



**JURONG PIONEER JUNIOR COLLEGE**  
**JC2 PRELIMINARY EXAMINATION 2019**

**CHEMISTRY**

**9729/01**

**Higher 2**

**26 September 2019**

Paper 1 Multiple Choice

**1 hour**

Candidates answer on separate paper.

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 and exam index number on the Answer Sheet in the spaces provided unless this has been done for you.

There are **thirty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A, B, C** or **D**.

Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

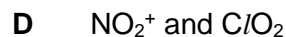
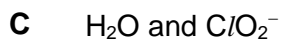
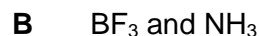
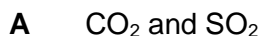
**Read the instructions on the Answer Sheet very carefully.**

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.

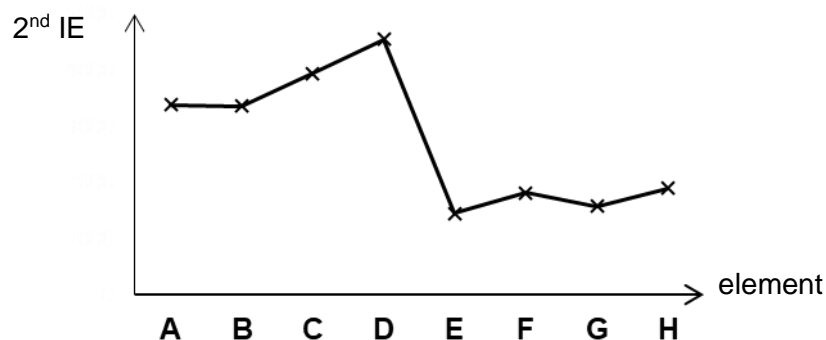
Any rough working should be done in this booklet.

The use of an approved scientific calculator is expected, where appropriate.

1 In which of the following pairs do the molecules have similar shapes?



2 **A** to **H** are consecutive elements with atomic numbers less than 20. The graph below shows their second ionisation energies ( $2^{\text{nd}}$  IE).



Which of the following statements is **incorrect**?

**A** Element **E** is from Group 2.

**B** **H** exists as tetraatomic molecules.

**C** The compound formed between **A** and **G** is a gas at room temperature.

**D** The  $2^{\text{nd}}$  IE of **B** is lower than that of **A** due to inter-electronic repulsion between its paired p electrons.

3 After an oil spillage at sea, a liquid hydrocarbon layer floats on the surface of the water.

Which statements help to explain this observation?

1 Hydrocarbon molecules are not solvated by water.

2 There are only instantaneous dipole-induced dipole interactions between hydrocarbon molecules.

3 Hydrogen bonding between water molecules causes water molecules to be packed closely together.

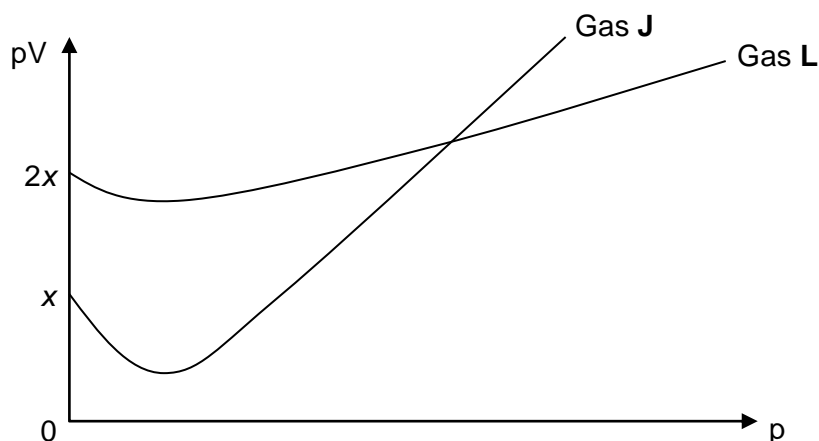
**A** 2 only

**B** 1 and 2 only

**C** 2 and 3 only

**D** 1, 2 and 3

- 4 The value of  $pV$  is plotted against  $p$  for two gases, **J** and **L**, where  $p$  is the pressure and  $V$  is the volume of the gas.



Which of the following could be the identities of the gases?

	Gas J	Gas L
1	0.5 mol of $\text{H}_2\text{O}$ at $25^\circ\text{C}$	0.5 mol of $\text{H}_2$ at $50^\circ\text{C}$
2	0.5 mol of $\text{NH}_3$ at $25^\circ\text{C}$	1 mol of $\text{CH}_4$ at $25^\circ\text{C}$
3	0.25 mol of $\text{SO}_2$ at $25^\circ\text{C}$	0.5 mol of $\text{H}_2$ at $25^\circ\text{C}$

- A** 2 only  
**B** 3 only  
**C** 2 and 3 only  
**D** 1, 2 and 3
- 5 *Use of the Data Booklet is relevant to this question.*

Which statement about 28.0 g of nitrogen gas is correct?

- A** It contains the same number of atoms as one mole of neon gas.  
**B** It contains the same number of molecules as 71.0 g of chlorine gas.  
**C** It has the same mass as one mole of carbon dioxide gas.  
**D** The gas occupies a volume of  $24\text{ dm}^3$  at standard temperature and pressure.

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

An element **M** can exist in a few oxidation states.

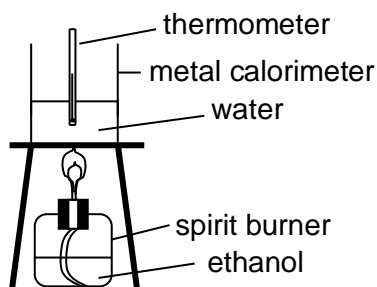
$15.00\text{ cm}^3$  of an aqueous solution of  $0.100\text{ mol dm}^{-3}$  of  $\text{M}^{n+}$  required  $20.00\text{ cm}^3$  of  $0.0250\text{ mol dm}^{-3}$  of acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  solution for a complete reaction.

What is the change in oxidation state of **M**?

- A** 2                      **B** 3                      **C** 4                      **D** 5

## 7 Use of the Data Booklet is relevant to this question.

A student carried out an experiment under laboratory conditions and the following results were obtained.

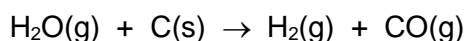


initial temperature of the water	28.0 °C
final temperature of the water	50.4 °C
mass of ethanol burner before burning	259.400 g
mass of ethanol burner after burning	259.286 g
mass of water used	30.000 g

Given that the enthalpy change of combustion of ethanol is  $-1367 \text{ kJ mol}^{-1}$ , what is the efficiency of heat transfer in the above experiment?

- A** 60.7%                      **B** 81.1%                      **C** 82.9%                      **D** 83.2%

## 8 Hydrogen can be made from steam as shown.



The Gibbs free energy change of the reaction is  $+78 \text{ kJ mol}^{-1}$  at 378K.

Which statement about the reaction is not correct?

- A** The entropy change is positive.  
**B** The products are energetically less stable than the reactants  
**C** The  $E_{\text{cell}}$  value of the reaction is positive.  
**D** The reverse reaction is spontaneous.

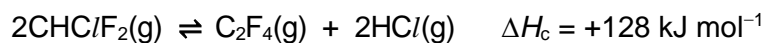
9 The table below gives data for the reaction between **N** and **Q** at constant temperature.

Experiment	[ <b>N</b> ] / $\text{mol dm}^{-3}$	[ <b>Q</b> ] / $\text{mol dm}^{-3}$	Initial rate / $\text{mol dm}^{-3} \text{ min}^{-1}$
1	0.003	0.2	$4.0 \times 10^{-4}$
2	0.006	0.4	$1.6 \times 10^{-3}$
3	0.006	0.8	$6.4 \times 10^{-3}$

Which statement about the reaction is not correct?

- A** The reaction is elementary.  
**B** The rate constant  $k$  has the units of  $\text{mol}^{-1} \text{ dm}^3 \text{ min}^{-1}$ .  
**C** The half-life of **N** is not constant.  
**D** The order of reaction with respect to [**Q**] is 2.

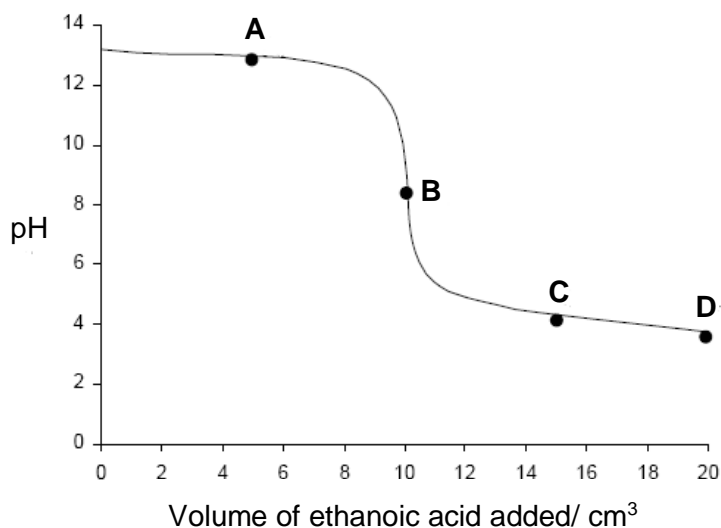
- 10 Poly(tetrafluoroethene) is a polymer used as a coating in non-stick kitchen utensils and for replacement of bone joints. One of the stages in the manufacture of the polymer is



Which statement correctly describes the effect of the change applied?

- A The equilibrium position will shift to the left when the reaction vessel is expanded.
  - B The equilibrium concentration of  $\text{CHClF}_2$  decreases when the reaction vessel is cooled.
  - C The addition of a catalyst will increase the equilibrium concentration of  $\text{C}_2\text{F}_4$ .
  - D The equilibrium constant,  $K_c$ , increases when the reaction vessel is heated.
- 11 The diagram below shows the change of pH produced by gradually adding  $0.100 \text{ mol dm}^{-3}$  aqueous ethanoic acid to  $10.0 \text{ cm}^3$  of  $0.100 \text{ mol dm}^{-3}$  aqueous sodium hydroxide.

At which point on the graph does  $\text{pH} = \text{p}K_a$ , where  $K_a$  is the acid dissociation constant of ethanoic acid?



- 12 The following tests were performed on an aqueous solution to identify the unknown ions it contains.

Step	Test	Observations
1	Add $\text{AgNO}_3(\text{aq})$ followed by excess dilute $\text{NH}_3(\text{aq})$ . Swirl and filter the mixture.	Yellow residue and colourless filtrate obtained.
2	Add $\text{Cl}_2(\text{aq})$ to filtrate.	Orange solution formed.

