3  + NO_2^+

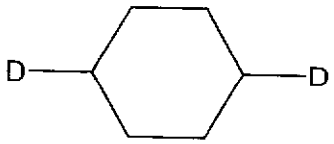
A 1, 2 and 3 **B** 1 and 2 only **C** 1 and 3 only **D** 2 only

26 Deuterium, D, is an isotope of hydrogen, ^2_1H.

Which compound can be formed by the addition of D_2 to another molecule, in the presence of a platinum catalyst?

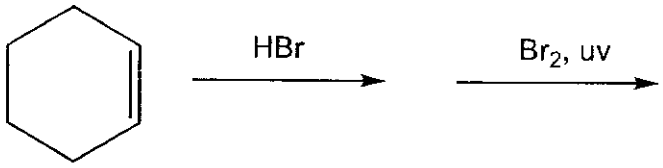
1 $CH_3CD_2ND_2$

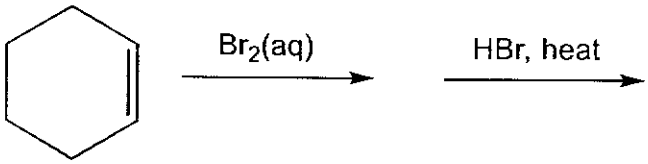
2 

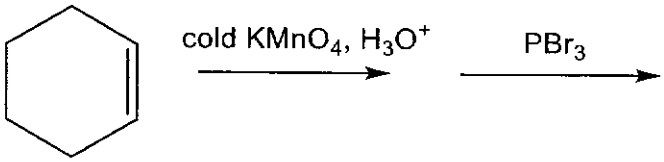
3 

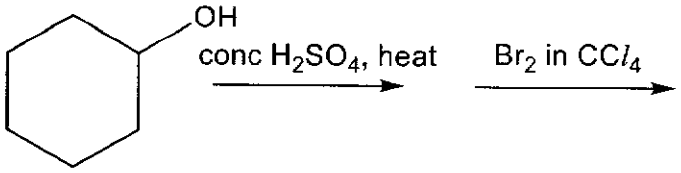
A 1, 2 and 3 **B** 1 and 2 only **C** 2 and 3 only **D** 1 only

27 Which two-step process will **not** give a good yield of 1,2-dibromocyclohexane?

A 

B 

C 

D 

28 The acid dissociation constants of amino acids, K_1 and K_2, can be illustrated using the equations below.

$NH_3^+CHRCO_2H + H_2O \ll NH_3^+CHRCO_2^- + H_3O^+ \quad K_1$

$NH_3^+CHRCO_2^- + H_2O \ll NH_2CHRCO_2^- + H_3O^+ \quad K_2$

Which statement is correct for **any** amino acid?

A $NH_3^+CHRCO_2^-$ is the most common species present at pH 7

B pK_1 is larger than pK_2

C Multiplying K_1 and K_2 gives K_w

D Equal concentrations of $NH_3^+CHRCO_2^-$ and $NH_2CHRCO_2^-$ are present at pH = pK_2

29 When propene is bubbled through iodine monochloride, IC*l*, dissolved in a suitable solvent, a reaction occurs.

Which product will be present in the greatest yield?

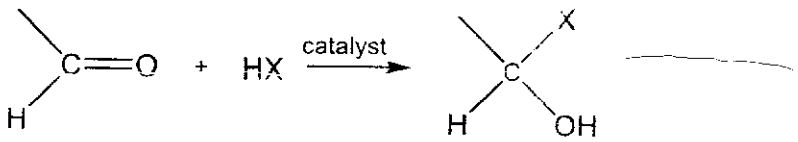
A CH_3CHCH_2I (Cl)

B CH_3CHCH_2I (I)

C CH_3CHCH_2Cl (I)

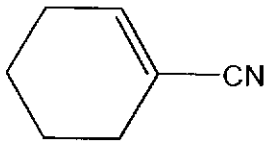
D CH_3CHCH_2Cl (Cl)

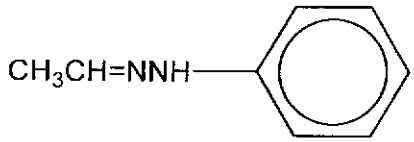
30 There are a range of reactions of the aldehyde group which have the pattern

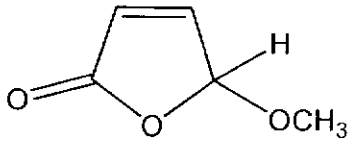


of which the formation of a cyanohydrin (where X = CN) is one.

Which compounds could be obtained by such an addition to an aldehyde group, followed by a dehydration?

1 

2 

3 

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

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Solutions

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

[A] =7

[B] =9

[C] =8

[D] =6

RIVER VALLEY HIGH SCHOOL
JC 2 PRELIMINARY EXAMINATION

CANDIDATE NAME								
CLASS	2	0	J					
CENTRE NUMBER	S					INDEX NUMBER		

H2 CHEMISTRY

9729/02

Paper 2 Structured Questions

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.

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.

(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**.

Table 1.1

source	CH_4	C_2H_x	C_3H_y	CO_2	N_2
J	80.3	8.1	2.3	1.4	7.9
K	82.1	14.0	3.5	0.1	0.3
L	88.0	0.8	0.7	10.4	0.1
M	77.5	4.0	0.9	3.3	14.3

In the formulae above, *x* and *y* are variables.

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

[3]

(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.

.....

..... [1]

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

.....

..... [1]

(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.

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

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

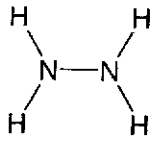
Use the data from Table 1.2 and the *Data Booklet*, construct a Born-Haber cycle to calculate $\Delta H_f(OH^-(g))$.

Table 1.2

	ΔH / kJ mol^{-1}
standard enthalpy change of atomisation of Mg(s)	+148
standard enthalpy change of formation of $Mg(OH)_2(s)$	–925
lattice energy of $Mg(OH)_2(s)$	–2993

[3]

(c) Hydrazine, N_2H_4, can be also used as an energy source and is stored as a liquid. It reacts exothermically with oxygen to give only gaseous products.



hydrazine

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

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

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*.

[2]

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

.....

.....

.....

.....

..... [2]

[Total: 12]

2 (a) (i) Describe the reactions of the chlorides, $MgCl_2$ and PCl_5, 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.

....

....

....

....

....

....

....

....

.... [3]

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

....

.... [1]

(b) Phosphorus exist in isotopes, mainly ^{31}P, ^{32}P and ^{33}P. ^{31}P is the most stable isotope.

(i) Define *isotopes*.

....

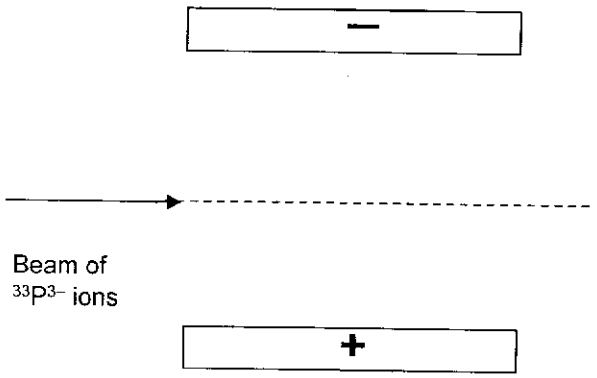
.... [1]

(ii) ^{31}P 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.

.... [1]

(iii) Phosphorus can exist as cations or anions.

The angle of deflection for a beam of $^{31}P^{+}$ ions in an electric field is 6°. Calculate the angle of deflection for a beam of $^{33}P^{3-}$ ions in the same electric field and show in the diagram below how a beam of $^{33}P^{3-}$ ions will deflect in the electric field.



[2]

(iv) ^{32}P 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.

..... [1]

[Total : 9]

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* /V**
$Ag^{2+} + e^- \ll Ag^+$	+2.00
$Ag_2S + 2e^- \ll 2Ag + S^{2-}$	−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.

....

....

.... [1]

(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.

....

....

....

....

....

....

.... [2]

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

When a silver coin is subjected to prolonged exposure to air and sulfide-containing compounds such as hydrogen sulfide, the surface will develop a tarnish which is predominantly silver(I) sulfide, Ag_2S.

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.

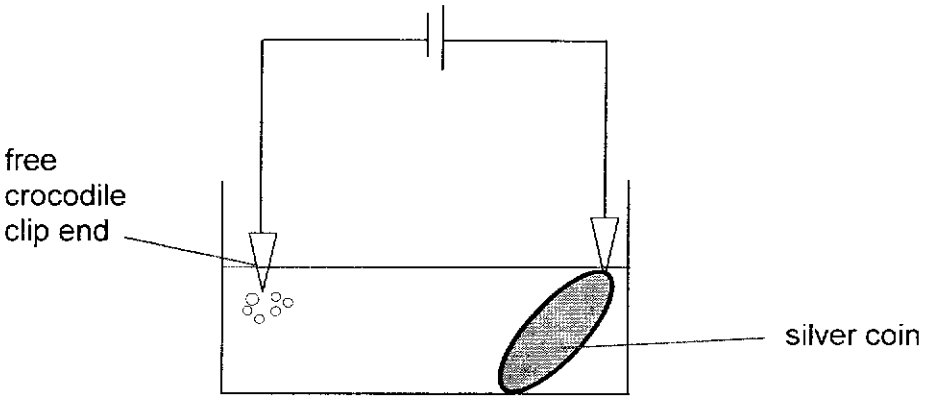
.... [1]

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

....

.... [1]

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



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.

.....

.....

.....

..... [2]

(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.

.....

.....

.....

..... [2]

(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.

Table 3.2

Silver halide	Experimental value / kJ mol^{-1}	Theoretical value / kJ mol^{-1}
AgF	−953	−920
AgC*l*	−908	−833
AgBr	−900	−815
AgI	−883	−778

(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.

.....

.....

.....

..... [2]

(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.

.....

..... [1]

[Total: 12]

4 Amines are a class of compounds widely used in the agricultural industry. Ethylamine, $CH_3CH_2NH_2$ (pK_b = 3.3), is widely used in the production of herbicides.

(a) 25.0 cm^3 of 0.888 mol dm^{-3} aqueous ethylamine was placed in a conical flask. 33.90 cm^3 of sulfuric acid was required to completely neutralise the ethylamine.

(i) Calculate the initial pH of aqueous ethylamine in the conical flask.

[2]

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

[1]

(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.

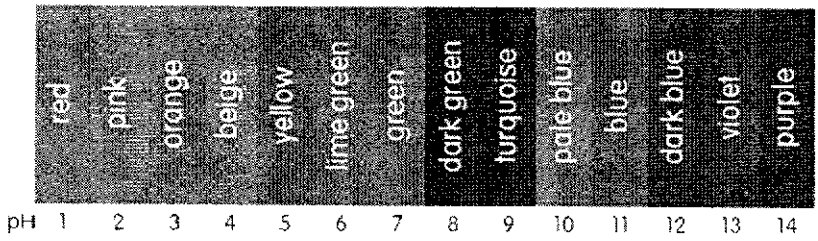


Fig. 4.1

[2]

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

Table 4.1

Indicator	Colour in acid	Colour in alkali	pH range over 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

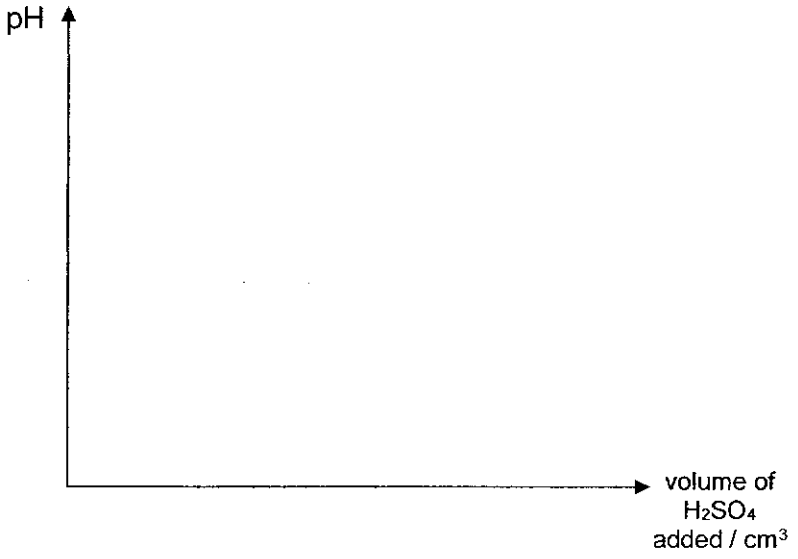
.....

..... [1]

(c) Calculate the pH of the solution mixture when 50.00 cm^3 of sulfuric acid has been added.

[1]

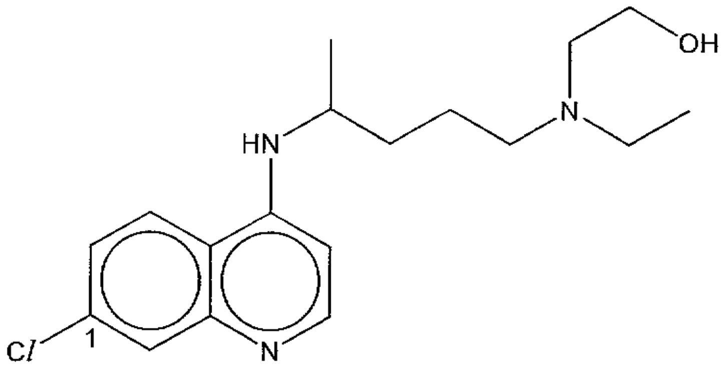
(d) Using information and your answers from **(a)**, **(b)** and **(c)**, sketch the shape of the pH curve of the titration between aqueous ethylamine and sulfuric acid.