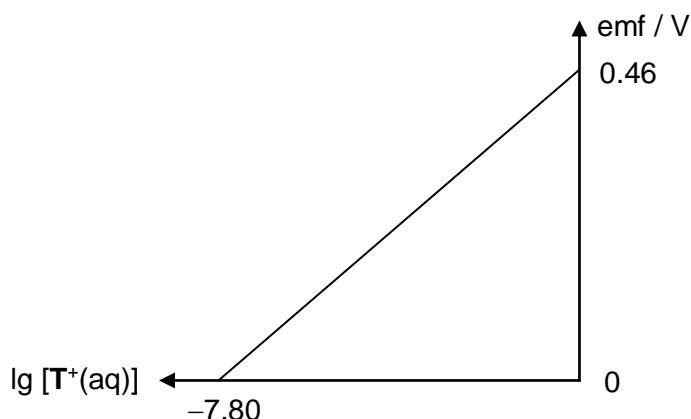
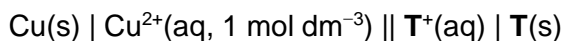
Which statements are correct?

- 1  $\text{I}^-$  ion is present in the mixture as the yellow  $\text{AgI}$  residue was obtained due to the low  $K_{\text{sp}}$  of  $\text{AgI}$ .
- 2  $\text{Br}^-$  ion is present in the mixture as it undergoes disproportionation reaction with  $\text{Cl}_2(\text{aq})$ .
- 3  $\text{Br}^-$  ion and  $[\text{Ag}(\text{NH}_3)_2]^+$  ion are present in the filtrate.

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

- 13 Use of the Data Booklet is relevant to this question.

The graph below shows the variation in electromotive force (emf) of the following electrochemical cell with  $\lg [\text{T}^+(\text{aq})]$  at 298 K.

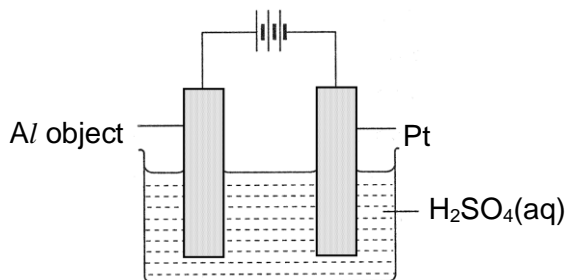


Which statement is not correct?

- A**  $\text{T(s)}$  is the positive electrode.  
**B** The direction of electron flow in the external circuit will be reversed when the concentration of  $\text{T}^+(\text{aq})$  is  $1.00 \times 10^{-5} \text{ mol dm}^{-3}$ .  
**C** The emf of the given cell under standard conditions will be +0.46 V.  
**D** The standard electrode potential of the  $\text{T}^+(\text{aq}) \mid \text{T(s)}$  half-cell is +0.80 V.

- 14 Use of the Data Booklet is relevant to this question.

A piece of aluminium object was placed in dilute sulfuric acid and anodised with a direct current of 1.5 A. After  $t$  minutes, the mass of the oxide layer formed is 3.7 g.



What is the time taken,  $t$ , for this anodisation process?

- A** 38.9                      **B** 58.3                      **C** 117                      **D** 233

- 15 Consider the following sequence of compounds:



What conclusions can be drawn about this sequence of compounds from left to right?

- 1 The electronegativity difference between the elements in each compound increases.
- 2 These compounds are isoelectronic.
- 3 The bonding becomes increasingly covalent.

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

- 16 A student carried out two experiments involving copper(II) sulfate.

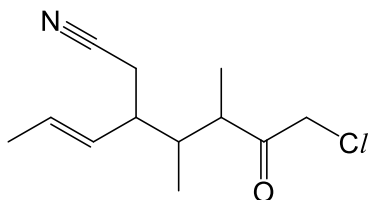
Experiment 1: Addition of aqueous ammonia causes a pale blue precipitate to form which dissolves in excess ammonia to give a deep-blue solution.

Experiment 2: Addition of aqueous potassium iodide produces a white precipitate and a brown solution.

What can be deduced from the experiments?

- A** The pale blue precipitate dissolves in excess ammonia due to the formation of a complex ion in experiment 1.  
**B** There is a redox reaction occurring in experiment 1.  
**C** The white precipitate formed in experiment 2 is  $\text{CuI}_2$ .  
**D** The brown solution in experiment 2 decolourises upon addition of sodium thiosulfate due to a ligand exchange reaction.

- 17 Which of the following options about the structure below is correct?



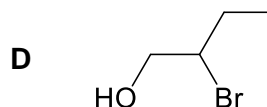
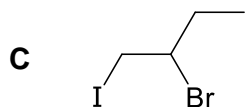
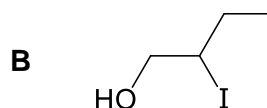
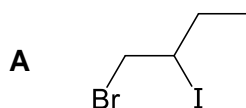
	Number of $sp$ hybridised C	Number of $sp^2$ hybridised C	Number of $sp^3$ hybridised C
A	1	3	8
B	1	3	6
C	0	4	8
D	0	4	6

- 18 3-methylpentane can undergo reaction with chlorine to form monosubstituted compounds that are optically active.

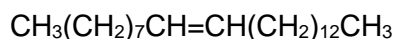
How many possible stereoisomers can be formed in the reaction?

- A 4                      B 5                      C 6                      D 8

- 19 Which of the following is not the product formed when but-1-ene reacts with IBr(aq)?



- 20 Fly paper is used as a non-toxic method of trapping houseflies. To increase its effectiveness and attractiveness, Muscalure, which is a fly sex pheromone, is added to the paper during its manufacture. Muscalure has the following structure:



Which of the following statements about Muscalure is not correct?

- A In the presence of excess bromine and UV light, it undergoes free radical substitution.  
 B It exists as a pair of cis-trans isomers.  
 C It gives a diol with cold dilute acidified potassium dichromate(VI).  
 D It can be extracted from the fly paper by soaking the paper in benzene.



**21** In which of the following reactions do benzene and methylbenzene behave differently?

- 1 Reacting with hot aqueous alkaline potassium manganate(VII)
- 2 Reacting with bromine in the presence of an iron catalyst
- 3 Reacting with bromine in the presence of light

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

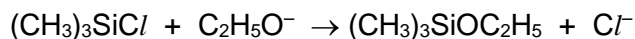
**22** A sample of bromoethane was warmed with ethanolic silver nitrate, and a cream precipitate was observed after about 4 minutes.

Under similar reaction conditions, which of the following compounds will result in precipitate formation only after 8 minutes?

- |                       |                           |
|-----------------------|---------------------------|
| <b>A</b> iodoethane   | <b>B</b> ethanoyl bromide |
| <b>C</b> bromobenzene | <b>D</b> chloroethane     |

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

Which of the following statements are likely to be true for the reaction:



- 1 It is likely to undergo a  $\text{S}_{\text{N}}1$  mechanism.
- 2  $\text{C}_2\text{H}_5\text{O}^-$  plays the role of the nucleophile.
- 3 Reaction proceeds faster if  $(\text{CH}_3)_3\text{CCl}$  is used instead.

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

- 24** Geraniol is found in rose oil and is used for the preparation of artificial scents. Upon controlled oxidation, geraniol yields  $\text{CH}_3\text{COCH}_3$ ,  $\text{CH}_3\text{COCH}_2\text{CH}_2\text{COOH}$  and  $(\text{CO}_2\text{H})_2$ . A possible structure of geraniol is:

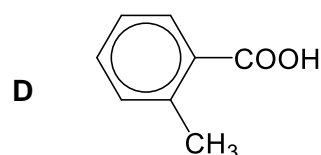
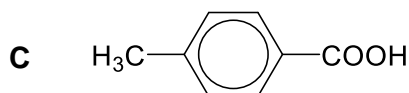
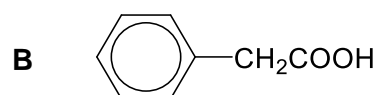
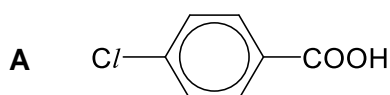
- A**  $\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)=\text{CHCH}_2\text{OH}$   
**B**  $(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{CH}_2\text{C}(\text{CH}_3)=\text{CHCH}_2\text{OH}$   
**C**  $(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)\text{CH}_2\text{C}(\text{CH}_3)=\text{CHCH}_2\text{OH}$   
**D**  $(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{CH}_2\text{C}(\text{CH}_2\text{OH})=\text{CHCH}_3$

- 25** The table below shows the relative rates of reaction for the addition of hydrogen cyanide to ketones under different conditions.

<i>condition</i>	<i>relative rate</i>
In water	slow
With small amount of acid	virtually zero
With small amount of base	very rapid

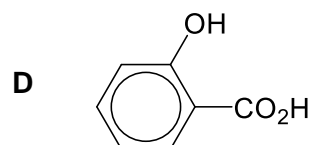
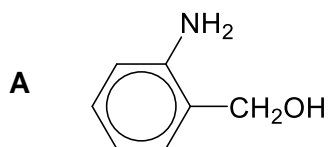
Which of the following statement can explain the above observations?

- A**  $\text{H}_2\text{O}$  is involved in the rate-determining step.  
**B** The small amount of base added acts as a catalyst.  
**C** Reaction in water is slow due to the low concentration of  $\text{CN}^-$ .  
**D**  $\text{H}^+$  is not a nucleophile.
- 26** Which of the following compounds react with both  $\text{NaBH}_4$  and Tollens' reagent?
- A** Both aldehydes and ketones  
**B** Aldehydes only  
**C** Ketones only  
**D** Neither aldehydes nor ketones
- 27** Which of the following compounds has the lowest  $\text{pK}_a$  value?



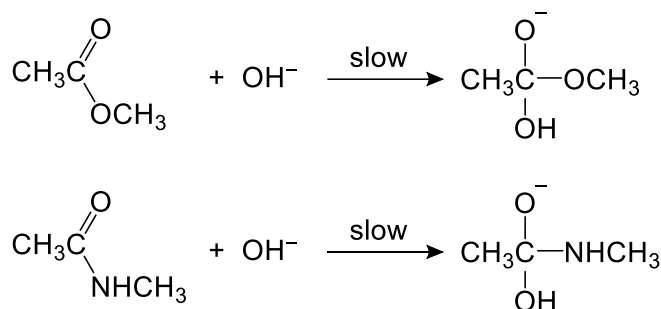
- 28** A compound **U** releases carbon dioxide from aqueous sodium hydrogencarbonate, and it readily decolourises aqueous bromine.

Which of the following could be **U**?



- 29** 1 mol of an ester ( $\text{CH}_3\text{CO}_2\text{CH}_3$ ) and an amide ( $\text{CH}_3\text{CONHCH}_3$ ) underwent base hydrolysis separately and the initial rate of reaction was measured. It was found that the ester undergoes hydrolysis approximately three times faster than the amide.

The slow step of the base hydrolysis of the ester and amide is the same and shown below.



Which statements help to explain the faster rate of base hydrolysis of the ester?

- 1 Oxygen is more electronegative than nitrogen.
- 2 The lone pair of electrons on the nitrogen atom in the amide interacts more with the carbonyl group.
- 3 There are two lone pairs of electrons on the oxygen atom in the ester and only one lone pair of electron on the nitrogen atom in the amide.

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

- 30** **X** is synthetic nonapeptide that is resynthesised from the amino acids found in honey bee venom. To investigate the sequence of amino acids in **X**, the nonapeptide was first hydrolysed by two enzymes. The protein fragments were then separated and their sequence determined.

The following protein fragments were obtained from the first enzyme which hydrolysed the peptide chain at the carboxylic end of the amino acid isoleucine, Ile.