[2]

[Total: 9]

5 **(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.

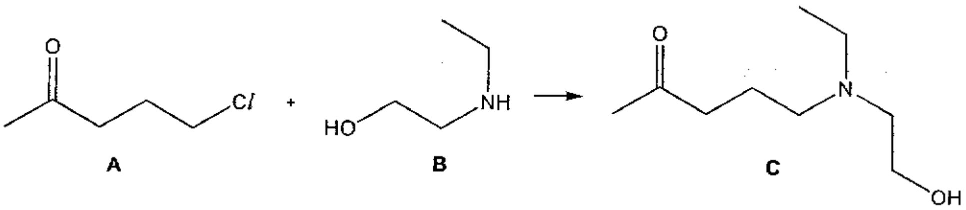


HCQ

State the oxidation number of carbon labelled 1 in HCQ.

.... [1]

(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 **very** alkaline conditions

.....

.....

..... [2]

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

.....

.....

..... [1]

(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.

.....

..... [1]

(ii) Experiments have shown that when $[O_2] = 8.1 \times 10^{-6}$ mol dm^{-3}, the concentration of Hb and $Hb(O_2)_4$ are equal.

Use this information to calculate a value for K_c.

[1]

(iii) All Singapore households are recently issued with an oximeter to monitor their blood oxygen saturation levels. Individuals whose blood oxygen levels are 94% and below should see a doctor immediately.

Use your value of K_c to calculate the $[O_2]$ necessary for 94% of the Hb to be converted to $Hb(O_2)_4$.

[1]

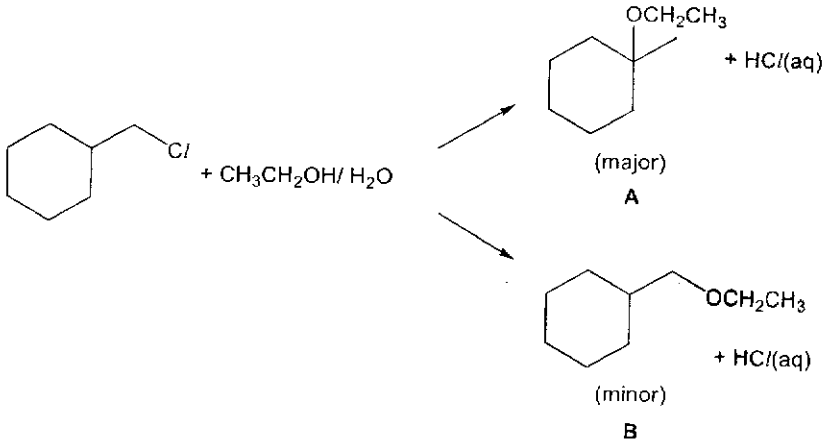
(iv) State what the K_c value indicates about the position of equilibrium.

....

.... [1]

[Total: 8]

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.

.....

..... [1]

The kinetics of the solvolysis of 0.0150 mol dm^{-3} (chloromethyl)cyclohexane 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 ($\mu S\ cm^{-1}$). The conductivity is directly proportional to the amount of isomer **A** present in the sample.

Fig. 6.1 shows the conductivity recorded against time for this experiment.

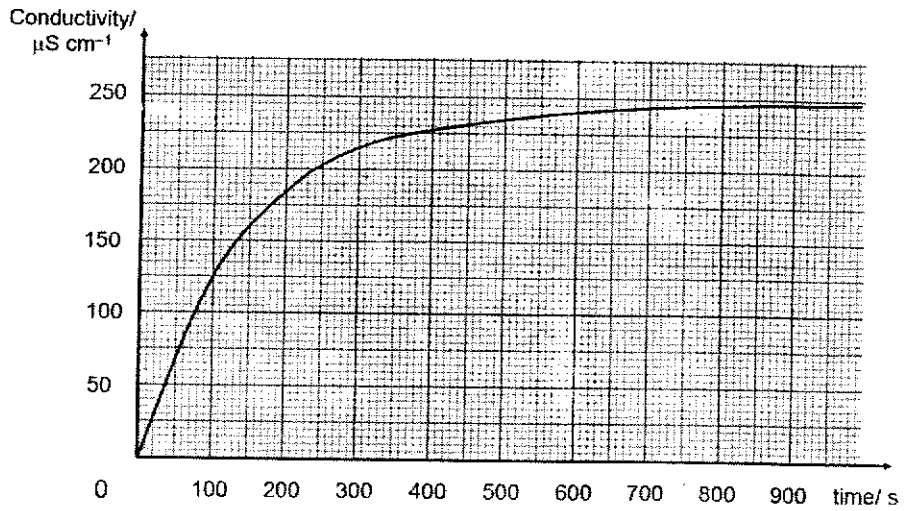


Fig 6.1

(b) In terms of structure and bonding, explain why

- the conductivity is zero initially
- the conductivity increases

.....

.....

.....

.....

..... [2]

(c) **(i)** Show how the initial rate of reaction for this experiment could be determined using Fig. 6.1.

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

[2]

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

.....

.....

.....

..... [2]

(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.

.....

.....

.....

..... [2]

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

..... [1]

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

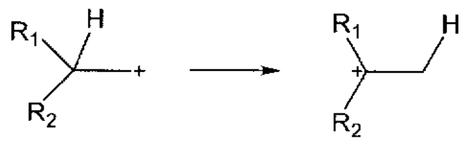
Conductivity = 7000[(chloromethyl)cyclohexane]

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)**.

[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.



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.

[3]

(d) Different halogenoalkanes have different reactivity towards nucleophilic substitution.

(i) Explain why (bromomethyl)cyclohexane reacts at a faster rate than (chloromethyl)cyclohexane.

.....

.....

..... [1]

(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.

Halide (X^-)	pK_a (HX)
F^-	+3
Cl^-	–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.

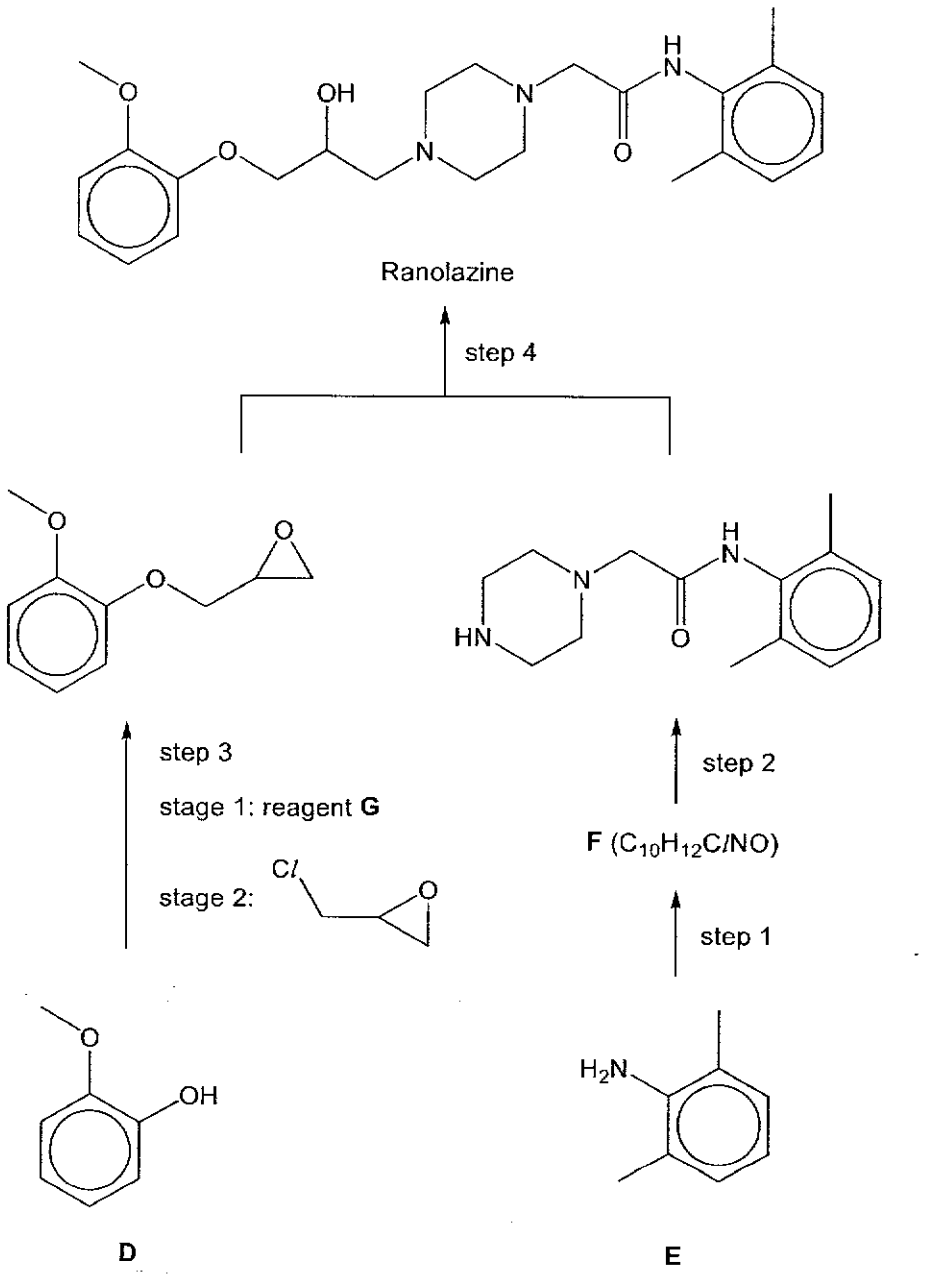
.....

.....

..... [1]

[Total: 18]

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



(i) Suggest a structure for the organic compound **F**.

[1]

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

Step 1: .....

Step 2: .....

Reagent **G**: ..... [3]

(b) **(i)** State the hybridisation of the unsaturated carbon in CH_3CN.

..... [1]

(ii) Hence, suggest the difference in bond length between the C–C bond acetonitrile (CH_3CN) and ethane (CH_3CH_3).

.....

.....

.....

..... [2]

[Total: 7]

RIVER VALLEY HIGH SCHOOL
JC 2 PRELIMINARY EXAMINATION

CANDIDATE NAME	**Suggested Answers**							
CLASS	2	0	J					
CENTRE NUMBER	S					INDEX NUMBER		

H2 CHEMISTRY

9729/02

Paper 2 Structured Questions

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.

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.

(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**.

Table 1.1

source	CH_4	C_2H_x	C_3H_y	CO_2	N_2
J	80.3	8.1	2.3	1.4	7.9
K	82.1	14.0	3.5	0.1	0.3
L	88.0	0.8	0.7	10.4	0.1
M	77.5	4.0	0.9	3.3	14.3

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)

- $CH_3CH_2CH_3$
- $CH_3CH{=}CH_2$
- $CH_3C{\equiv}CH$
- $CH_2{=}C{=}CH_2$
- Δ (cyclopropane)

[3]

(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.

K, since it has the greatest % of hydrocarbons / carbon-containing compounds [1]

(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

[1]

(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.

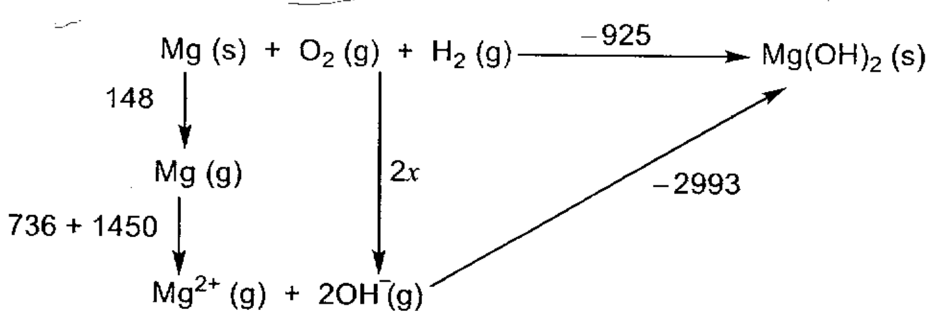
(i) The equation for the formation of the gaseous hydroxide ion is shown.

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

Use the data from Table 1.2 and the *Data Booklet*, construct a Born-Haber cycle to calculate $\Delta H_f(OH^-(g))$.

Table 1.2

	ΔH / kJ mol^{-1}
standard enthalpy change of atomisation of Mg(s)	+148
standard enthalpy change of formation of $Mg(OH)_2(s)$	–925
lattice energy of $Mg(OH)_2(s)$	–2993



(All values in kJ mol^{-1})

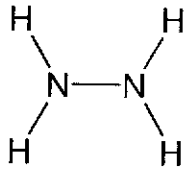
Let $\Delta H = \Delta H_f$ (OH$^-$(g)) be x kJ mol^{-1}

148 + 736 + 1450 + 2x + (–2993) = –925

x = –133

ΔH_f (OH$^-$(g)) = **–133 kJ mol^{-1}** [3]

(c) Hydrazine, N_2H_4, can be also used as an energy source and is stored as a liquid. It reacts exothermically with oxygen to give only gaseous products.

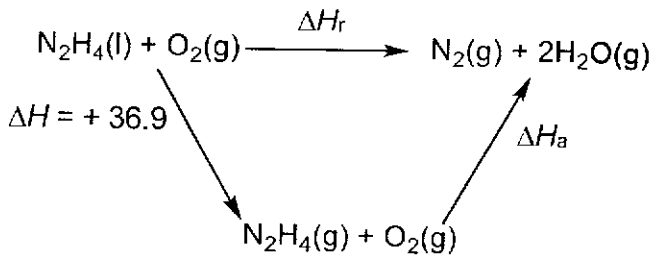


hydrazine

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

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

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.*



Bonds broken	Bonds formed
1 N–N	N≡N
4 N–H	4 O–H
1 O=O	

ΔH_a = **160 + 496 + 4(390) – 944 – 4(460)** = –568 kJ mol^{-1}

ΔH_r = +36.9 + (–568) = –531.1 = –531 kJ mol^{-1} [2]

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

$\Delta G_r = \Delta H_r - T\Delta S_r$

ΔS_r is **positive since there is an increase in number of gaseous particles** from 1 to 3.