Arg-Ile  
Ser-Lys-Trp-Ile  
Lys-Leu-Arg

The second enzyme, which hydrolysed the peptide chain at the carboxylic end of the amino acid lysine, Lys, yielded the following fragments

Arg-Ile-Ser-Lys  
Trp-Ile-Lys  
Leu-Arg

Which of the following is the correct primary structure of the nonapeptide **X**?

- A** Lys-Leu-Arg-Ile-Ser-Lys-Trp-Ile-Lys
- B** Trp-Ile-Lys-Leu-Arg-Ile-Ser-Lys-Trp
- C** Arg-Ile-Ser-Lys-Trp-Ile-Lys-Leu-Arg
- D** Arg-Ile-Ser-Lys-Leu-Arg-Trp-Ile-Lys



**JURONG PIONEER JUNIOR COLLEGE**  
**JC2 H2 CHEMISTRY (9729) PRELIMINARY EXAM 2019**  
**(PAPER 1) – Suggested Worked Solutions**

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

NAME \_\_\_\_\_

CLASS **18S****JURONG PIONEER JUNIOR COLLEGE**  
**JC2 PRELIMINARY EXAMINATION 2019****CHEMISTRY****9729/02****Higher 2****17 September 2019**

Paper 2 Structured Questions

**2 hours**

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

**READ THESE INSTRUCTIONS FIRST**

Write your name, class and exam index number on all the work you hand in.

Write in dark blue or black pen on both sides of the paper.

You may use a HB pencil for any diagrams, graphs.

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

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

The use of an approved scientific calculator is expected, where appropriate.

A *Data Booklet* is provided.

At the end of the examination, fasten all your work securely together.

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

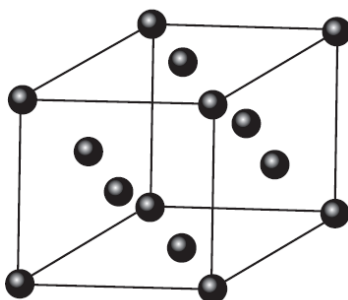
For Examiner's Use	
1	17
2	17
3	19
4	22
Penalty (delete accordingly)	
Bond linkages	-1 / NA
Total	75

This document consists of **18** printed pages.

Answer **all** the questions.

For  
Examiner's  
Use

- 1 Copper, a transition element, and iodine, a Group 17 halogen, are both shiny crystalline solids. The crystal structures of copper and iodine are both face-centred cubic. **Figure 1.1** shows the arrangement of the particles in this type of crystal lattice.



**Figure 1.1**

In **Figure 1.1**, the particles present are represented by .

- (a) (i) What type of particles is present in the copper crystal? State the interactions within the crystal.

Particles : .....

Interactions : ..... [1]

- (ii) What type of particles is present in the iodine crystal? State the interactions within the crystal.

Particles : .....

Interactions : ..... [1]

- (b) Explain why copper is malleable and ductile.

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

- (c) Give an example of another physical property that is present in one of the above solids but absent in the other. Explain.

.....

.....

.....

.....

[2]

- (d) A sample of copper contains the two isotopes  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$  only. An experiment is conducted to find the relative atomic mass of this sample and is found to be 63.9.

- (i) Explain why the value found is not a whole number.

.....

[1]

- (ii) Suggest why the relative atomic mass stated above differs from the value obtained from the Periodic Table.

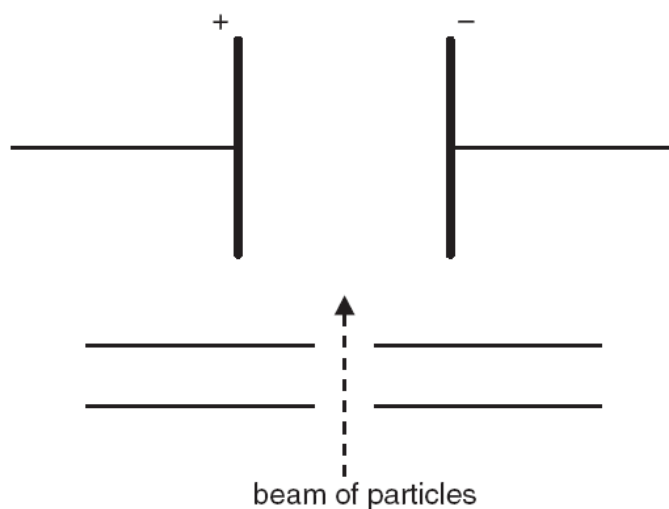
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[1]

- (e) When separate beams of  $^{63}\text{Cu}^{2+}$  and  $^{127}\text{I}^{-}$  are passed through an electric field in **Figure 1.2**, they behave differently.

On **Figure 1.2**, sketch the paths taken by beams of  $^{63}\text{Cu}^{2+}$  and  $^{127}\text{I}^{-}$  in the presence of electric field, given that the angle of deflection of the  $\text{Cu}^{2+}$  beam is  $7.0^\circ$ .



**Figure 1.2**

[2]



- (f) Group 17 halogens  $\text{Cl}_2$ ,  $\text{Br}_2$  and  $\text{I}_2$  are often used as oxidising agents in chemical reactions.

Describe, using relevant  $E$  values from the *Data Booklet*, the trend in the reactivity of the halogens,  $\text{Cl}_2$ ,  $\text{Br}_2$  and  $\text{I}_2$  as oxidising agents.

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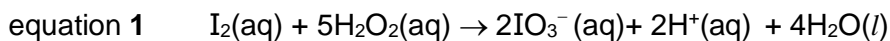
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[2]

- (g) In acidic solutions,  $\text{H}_2\text{O}_2$  is one of the most powerful oxidising agents known and is stronger than the halogens.  $\text{H}_2\text{O}_2$  reacts with aqueous iodine as shown in equation 1.



$$E_{\text{cell}} = +0.57 \text{ V}$$

- (i) Write the half-equations for the above reaction between  $\text{H}_2\text{O}_2$  and  $\text{I}_2$ . Hence, use relevant data from the *Data Booklet* to calculate  $E$  ( $\text{IO}_3^-/\text{I}_2$ ).

[2]

- (ii) Draw a fully labelled diagram of the electrochemical cell you would set up in order to measure the cell potential of reaction **1** under standard conditions.

In your answer, you should include the following:

- describe the measurement you would make determine the cell potential,
- polarity of electrodes and,
- direction of electron flow.

[4]

[Total: 17]

2 **Table 2.1** lists the solubility of the Group 2 carbonates at 25 °C.

**Table 2.1**

Group 2 element, <b>M</b>	Solubility of <b>MCO<sub>3</sub></b> / mol dm <sup>-3</sup>
Mg	$1.87 \times 10^{-4}$
Ca	$6.16 \times 10^{-5}$
Sr	$1.05 \times 10^{-5}$

- (a) By considering the relationship between  $\Delta H_{\text{soln}}$ , lattice energy and  $\Delta H_{\text{hyd}}$ , explain why the solubility of Group 2 carbonates, decreases down the group.

.....

.....

.....

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.....

.....

[2]

- (b) Selective precipitation is a technique of separating two or more ions from a solution by adding a suitable reagent that selectively precipitates one ion over the other ions.

A student carried out a selective precipitation experiment by slowly adding, dropwise, volumes of aqueous  $\text{Sr}(\text{NO}_3)_2$  solution to 1.0 dm<sup>3</sup> solution containing 0.020 mol of  $\text{CO}_3^{2-}(\text{aq})$  and 0.10 mol of  $\text{F}^{-}(\text{aq})$  at 25 °C.

You may assume that the volume of aqueous  $\text{Sr}(\text{NO}_3)_2$  added is negligible to the total volume of the solution in the experiment.

- (i) Calculate the value of  $K_{\text{sp}}$  for strontium carbonate,  $\text{SrCO}_3$ .

[1]

- (ii) Given that at 25 °C, the numerical value of the solubility product,  $K_{sp}$ , for strontium fluoride,  $SrF_2$ , is  $2.5 \times 10^{-9}$  and using your answer in (b)(i), deduce which salt will precipitate first in the selective precipitation experiment.

Show your working clearly.

[3]

- (c) A teacher asked the students in her class to explain which compound, calcium carbonate or strontium carbonate, has a higher decomposition temperature.

The following response was given by one of her students:

*'Calcium carbonate has a higher decomposition temperature than strontium carbonate. The  $Ca^{2+}$  ion is a smaller ion than  $Sr^{2+}$ , hence the lattice energy of calcium carbonate is more exothermic than that of strontium carbonate.'*

Comment on the student's response.

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.....

[3]

- (d) A current is passed through three cells connected in series, as shown in Figure 2.2.

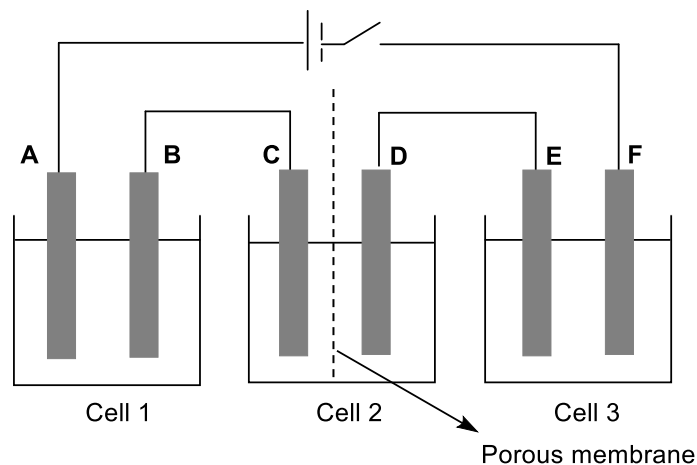


Figure 2.2

Cell 1 contains lead electrodes, **A** and **B**, and electrolyte  $\text{Pb}(\text{NO}_3)_2(\text{aq})$ .

Cell 2 contains platinum electrodes, **C** and **D**, and electrolyte  $\text{Mg}(\text{OH})_2(l)$ .

Cell 3 contains platinum electrodes, **E** and **F**, and electrolyte containing  $\text{X}^{n+}(\text{aq})$ .

- (i) Give the ion–electron equations for the reactions that occur at each of the electrodes, **A** to **C**, when the switch is closed.

Electrode **A**: .....

Electrode **B**: .....

Electrode **C**: .....

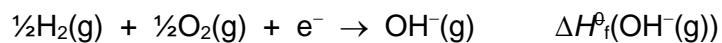
[3]

- (ii) It was found that 3240 coulombs of electricity cause the deposition of 1 g of **X** ( $A_r = 119$ ) at electrode **F** in Cell 3.

Find the value of  $n$  in  $\text{X}^{n+}(\text{aq})$ .

[2]

- (e) The equation for the formation of the gaseous hydroxide ion is shown below.



Using the data in **Table 2.3** and relevant data from the *Data Booklet*, complete the energy level diagram to calculate  $\Delta H_f^\ominus(\text{OH}^-(\text{g}))$ .