Since both the **ΔH_r and $-T\Delta S_r$ terms are negative**, **ΔG_r is always negative**. Hence, the reaction is spontaneous at all temperatures. [2]

[Total: 12]

2 (a) (i) Describe the reactions, if any, of the chlorides $MgCl_2$ and PCl_5 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.

$MgCl_2$ has a **giant ionic lattice structure** and **strong electrostatic attraction between Mg^{2+} and Cl^- ions**. $MgCl_2$ dissolves in water readily to form an acidic solution of **pH 6.5**. Both hydration of ions and partial hydrolysis of $Mg^{2+}(aq)$ occurs. Hydrolysis occurs due to the polarisation of water molecules by the Mg^{2+} ion

$$MgCl_2(s) + 6H_2O(l) \rightarrow [Mg(H_2O)_6]^{2+}(aq) + 2Cl^-(aq)$$

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

PCl_5 has a **simple covalent structure**. PCl_5 dissolves and undergoes hydrolysis in water to form an acidic solution of **pH 2**. P atom in PCl_5 has **energetically accessible vacant 3d orbitals to 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.

CCl_4 **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. [1]

(b) Phosphorus exist in isotopes, mainly ^{31}P, ^{32}P and ^{33}P. ^{31}P is the most stable isotope.

(i) Define *isotopes*.

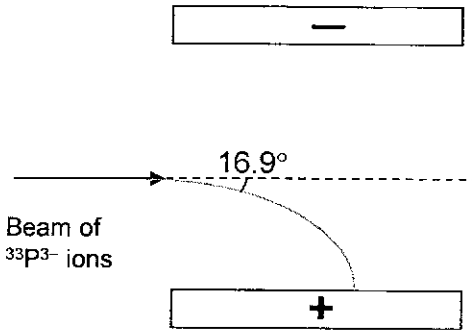
Isotopes are **atoms of the same element with the same number of protons but different number of neutrons**. [1]

(ii) ^{31}P 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]

(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.



$\frac{\text{charge}}{\text{mass}}$ for $^{31}P^{+} = \frac{+1}{31} = 0.03225$

$\frac{\text{charge}}{\text{mass}}$ for $^{33}P^{3-} = \frac{-3}{33} = 0.09091$

Since angle of deflection $\propto \frac{\text{charge}}{\text{mass}}$,

Angle of deflection $= \frac{0.09091}{0.03225} \times 6 = 16.9°$

[2]

(iv) ^{32}P 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.

$^{32}P \rightarrow {}^{32}S^{+} + e^{-}$ [1]

[Total : 9]

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* /V
$Ag^{2+} + e^- \ll Ag^+$	+2.00
$Ag_2S + 2e^- \ll 2Ag^+ + S^{2-}$	−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 **disproportionation** to form Cu^{2+} and Cu.

E_{cell} = +0.52 – (+0.15) = **+0.37** V (spontaneous) [1]

(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

E_{cell} for Ag^+ [R] and water [O] = +0.80 – (+1.23) = **−0.43 V** (non-spontaneous*)

OR

E_{cell} for Ag^+ [O] and water [R] = −0.83 – (+2.00) = **−2.83 V** (non-spontaneous*) [2]

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

When a silver coin is subjected to prolonged exposure to air and sulfide-containing compounds such as hydrogen sulfide, the surface will develop a tarnish which is predominantly silver(I) sulfide, Ag_2S.

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.

$\mathbf{O_2 + 2H_2S + 4Ag \rightarrow 2H_2O + 2Ag_2S}$ [1]

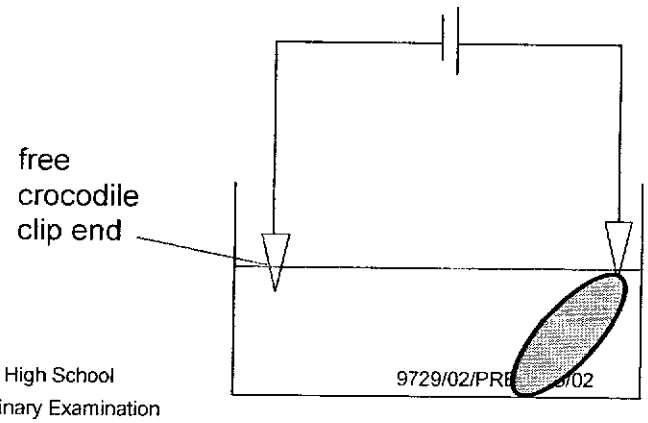
(ii) Calculate the E_{cell} for this reaction.

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

$= +1.23 - (-0.69)$

$= \mathbf{+1.92\ V}$ [1]

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



silver coin

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.

Gas is **H_2**. ($2H_2O + 2e^- \rightarrow H_2 + 2OH^-$)

H_2O is preferentially reduced, **as $E(H_2O/H_2)$** (= −0.83 V) **is more positive than $E(Na^+/Na)$** (= −2.71 V). [2]

(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 Ag_2S

= 6.051×10^{-7} mol of Ag_2S

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 ➔ **2.34 s** [2]

(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.

Table 3.2

Silver halide	Experimental value / kJ mol^{-1}	Theoretical value / kJ mol^{-1}
AgF	−953	−920
AgC*l*	−908	−833
AgBr	−900	−815

AgI	−883	−778

(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 **ionic radii of F^-, Cl^-, Br^- and I^- are 0.136 nm, 0.181 nm, 0.195 nm and 0.216 nm** respectively. As $|LE| \propto \frac{q_+ q_-}{r_+ + r_-}$ and the **ionic radii** of the halide ions **increases from F^- to I^-**, the values of the theoretical lattice energies of the silver halides decrease from AgF to AgI. [2]

(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.

I^- is a large anion and is **polarised by Ag^+ ion** which results in the ionic bond in AgI having **some covalent character**, 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). [1]

[Total: 12]

4 Amines are a class of compounds widely used in the agricultural industry. Ethylamine, $CH_3CH_2NH_2$ (pK_b = 3.3), is widely used in the production of herbicides.

(a) 25.0 cm^3 of 0.888 mol dm^{-3} aqueous ethylamine was placed in a conical flask. 33.90 cm^3 of sulfuric acid was required to completely neutralise the ethylamine.

(i) Calculate the initial pH of aqueous ethylamine in the conical flask.