**Table 2.3**

Enthalpy change of atomisation of Mg(s)	+148 kJ mol <sup>-1</sup>
Enthalpy change of formation of Mg(OH) <sub>2</sub> (s)	-925 kJ mol <sup>-1</sup>
Lattice energy of Mg(OH) <sub>2</sub> (s)	-2993 kJ mol <sup>-1</sup>



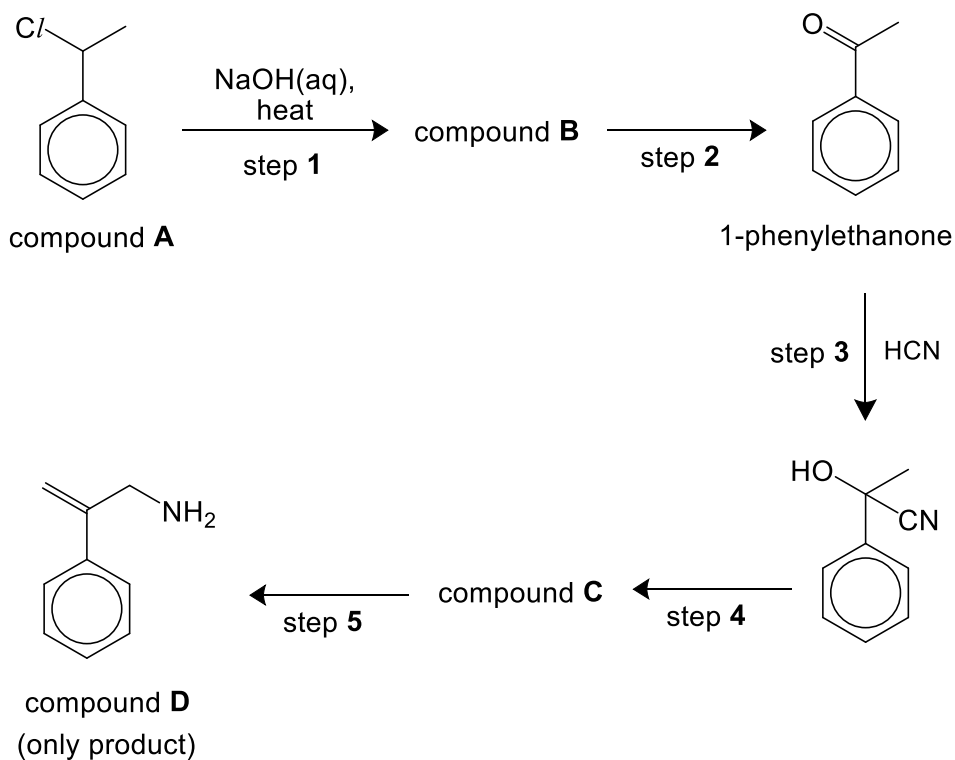
[3]

[Total: 17]

For  
Examiner's  
Use

- 3 (a) Amines are found commonly in polymers used in plastics or textiles.

Compound **D** is an amino-containing monomer, which is used in polymerisation to form plastic materials. **Figure 3.1** outlines the formation of compound **D** from **A**.



**Figure 3.1**

- (i) Draw the structures of the compounds **B** and **C** in the boxes provided below.

Compound <b>B</b>	Compound <b>C</b>

[2]

- (ii) Give the reagents and conditions for steps 2, 4 and 5.

step 2 : .....

step 4 : .....

step 5 : .....

[3]

- (iii) Name and describe the mechanism of the reaction that occurs in step 3.  
Show relevant lone pairs and dipoles, and use curly arrows to indicate the movement of electron pairs.

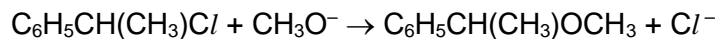
Type of mechanism: .....

[4]

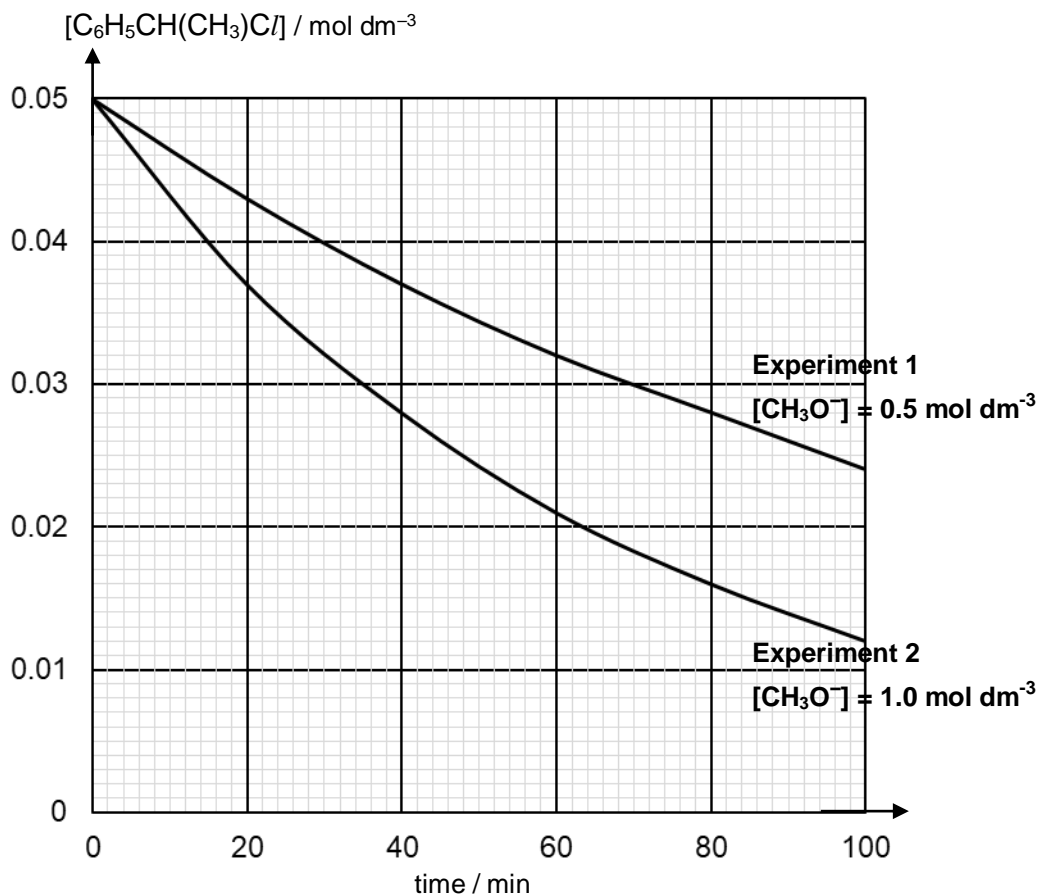
**Question 3 continues on the next page.**



- (b) Compound **A**,  $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{Cl}$ , undergoes hydrolysis reaction according to the following equation.



The graphs in **Figure 3.2** were obtained from two hydrolysis experiments. In each experiment, the overall  $[\text{CH}_3\text{O}^-]$  remained virtually constant.



**Figure 3.2**

- (i) Deduce the order of reaction with respect to  $[\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{Cl}]$ .

.....  
 ..... [2]

- (ii) Deduce the order of reaction with respect to  $[\text{CH}_3\text{O}^-]$ .

[2]

- (iii) Hence, construct a rate equation for the reaction, stating clearly the units for the rate constant.

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

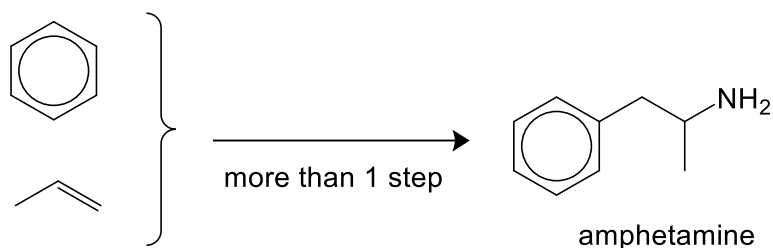
- (iv) Determine the half-life of the reaction if Experiment 3 is repeated with both the concentrations of  $\text{CH}_3\text{O}^-(\text{aq})$  and  $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{Cl}$  doubled that in Experiment 2.

..... [1]

- (c) Amphetamine,  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{CH}_3)\text{NH}_2$ , is a central nervous system stimulant that is used to improve brain development and nerve growth, and the treatment of obesity.

Suggest a synthesis of amphetamine starting from benzene and propene.

Include reagents and conditions for all reactions and the structures of all other intermediate compounds, in your answer.



[4]

[Total: 19]

- 4 (a) Methanoic acid,  $\text{HCO}_2\text{H}$ , was formerly known as formic acid because it is present in the sting of ants and the Latin name for ant is *formica*. It was first isolated in 1671 by John Ray who collected a large number of dead ants and extracted the acid from them by distillation.

When stung by one typical ant, about 80 % of its methanoic acid is injected into the skin. This volume of methanoic acid injected is equivalent to  $7.5 \times 10^{-3} \text{ cm}^3$  of a laboratory-prepared solution **A** which contains 50 % by volume of pure methanoic acid.

The sting of bees also contain high amounts of methanoic acid. In a typical bee sting, the mass of methanoic acid injected into skin is  $5.4 \times 10^{-3} \text{ g}$ .

The lethal dose of formic acid on mouse is 1.8 g per kg of mouse.

One simple treatment for ant or bee stings is to use washing soda, which contain sodium carbonate.

- (i) Use the given information, calculate how many ants would have to be distilled to produce at least  $1 \text{ cm}^3$  of pure methanoic acid.

[2]

- (ii) Determine the number of ants required to inject a lethal dose on a 0.2 kg mouse.

The density of pure methanoic acid is  $1.2 \text{ g cm}^{-3}$ .

[2]

- (iii) Write a balanced chemical equation for the reaction between methanoic acid and sodium carbonate.

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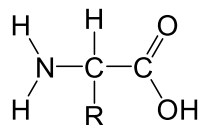
[1]

- (iv) Calculate the mass of sodium carbonate required to neutralise one bee sting.

[2]

- (b) Many ants forage at extrafloral nectar on plants and provide the plant with some measure of protection from herbivory. These nectars contain sugars, amino acids and, often, other compounds.

Amino acids are the building blocks of protein. The general structure of amino acid is as shown below



where R represents the side-chain on the  $\alpha$ -carbon of amino acid.

Information on three amino acids is given in **Table 4.1**.

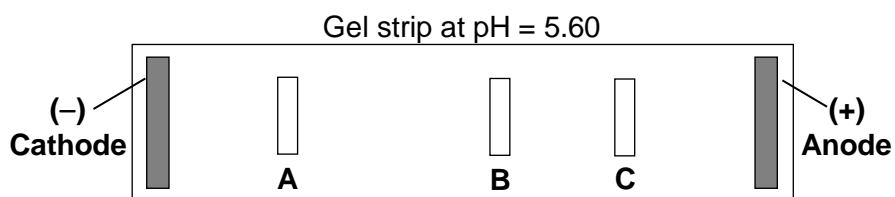
**Table 4.1**

Amino Acid	Formula of side-chain (R in $\text{NH}_2\text{CHRCOOH}$ )	$pK_a$		
		$\alpha\text{-COOH}$	$\alpha\text{-NH}_2$	R group
aspartic acid (asp)	$-\text{CH}_2\text{COOH}$	1.88	9.60	3.65
glutamic acid (glu)	$-\text{CH}_2\text{CH}_2\text{COOH}$	2.19	9.67	4.25
lysine (lys)	$-(\text{CH}_2)_4\text{NH}_2$	2.18	8.95	10.53

Electrophoresis is a technique of separating and identifying amino acids.