$CH_3CH_2NH_2(aq) + H_2O(l) \rightleftharpoons CH_3CH_2NH_3^+(aq) + OH^-(aq)$

$K_b = 10^{-3.3} = 5.012 \times 10^{-4}$ mol dm^{-3}

$$= \frac{x^2}{0.888}$$

$x = [OH^-] =$ **0.02110** mol dm^{-3} [2]

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 $H_2SO_4 = \frac{0.0222}{2} = 0.0111$ mol

$[H_2SO_4] = \frac{0.0111}{33.90 \times 10^{-3}}$ = **<u>0.327</u>** mol dm`3 (Accept: 0.311 mol dm`3) [1]

(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.

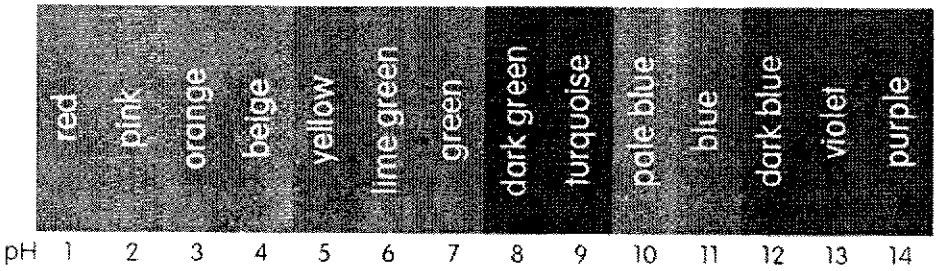


Fig. 4.1

At equivalence point, only the ethylammonium salt is present:

$CH_3CH_2NH_3^+(aq) + H_2O(l) \rightleftharpoons CH_3CH_2NH_2(aq) + H_3O^+(aq)$

$[CH_3CH_2NH_3^+] = \frac{0.0222}{(25 + 33.9) \times 10^{-3}} = 0.377$ mol dm`3

$x^2 = (10^{`(14 - 3.3)})(0.377)$

~~$x = 2.74 \times 10^{-6}$~~

pH = **<u>5.56</u>**

Accept: **<u>yellow / yellow green / lime green</u>** [2]

(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 in acid	Colour in alkali	pH range over 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

Table 4.1

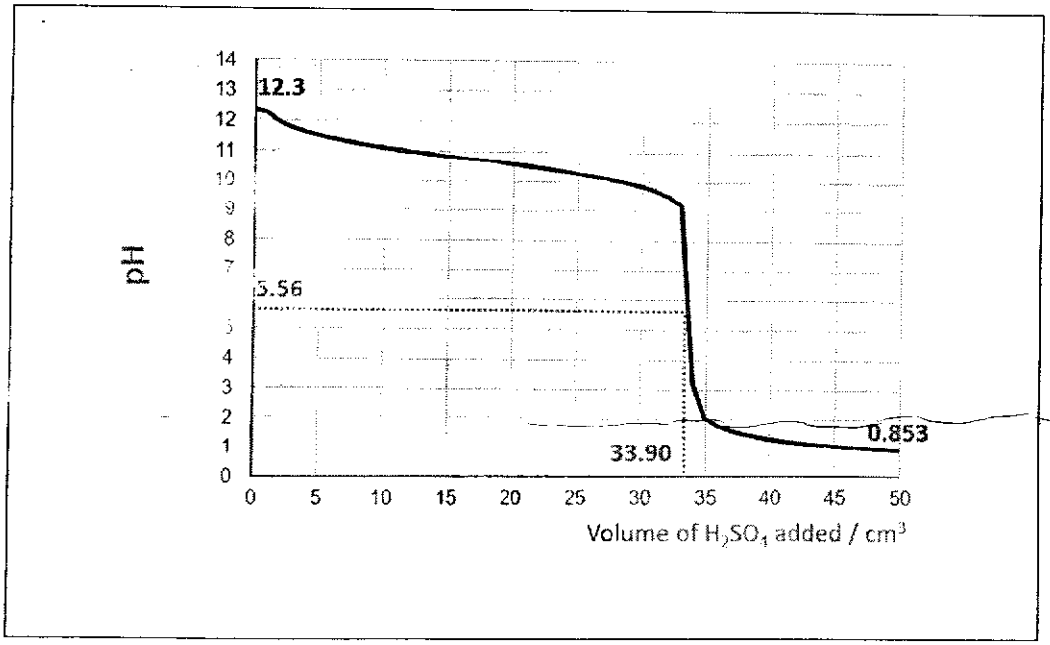
Chlorophenol red. The **working pH range of chlorophenol red lies within the sharp pH change near the equivalence point**. [1]

(c) Calculate the pH of the solution mixture when 50.00 cm^3 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 = **0.853** [1]

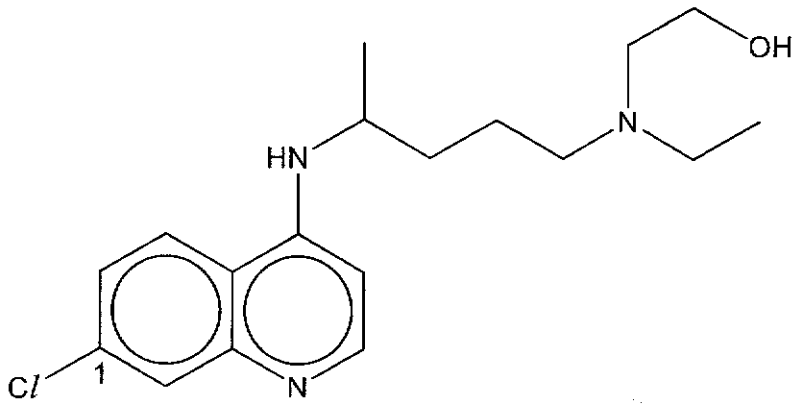
(d) Using relevant information above and your answers from **(a)(i)**, **(b)(i)** and **(c)**, sketch the shape of the pH curve of the titration between aqueous ethylamine and sulfuric acid.



[2]

[Total: 9]

5 **(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.



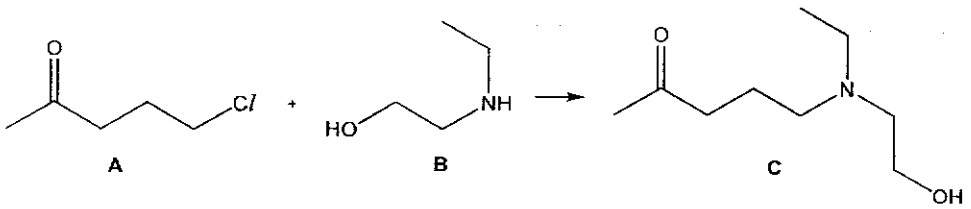
HCQ

State the oxidation number of carbon labelled 1 in HCQ.

+1

[1]

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



A B C

(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

Under very alkaline conditions, the alcohol functional group on B will be **deprotonated/lose its proton**. The alkoxide ion formed can also **act as a nucleophile** to attack **A**. There will be side products formed/**C** will not be formed/yield of **C** will be low. [2]

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 **further nucleophilic substitution**, resulting in the formation of the quaternary ammonium salt which will lower the yield of **C**. [1]

(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.