A solution of amino acids is absorbed into paper that is moistened with a buffer solution and stretched between two electrodes.

An electrophoresis experiment is run on a solution containing aspartic acid, lysine, and glutamic acid in **Table 4.1** at pH 5.60. The relative positions of the three amino acids obtained after electrophoresis is as shown **Figure 4.2**.



**Figure 4.2**

Draw the structural formulae of the species found at positions **A**, **B** and **C** at the end of the experiment.

<b>A</b>	<b>B</b>	<b>C</b>

[3]

- (c) Compound **J**, which contains only carbon, hydrogen and oxygen atoms, is a non-narcotic analgesic commonly sold in pharmacy.

The chemical composition of liquid **J** can be analysed by combustion:

- 0.1 cm<sup>3</sup> of liquid **J** was burnt with 150 cm<sup>3</sup> of oxygen gas.
  - Before cooling to room temperature, the gaseous mixture was passed through a tube containing anhydrous calcium chloride. The mass of the tube increased by 0.038 g.
  - The resulting gas mixture was then cooled to room temperature and the volume of the gaseous mixture is 140 cm<sup>3</sup>.
  - The gaseous mixture further contracted by 90 cm<sup>3</sup> when it is passed through aqueous sodium hydroxide.
  - All volumes are measured at room temperature and pressure.
- (i) Using the combustion data of compound **J**, show that the molecular formula of compound **J** is C<sub>9</sub>H<sub>10</sub>O<sub>3</sub>.

[3]

In another experiment, compound **J** is hydrolysed with hot NaOH(aq) and the resulting mixture acidified with a mineral acid such as sulfuric acid. Two products **K** and **M** are formed. Methanoic acid, HCO<sub>2</sub>H, is **not** among the products.

**Table 4.3** shows the results of the analysis of compounds **K** and **M** with the following reagents.

**Table 4.3**

Reaction	Reagent and condition	Result
1	excess Br <sub>2</sub> (aq)	Only <b>K</b> forms a white solid, <b>L</b> ( <i>M<sub>r</sub></i> = 295.8) but not <b>M</b> .
2	Na <sub>2</sub> CO <sub>3</sub> (aq)	Effervescence observed for <b>K</b> but not <b>M</b> .
3	Na(s)	Effervescence observed for both <b>K</b> and <b>M</b> .
4	NaOH(aq), I <sub>2</sub> (aq), heat	Pale yellow precipitate observed for <b>M</b> but not <b>K</b> .

- (ii) Name the functional group that reactions **1** and **2** show to be present in compound **K**.

reaction **1** .....

reaction **2** ..... [2]

- (iii) Give the molecular formula of compound **K**.

..... [1]

- (iv) State the structural feature present in compound **M**.

..... [1]

- (v) Use the deduction made in (c)(i) to (c)(iv), suggest a possible structural formulae for the compound **J**,  $C_9H_{10}O_3$ .

[1]

Question 4 continues on the next page.

Values of the acid dissociation constants,  $K_a$ , for some organic acids are given in **Table 4.4** below.

**Table 4.4**

acid	Formula	$K_a / \text{mol dm}^{-3}$
benzoic acid	$\text{C}_6\text{H}_5\text{CO}_2\text{H}$	$6.3 \times 10^{-5}$
phenol	$\text{C}_6\text{H}_5\text{OH}$	$1.3 \times 10^{-10}$
ethanoic acid	$\text{CH}_3\text{CO}_2\text{H}$	$1.8 \times 10^{-5}$
trifluoroethanoic acid	$\text{CF}_3\text{CO}_2\text{H}$	$5.0 \times 10^{-3}$

- (vi) After compound **J** is hydrolysed with hot  $\text{NaOH(aq)}$ , the resulting mixture acidified with a mineral acid such as sulfuric acid to give compound **K**.

Suggest, whether ethanoic acid or trifluoroethanoic acid, can be used as a replacement for sulfuric acid. Explain your answer.

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.....

[2]

- (vii) With reference to **Table 4.4**, account for the difference in  $K_a$  values of:

- $K_a$  of ethanoic acid is higher than that of phenol,

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- $K_a$  of trifluoroethanoic acid is higher than that of ethanoic acid.

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[2]

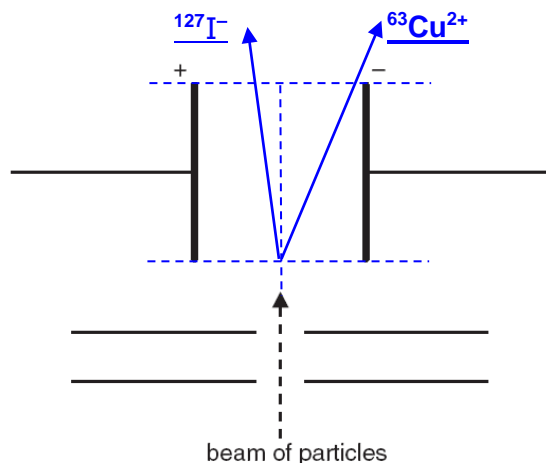
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**JURONG PIONEER JUNIOR COLLEGE**  
**2019 JC2 H2 CHEMISTRY (9729)**  
**Preliminary Examination Paper 2**  
**(Suggested Answers)**

- 1 (a) (i) Particles:  $\text{Cu}^{2+}$  cation  
Interactions: metallic bonding
- (ii) Particles:  $\text{I}_2$  molecule  
Interactions: instantaneous dipole–induced dipole interactions
- (b) The layers of  $\text{Cu}^{2+}$  cations can slide past each other without breaking the metallic bond (or with the mobile valence electrons holding them together).
- (c) Electrical conductivity: Mobile valence electrons available to conduct electricity in copper but no mobile charge carriers available in iodine to conduct electricity.  
or  
Solubility in organic solvent: Iodine is able to form favourable instantaneous dipole–induced dipole interactions with the organic solvent, but copper is unable to form favourable interactions with the organic solvent.
- (d) (i) Atomic mass is the weighted average of the mass of isotopes.
- (ii) Percentage abundance of the isotopes in this sample differs from what is normally obtained.  
or  
There are more than 2 types of isotopes of copper present in the sample.

(e)



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

angle of deflection of  $\text{I}^-$

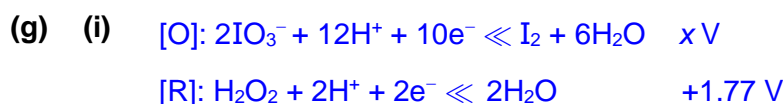
$$= \left| \frac{-1/127}{+2/63} \right| \times (7.0^\circ) = \underline{1.7^\circ} \text{ (1dp)}$$

(f)

X	Cl	Br	I
$E(\text{X}_2/\text{X}^-) / \text{V}$	+1.36	+1.07	+0.54

Since  $E(\text{X}_2/\text{X}^-)$  becomes less positive down the group, it implies that the tendency of  $\text{X}_2$  to be reduced to  $\text{X}^-$  decreases and hence, the oxidising power of  $\text{X}_2$  decreases down the group.



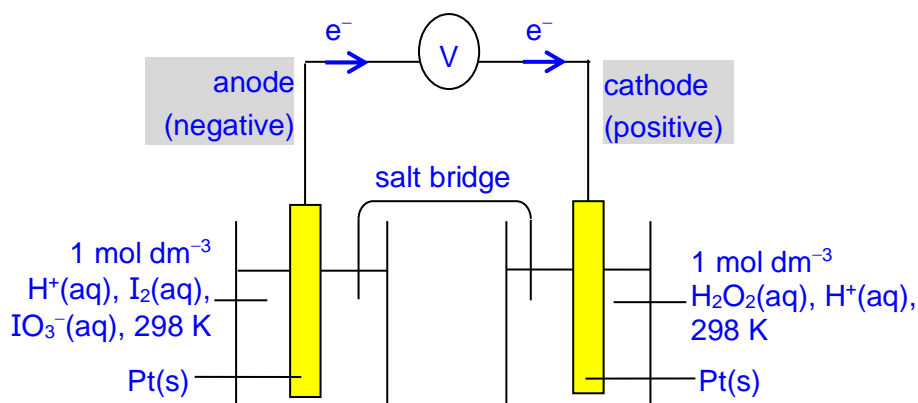


$$E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}}$$

$$+0.57 = (+1.77) - E(\text{IO}_3^-/\text{I}_2)$$

$$E(\text{IO}_3^-/\text{I}_2) = +1.20\text{ V}$$

(ii)



Note the  $E_{\text{cell}}$  value on the voltmeter at first instance of cell being connected.

2 (a) 
$$\Delta H_{\text{soln}} = -LE + \underbrace{\sum \Delta H_{\text{hyd}}}_{\substack{-\text{ve} \\ +\text{ve}}}$$

Down the group, both LE of  $\text{MCO}_3$  and  $\Delta H_{\text{hyd}}$  of  $\text{M}^{2+}$  becomes less exothermic (or more endothermic or magnitude/value of LE of  $\text{MCO}_3$  and  $\Delta H_{\text{hyd}}$  of  $\text{M}^{2+}$  decreases) since the radius of  $\text{M}^{2+}$  increases down the group.

However, the decrease in LE is less than the decrease in  $\Delta H_{\text{hyd}}$  since  $\text{M}^{2+}$  is smaller than  $\text{CO}_3^{2-}$ .

Hence,  $\Delta H_{\text{soln}}$  becomes less exothermic and the solubility of  $\text{MCO}_3$  decreases down the group.

(b) (i)  $K_{\text{sp}}$  of  $\text{SrCO}_3 = [\text{Sr}^{2+}][\text{CO}_3^{2-}] = (1.05 \times 10^{-5})^2 = 1.10 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$

(ii) For precipitation to occur, ionic product  $\geq K_{\text{sp}}$ .

$$\text{ionic product of SrCO}_3 = [\text{Sr}^{2+}]_{\text{min}}[\text{CO}_3^{2-}] \geq K_{\text{sp}}$$

$$[\text{Sr}^{2+}]_{\text{min}}(0.02) = 1.1 \times 10^{-10}$$

$$\text{minimum } [\text{Sr}^{2+}] \text{ to precipitate SrCO}_3 = 5.50 \times 10^{-9} \text{ mol dm}^{-3}$$

$$\text{ionic of SrF}_2 = [\text{Sr}^{2+}]_{\text{min}}[\text{F}^-]^2 \geq K_{\text{sp}}$$

$$[\text{Sr}^{2+}]_{\text{min}}(0.1)^2 = 2.5 \times 10^{-9}$$

$$\text{minimum } [\text{Sr}^{2+}] \text{ to precipitate SrF}_2 = 2.50 \times 10^{-7} \text{ mol dm}^{-3}$$

$\text{SrCO}_3$  will precipitate first because a lower  $[\text{Sr}^{2+}]$  is required to form the precipitate.

- (c) The student's response is incorrect as  $\text{SrCO}_3$  has a higher decomposition temperature than  $\text{CaCO}_3$ .

Thermal stability of Group 2 carbonate depends on the charge density of  $\text{M}^{2+}$ , not lattice energy.

Since  $\text{Sr}^{2+}$  has a larger radius,  $\text{Sr}^{2+}$  has a lower charge density than  $\text{Ca}^{2+}$ . Hence,  $\text{Sr}^{2+}$  polarises large  $\text{CO}_3^{2-}$  less and weakens the C–O bond to a smaller extent than that in  $\text{BaCO}_3$ .

Hence,  $\text{SrCO}_3$  has a higher thermal stability and has a higher decomposition temperature.

- (d) (i) Electrode A:  $\text{Pb(s)} \rightarrow \text{Pb}^{2+}(\text{aq}) + 2\text{e}^-$   
 Electrode B:  $\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Pb(s)}$   
 Electrode C:  $4\text{OH}^-(\text{l}) \rightarrow \text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g/l}) + 4\text{e}^-$

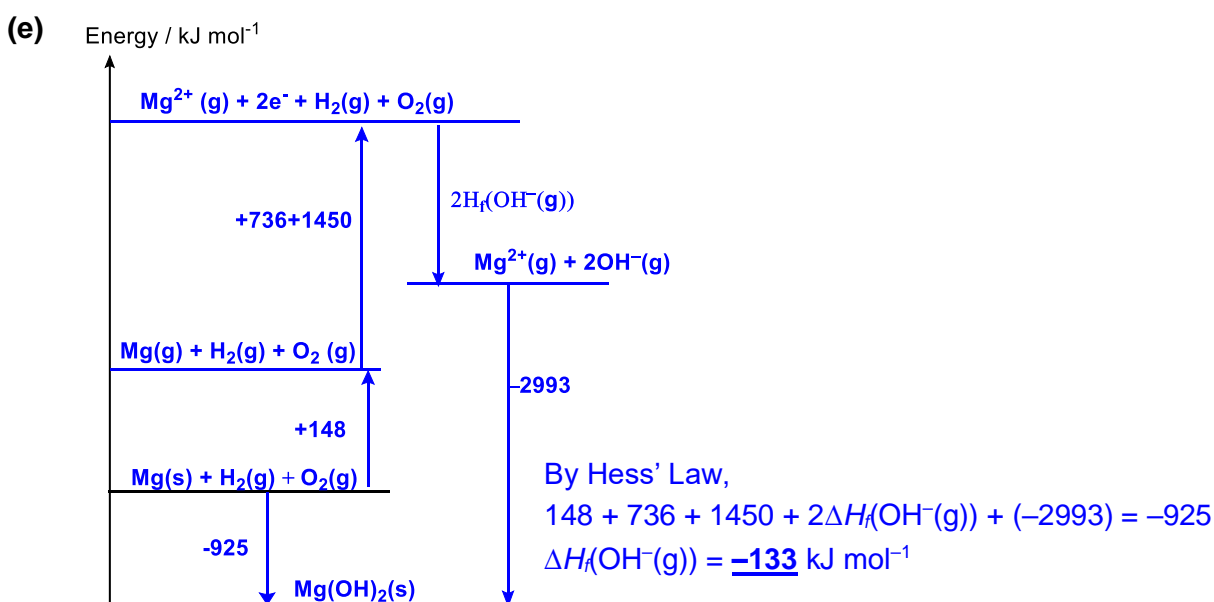
- (ii)  $\text{X}^{n+} + \text{n e}^- \rightarrow \text{X}$

$$n(\text{X}) \text{ deposited} = 1 \div 119 = 0.008403 \text{ mol}$$

$$n_{\text{e}} \text{ passed} = 3240 \div 96500 = 0.03358 \text{ mol}$$

mole ratio	X	:	$\text{e}^-$
	0.008403	:	0.03358
	1	:	4

Hence, the value of n is 4.



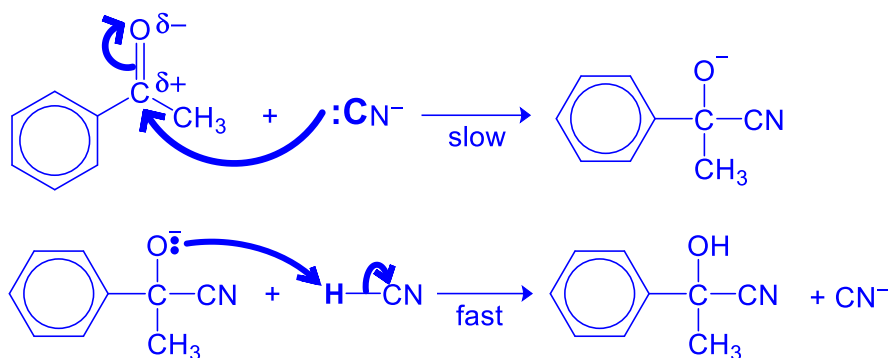
3 (a) (i)

Compound B	Compound C

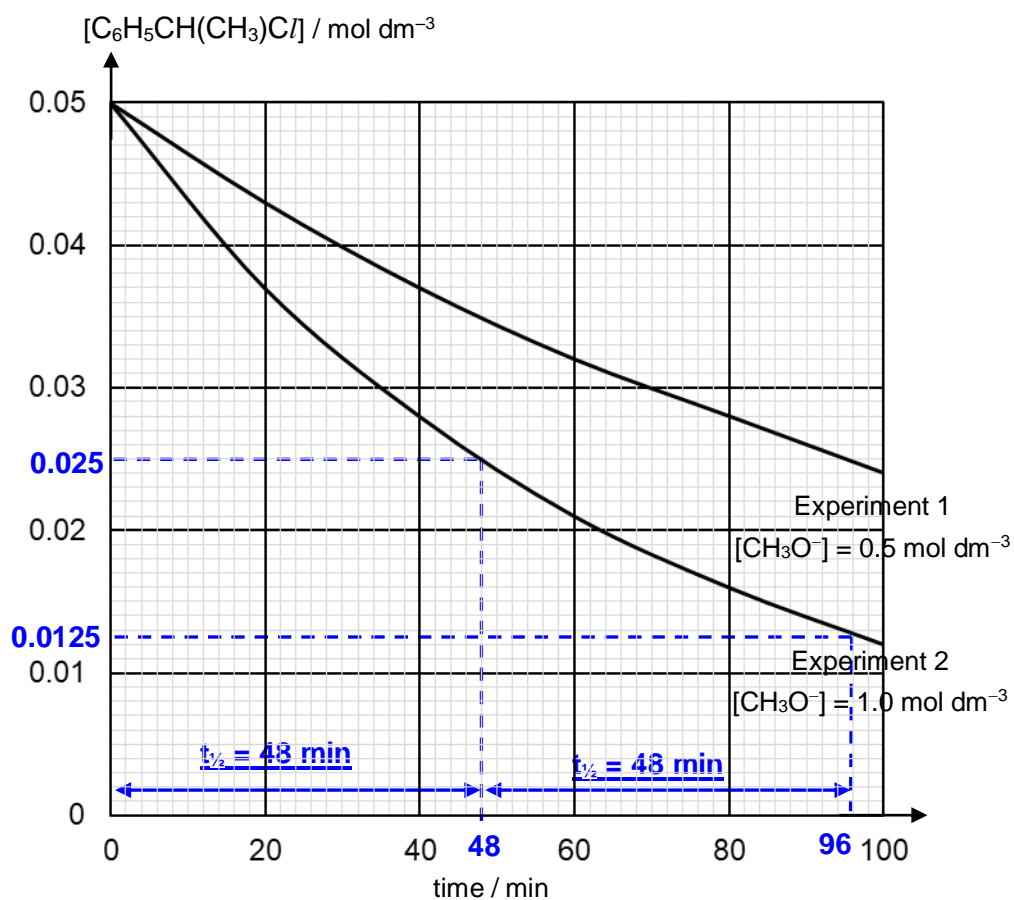
- (ii) step 2 : acidified  $\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$ , heat under reflux  
 step 4 :  $\text{Al}_2\text{O}_3$ , heat (or excess conc.  $\text{H}_2\text{SO}_4(\text{l})$ , heat)

step 5 : LiA/H<sub>4</sub>, dry ether

(iii) Type of mechanism: nucleophilic addition

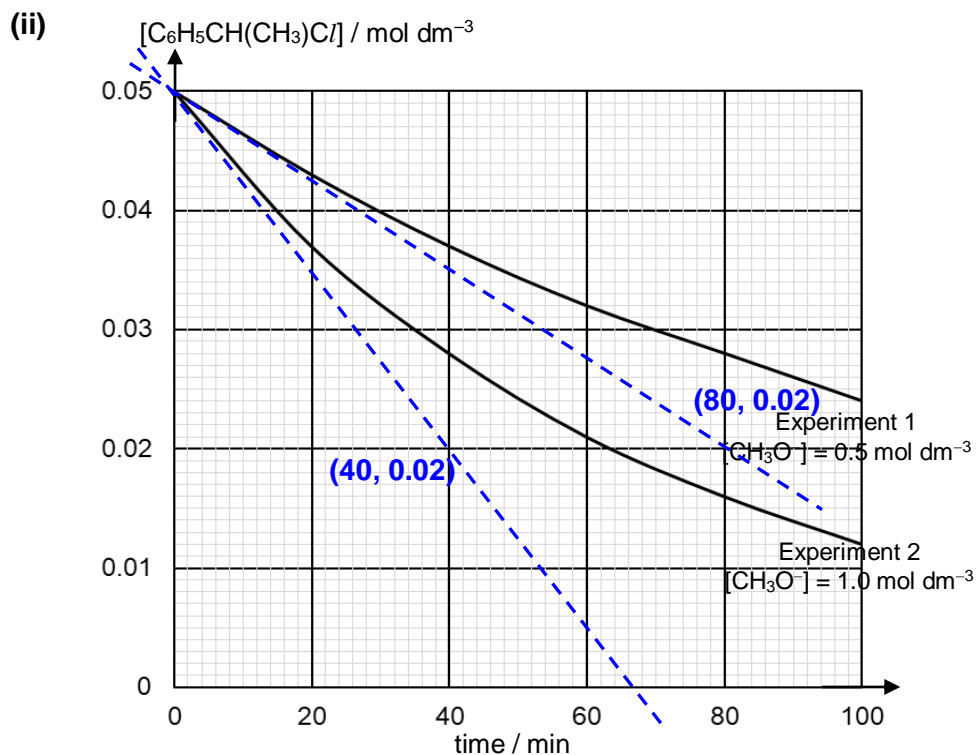


(b) (i)



average  $t_{1/2} = \frac{1}{2} (48 + 48) = 48 \text{ min}$

Since the half-lives are constant at about 48 min, the order of reaction with respect to  $[\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{Cl}]$  is 1.