$K_c = \dfrac{[Hb(O_2)_4]}{[Hb][O_2]^4}$ Units: **mol^{-4} dm^{12}** [1]

(ii) Experiments have shown that when $[O_2] = 3.10 \times 10^{-6}$ mol dm^{-3}, the concentration of Hb and $Hb(O_2)_4$ are equal.

Use this information to calculate a value for K_c.

$K_c = \dfrac{[Hb(O_2)_4]}{[Hb][8.1\times10^{-6}]^4}$ = **2.32×10^{20}** mol^{-4} dm^{12} [1]

(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 $[O_2]$ necessary for 94% of the Hb to be converted to $Hb(O_2)_4$.

$K_c = \frac{[Hb(O_2)_4]}{[Hb][O_2]^4}$

94% conversion means that ratio of $Hb(O_2)_4$:Hb is 94:6

$2.32 \times 10^{20} = \frac{94}{6[O_2]^4}$

$[O_2]$ = **<u>1.61×10^{-5}</u>** mol dm^{-3}

[1]

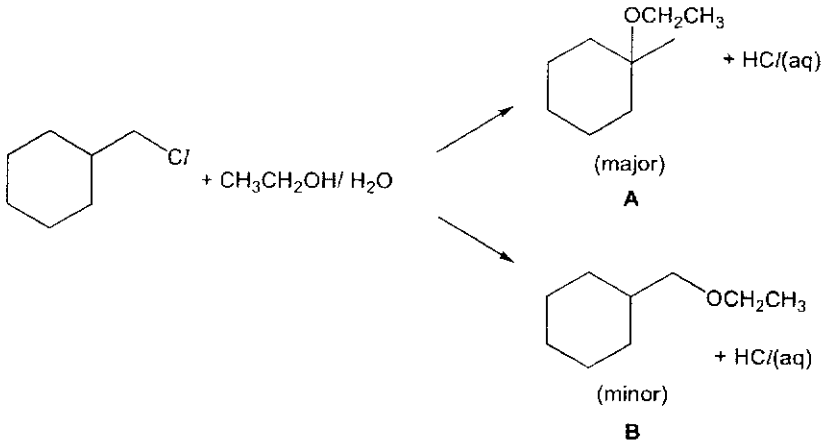
(iv) State what the K_c value indicates about the position of equilibrium.

A very large K_c value that is greater than 1 suggests that the **<u>equilibrium position lies very much to the right</u>**.

[1]

[Total: 8]

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 **electron-donating ethyl group increases the availability of lone pair of electrons** on O in ethanol, making it a stronger nucleophile than water. [1]

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 ($\mu S\ cm^{-1}$). The conductivity is directly proportional to the amount of isomer **A** present in the sample.

Fig. 6.1 shows the conductivity recorded against time for this experiment.

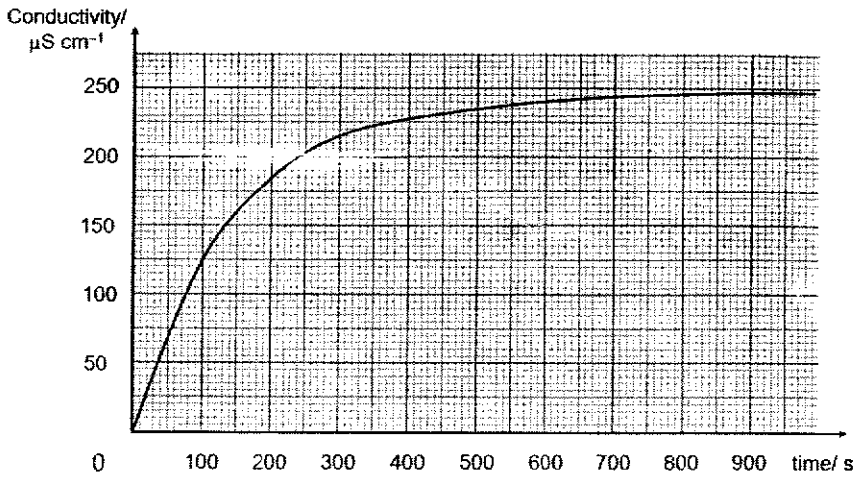


Fig. 6.1

(b) In terms of structure and bonding, explain why

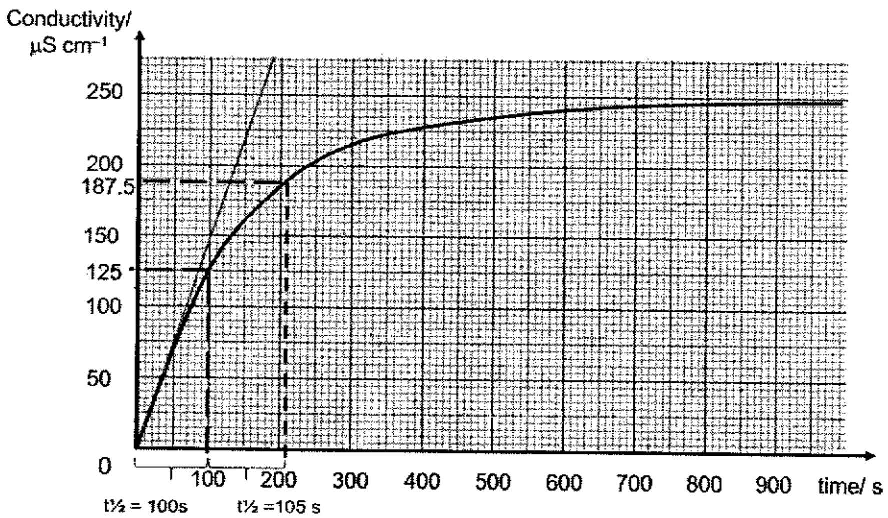
- the conductivity is zero initially
- the conductivity increases

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

HCl, which has a **simple covalent structure**, **dissociates in water** completely to give **H^+ and Cl^- ions**, which can act as **charge carriers**. Hence, as the reaction progresses/ HCl is formed, the conductivity of the solution increases. [2]

(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.]