From the graph of  $[\text{OH}^-] = 1.0 \text{ mol dm}^{-3}$

$$\text{Initial rate} = \frac{|0.02 - 0.05|}{40 - 0} = 7.50 \times 10^{-4} \text{ mol dm}^{-3} \text{ min}^{-1}$$

From the graph of  $[\text{OH}^-] = 1.0 \text{ mol dm}^{-3}$

$$\text{Initial rate} = \frac{|0.02 - 0.05|}{80 - 0} = 3.75 \times 10^{-4} \text{ mol dm}^{-3} \text{ min}^{-1}$$

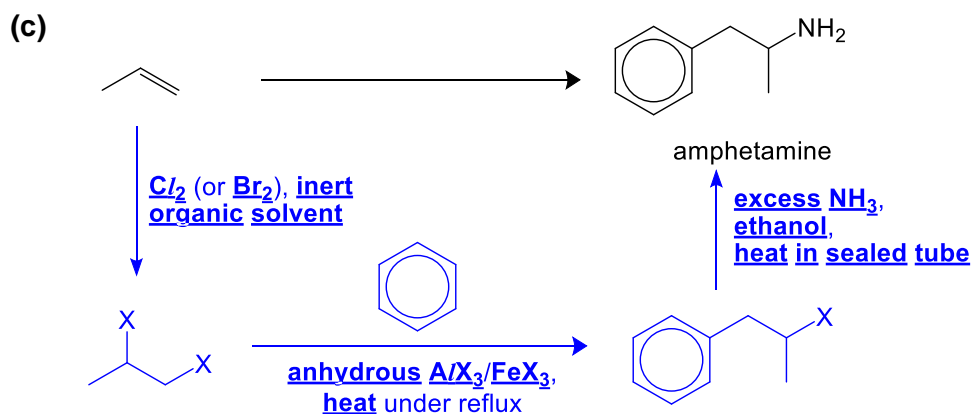
When  $[\text{CH}_3\text{O}^-]$  doubles, the rate is doubled.

Hence, the order of reaction with respect to  $[\text{CH}_3\text{O}^-]$  is 1.

(iii)  $\text{rate} = k [\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{Cl}] [\text{CH}_3\text{O}^-]$

$$\text{units of } k = \frac{\text{mol dm}^{-3} \text{ min}^{-1}}{(\text{mol dm}^{-3})^2} = \text{mol}^{-1} \text{ dm}^3 \text{ min}^{-1}$$

(iv) Experiment 3:  $t_{1/2} \text{ of } \text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{Cl} = \frac{\ln 2}{k(2.0)} = \frac{1}{2} \times 48 = \underline{24 \text{ min}}$

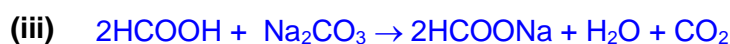


- 4 (a) (i) Volume of pure methanoic acid in one ant  

$$= (7.5 \times 10^{-3}) \times \frac{50}{100} \times \frac{100}{80} = 4.688 \times 10^{-3} \text{ cm}^3$$
  
 No. of ants required to produce  $1 \text{ cm}^3$  of pure methanoic acid  

$$= \frac{1}{1000} \div (4.688 \times 10^{-3}) = 214$$

- (ii) volume of HCOOH injected by one ant  $= (7.5 \times 10^{-3}) \times \frac{50}{100} = 3.75 \times 10^{-3} \text{ dm}^3$   
 mass of HCOOH injected by one ant  $= (3.75 \times 10^{-3}) \times 1.2 = 4.50 \times 10^{-3} \text{ g}$   
 no. of ants needed  $= (1.8 \times 0.2) \div (4.50 \times 10^{-3}) = 80$



- (iv)  $n(\text{HCOOH})$  injected by one bee  $= (5.4 \times 10^{-3}) \div 30.0 = 1.80 \times 10^{-4} \text{ mol}$   
 Since  $1\text{Na}_2\text{CO}_3 \equiv 2\text{HCOOH}$ ,  
 $n(\text{Na}_2\text{CO}_3)$  required  $= \frac{1}{2} \times (1.80 \times 10^{-4}) = 9.00 \times 10^{-5} \text{ mol}$   
 Mass of  $\text{Na}_2\text{CO}_3$  needed to neutralise one bee sting  
 $= (9.00 \times 10^{-5}) \times 106.0 = 0.00954 \text{ g}$

(b)

A	B	C
$\begin{array}{c} \text{H} \\   \\ \text{H}_3\text{N}^+ - \text{C} - \text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{O}^- \end{array} \\   \\ (\text{CH}_2)_4 \\   \\ \text{NH}_3^+ \end{array}$	$\begin{array}{c} \text{H} \\   \\ \text{H}_3\text{N}^+ - \text{C} - \text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{O}^- \end{array} \\   \\ \text{CH}_2 \\   \\ \text{CH}_2 \\   \\ \text{COO}^- \end{array}$	$\begin{array}{c} \text{H} \\   \\ \text{H}_3\text{N}^+ - \text{C} - \text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{O}^- \end{array} \\   \\ \text{CH}_2 \\   \\ \text{COO}^- \end{array}$

- (c) (i) Let compound J be  $\text{C}_x\text{H}_y\text{O}_z$ .  

$$\text{C}_x\text{H}_y\text{O}_z + (x + \frac{y}{4} - \frac{z}{2})\text{O}_2 \rightarrow x\text{CO}_2 + (\frac{y}{2})\text{H}_2\text{O}$$
  
 $n(\text{H}_2\text{O})$  collected  $= 0.038 \div 18.0 = 0.002111 \text{ mol}$

After cooling:

$$\text{volume of gases} = V(\text{unreacted O}_2) + V(\text{CO}_2) = 140 \text{ cm}^3$$

After reaction with NaOH:

$$V(\text{CO}_2) = 90 \text{ cm}^3$$

$$V(\text{unreacted O}_2) = 50 \text{ cm}^3$$

$$V(\text{reacted O}_2) = 150 - 50 = 100 \text{ cm}^3$$

$$n(\text{CO}_2) \text{ evolved} = \frac{90}{1000} \div 24.0 = 0.00380 \text{ mol}$$

$$n(\text{reacted O}_2) = \frac{100}{1000} \div 24.0 = 0.00417 \text{ mol}$$

$$\begin{array}{ccccccc}
 \text{C}_x\text{H}_y\text{O}_z & + & (x + \frac{y}{4} - \frac{z}{2})\text{O}_2 & \rightarrow & x\text{CO}_2 & + & (\frac{y}{2})\text{H}_2\text{O} \\
 & & 0.00417 & & 0.00380 & & 0.00211 \\
 & & 2 & & 1.8 & & 1 \\
 & & 10 & & 9 & & 5
 \end{array}$$

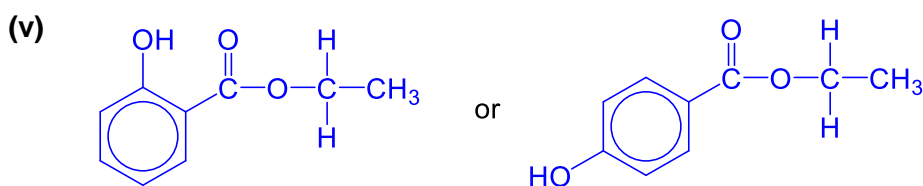
$x = 9$ ,  $y = 10$  and  $z =$

Hence, the molecular formula of J is  $\text{C}_9\text{H}_{10}\text{O}_3$ .

- (ii) reaction 1 phenol  
reaction 2 carboxylic acid

- (iii)  $\text{C}_7\text{H}_6\text{O}_3$

- (iv)  $-\text{CH}(\text{CH}_3)\text{OH}$  is present.



- (vi) To form K (*i.e.* benzoic acid and phenol), the acid used must be a stronger acid than benzoic acid and phenol (e.g.  $\text{H}_2\text{SO}_4$  which is a strong acid).

Since the  $K_a$  of  $\text{CF}_3\text{CO}_2\text{H}$  is higher than that of benzoic acid and phenol,  $\text{CF}_3\text{CO}_2\text{H}$  is a stronger acid and hence, it can be used as a replacement for sulfuric acid.

- (vii) •  $K_a$  of ethanoic acid is higher than that of phenol,

p-p orbital overlap results in the delocalisation of lone pair on  $\text{O}^-$  into  $\text{C}=\text{O}$  of  $\text{CH}_3\text{COO}^-$ , dispersing the negative charge over two electronegative O atoms and stabilises  $\text{CH}_3\text{COO}^-$  more than phenoxide ion. Hence, ethanoic acid is a stronger acid and has a higher  $K_a$  than phenol.

- $K_a$  of trifluoroethanoic acid is higher than that of ethanoic acid.

The three electron-withdrawing (or electronegative) F atoms disperses the negative charge on  $\text{O}^-$  of  $\text{CF}_3\text{COO}^-$  and stabilises  $\text{CF}_3\text{COO}^-$  more than  $\text{CH}_3\text{COO}^-$ . Hence, trifluoroethanoic acid is a stronger acid and has a higher  $K_a$  than ethanoic acid.



**JURONG PIONEER JUNIOR COLLEGE**  
**JC2 PRELIMINARY EXAMINATION 2019**

**CHEMISTRY**

**Higher 2**

Paper 3 Free Response

**9729/03**

**23 September 2019**

**2 hours**

Candidates answer on separate paper.

Additional Materials:      Answer Paper  
                                    Cover Page for Answer  
                                    Data Booklet

**READ THESE INSTRUCTIONS FIRST**

Write your name, class and exam index number on all the work you hand in.

Write in dark blue or black pen on both sides of the paper.

You may use a HB pencil for any diagrams, graphs.

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

**Section A**

Answer **all** questions.

**Section B**

Answer **one** question.

The use of an approved scientific calculator is expected, where appropriate.

A *Data Booklet* is provided.

At the end of the examination, fasten all your work securely together.

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

## Section A

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

- 1 (a) When a red-hot wire is plunged into separate samples of the gaseous  $\text{HCl}$  and  $\text{HI}$ , a colour change was observed in one of the samples.  
Suggest which sample gave the colour change. Use data from the *Data Booklet* to explain your answer. [2]
- (b) Chlorine gas can be prepared by reacting concentrated hydrochloric acid with manganese(IV) oxide. Manganese(II) chloride and water are also formed. Chlorine gas evolved is passed through a drying agent.
- (i) Write an ion-electron equation for the reduction of manganese(IV) oxide,  $\text{MnO}_2$ . [1]
- (ii) The standard reduction potential,  $E^\circ$ , of the half-reaction in (b)(i) is +1.23 V.  
Calculate  $\Delta G^\circ$ , in  $\text{kJ mol}^{-1}$ , for the overall reaction and use it to explain why the reaction is unlikely to occur. [3]
- (iii) Give **two** possible reasons why the reaction does occur. Explain your answer. [2]
- (c) Alkenes or alcohols can react with gaseous  $\text{HCl}$  to form alkyl chlorides. However, carboxylic acids do not react with gaseous  $\text{HCl}$ .
- (i) Describe the mechanism for the reaction of propene with  $\text{HCl}$ . [2]
- (ii) With reference to your mechanism in (c)(i), suggest how propene can act as a Bronsted-Lowry base. [1]
- (iii) State the *type* of reaction that occurs between ethanol and gaseous  $\text{HCl}$ . [1]
- (iv) Explain why ethanoic acid does not react with gaseous  $\text{HCl}$ . [1]



- (d)  $\text{HClO}_4$  can be used to prepare perchloric acid,  $\text{HClO}_4$ .

In the presence of  $\text{HClO}_4$ , alcohols react with nitriles to form *N*-alkylamides. This is known as the *Ritter reaction*, as shown in Fig. 1.1.