Initial rate = $\dfrac{275}{190} = 1.447 = 1.45\ \mu S\ cm^{-1}\ s^{-1}$ [2]

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

Graphwork to show 2 $t_{1/2}$ values

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

(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 **rate did not change**, the rate of reaction is **independent of [ethanol]**, the reaction is **zero order** with respect to ethanol. [2]

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

Rate = *k*[(chloromethyl)cyclohexane] [1]

(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)**.

$$\text{Initial rate} = \frac{1.447}{7000} = 2.067 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$$

$$\text{Rate constant} = \frac{2.067 \times 10^{-4}}{0.015} = 0.01378 = 0.0138 \text{ s}^{-1}$$

[3]

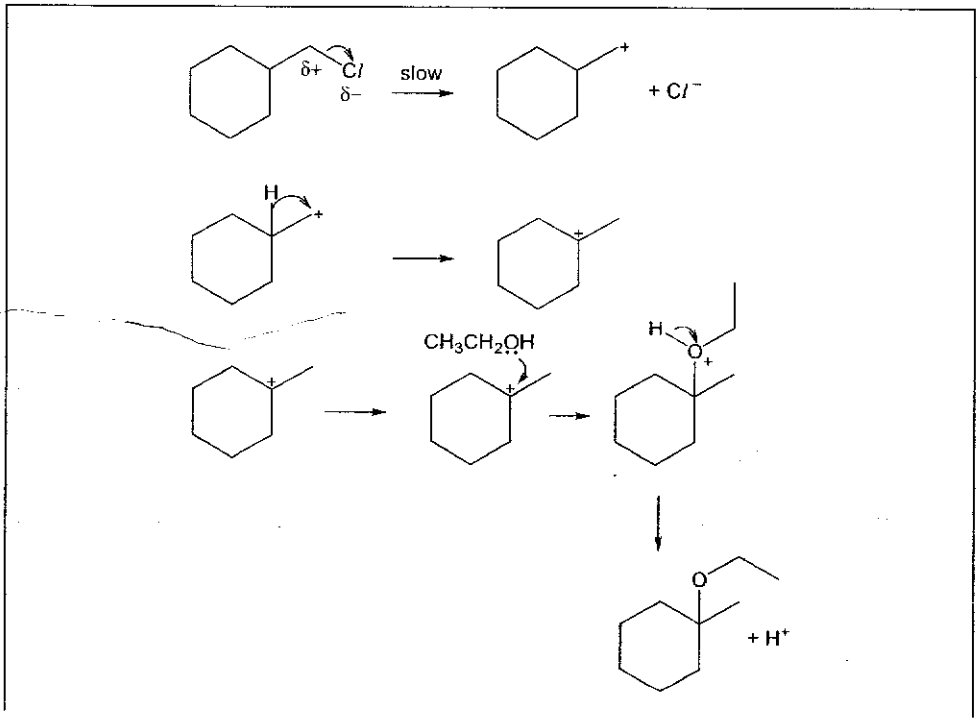
(vi) The solvolysis reaction proceeds via two intermediates.

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.

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.



[3]

(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

[1]

(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.

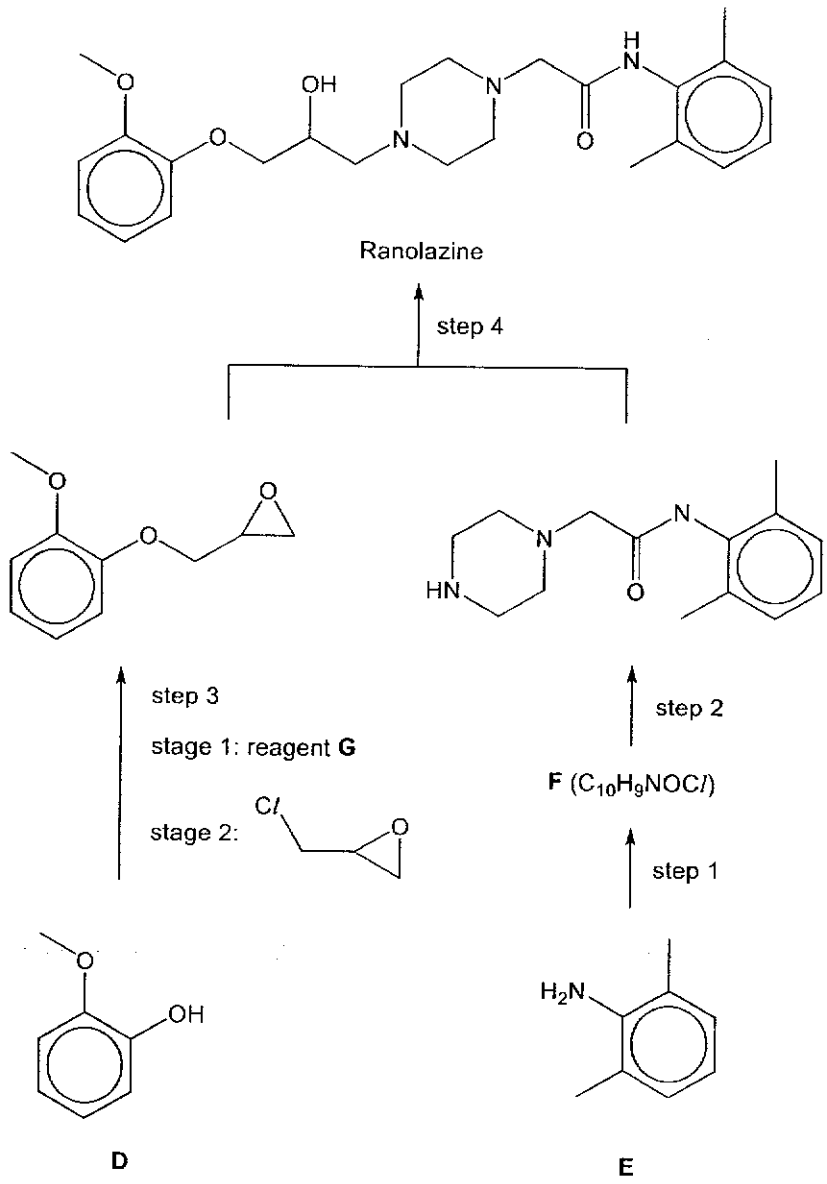
Halide (X^-)	pK_a (HX)
F^-	+3
Cl^-	–7
Br^-	–9
I^-	–10

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 **lower** pK_a, so Br^- is a **more stable anion** than Cl^-, the activation energy is lower and the reaction is faster. [1]

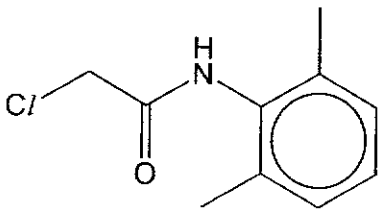
[Total: 18]

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



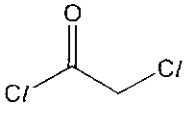
(i) Suggest a structure for the organic compound **F**.

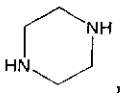
Structure of **F**:



[1]

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

Step 1: anhydrous 

Step 2: excess ethanolic  , heat (under reflux)

Reagent **G**: NaOH(aq)

[3]

(b) **(i)** State the hybridisation of the unsaturated carbon in CH_3CN.

sp

[1]

(ii) Hence, suggest the difference in bond length between the C–C bond acetonitrile (CH_3CN) and ethane (CH_3CH_3).

Acetonitrile consists **sp^3 C – sp C bond**, while **ethane contains sp^3 C – sp^3 C bond**. An sp-hybridised orbital has a **greater s-character** than an sp^3-hybridised orbital and **smaller in size/ electron in it is closer to the nucleus**. Hence, the sp^3 C – sp C bond in CH_3CN is **shorter** than the sp^3 C – sp^3 C bond in ethane.

[2]

[Total: 7]