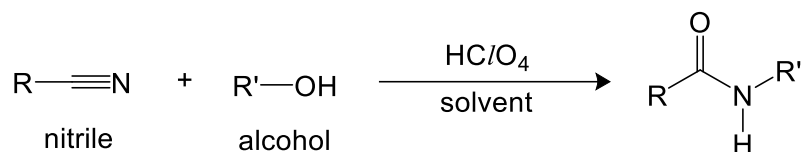


Fig. 1.1

Consider the following reaction which employs the *Ritter reaction* in the last step.

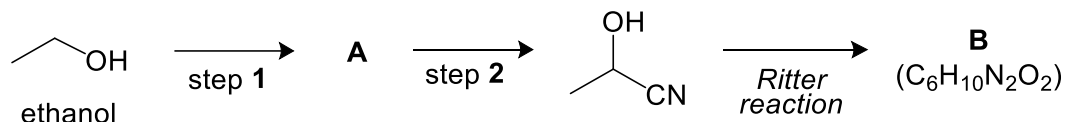


Fig. 1.2

Suggest appropriate reagents and conditions necessary for steps 1 and 2, and draw the structures of the compounds A and B. [4]

- (e) *Lingzhi* (*Ganoderma lucidum*) is a mushroom that has been used in Chinese medicines for more than 2000 years due to its numerous health benefits.

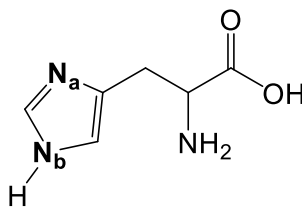
When *Lingzhi* is ingested, gastric juice in the stomach which comprises mainly hydrochloric acid, activates digestive enzymes to breakdown proteins into smaller peptides and amino acids.

- (i) A peptide, isolated from *Lingzhi*, consists of 10 amino acid residues. It is partially hydrolysed into the following tripeptides:

ala-val-ser, leu-gly-val, ser-gly-arg,  
val-ala-val, arg-asn-leu, gly-arg-asn

Suggest the primary structure of this peptide. [1]

- (ii) Histidine is an amino acid also found in *Lingzhi*.



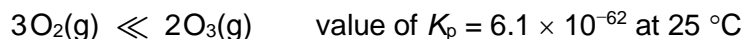
histidine (his)

Both  $\text{N}_a$  and  $\text{N}_b$  are  $\text{sp}^2$  hybridised.

By considering the hybridisation state and the orientation of the p orbitals of the two nitrogen atoms, explain why  $\text{N}_a$  is a stronger base than  $\text{N}_b$ . [1]

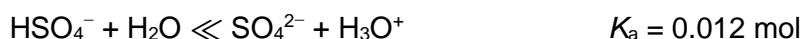
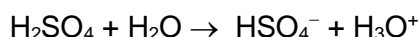


- 2 (a) The kinetic theory of gases makes assumptions about the behaviour of an ideal gas. State **two** assumptions of the kinetic theory of gases. [2]
- (b) Ozone,  $O_3$ , is produced naturally in the stratosphere when highly energetic solar radiation strikes molecules of oxygen,  $O_2$ .



- (i) Write  $K_p$  expression for this reaction. [1]
- (ii) Assuming gaseous oxygen and ozone obey the ideal gas equation, use your answer in (b)(i) to express  $K_c$  in terms of  $K_p$  and hence, show that the value of  $K_c$  is  $1.5 \times 10^{-55}$ . [2]
- (iii) Based on the numerical value of  $K_c$  given in (b)(ii), how does the amount of product compare to the amount of reactant in this reaction at equilibrium? [1]
- (iv) If a  $4 \text{ dm}^3$  flask is initially filled with 10.0 moles of  $O_2$ , calculate the equilibrium concentration of ozone. [2]  
You may use your conclusion in (b)(iii) to make suitable approximation in your calculations.
- (c) Ozone reacts with water and sulfur dioxide,  $SO_2$  to form sulfuric acid,  $H_2SO_4$ , as the only product.
- (i) Construct a balanced equation for this reaction. [1]

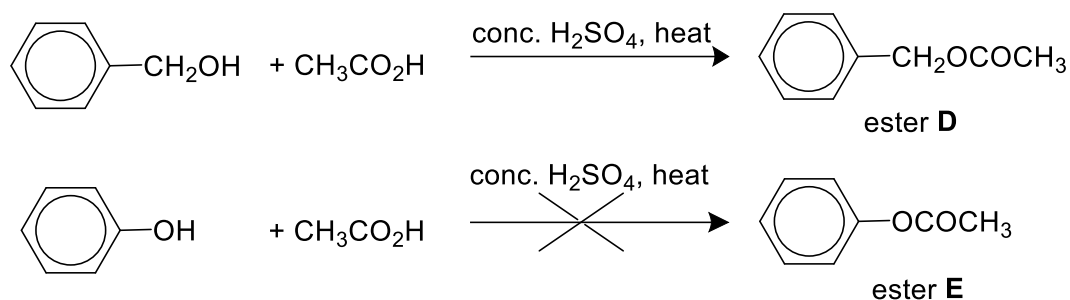
$H_2SO_4$ , a dibasic acid, dissociates in two stages.



$\text{dm}^{-3}$

- (ii) Suggest a reason for the difference in the extent of dissociation of  $H_2SO_4$  and  $HSO_4^-$ . [1]
- (iii) Calculate the pH of the buffer solution formed when  $5 \text{ cm}^3$  of  $0.100 \text{ mol dm}^{-3}$  HCl solution was added to  $10 \text{ cm}^3$  of  $0.200 \text{ mol dm}^{-3}$   $Na_2SO_4$  solution. [2]

- (d) Concentrated sulfuric acid can be used to form ester by reacting alcohol with ethanoic acid. However, under the same condition, phenol cannot react with ethanoic acid to form ester **E**.

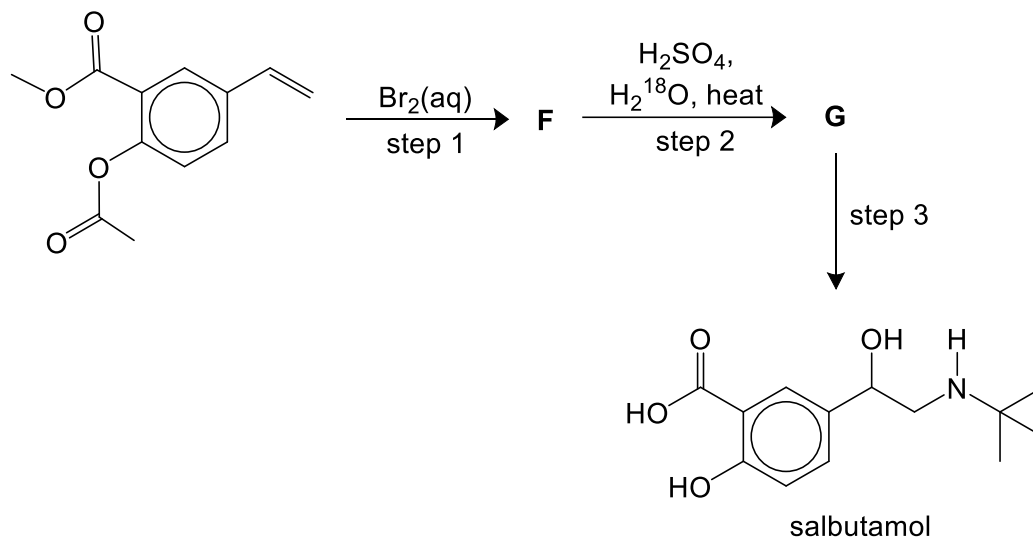


**Fig. 2.1**

Explain why ester **E** cannot be formed from phenol and ethanoic acid.

Suggest suitable reagent and conditions for the formation of ester **E** from phenol. [2]

- (e) **Fig. 2.2** shows the reaction scheme for the conversion of a diester into salbutamol, a drug used to treat asthma.

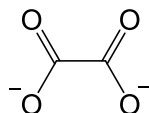


**Fig. 2.2**

- Draw the structure of **F**. [1]
- Isotopic labelling experiment is often used to elucidate the mechanism of organic reaction. In step 2 of **Fig 2.2**, the water used in the hydrolysis of **F** was labelled using the oxygen isotope  $^{18}\text{O}$ .  
Draw the structure of **G**, stating clearly the  $^{18}\text{O}$  isotope if present. [2]
- Suggest the reagent and conditions necessary for step 3. [1]
- Suggest why step 2 cannot be carried out before step 1. [1]
- Explain why the reaction in step 3 is likely to give a low yield of salbutamol. [1]

[Total: 20]

- 3 (a) (i) Write the full electronic configurations for a Cr atom. [1]
- (ii) Transition elements exhibit a range of different oxidation states.  
Describe and explain the pattern of **maximum** oxidation states for the elements from Sc to Zn. [2]
- (iii) Explain why iron(III) salts are usually coloured while scandium(III) salts are white or colourless. [3]
- (iv) When a solution of cobalt(II) sulfate is warmed with potassium ethanedioate,  $K_2C_2O_4$ , sulfuric acid and hydrogen peroxide, a complex with the formula  $K_3[Co(C_2O_4)_3]$  is formed. The structure of ethanedioate ion is given below.



ethanedioate ion

Draw the three-dimensional diagram to show the shape of the cobalt-containing anion. [1]

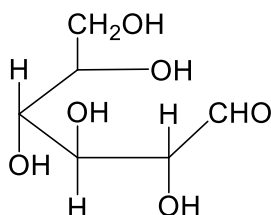
- (b) Copper in oxidation state of +1 is unstable in aqueous solution but can be stabilised as insoluble salts and in some complexes.

Step 1: On boiling with copper metal, 1 mole of blue aqueous  $CuCl_2$  reacts with 2 moles of dilute  $HCl$  to give a colourless solution **P**, which contains complex ion of copper and chlorine.

Step 2: After filtering off the excess copper metal and diluting the solution with water, a white solid **Q**, containing copper and chlorine only, is formed. The oxidation number of copper in **P** and **Q** are the same.

- (i) Explain the observations in step 1.  
Your answer should include the type of reactions that have occurred and give the formula of any insoluble salt and complex formed. Write an equation for the reaction that occurred. [2]
- (ii) Identify the white solid **Q** formed in step 2. [1]

- (c) Fehling's solution can be used to screen for glucose in urine, thus detecting diabetes. It gives a positive test due to the presence of an aliphatic aldehyde functional group in the open structure of glucose.

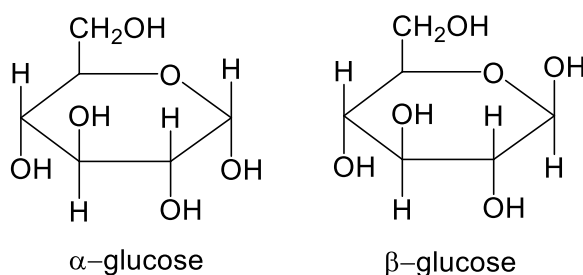


open structure of glucose

Fehling's solution is prepared by mixing  $\text{CuSO}_4(\text{aq})$  and an alkaline solution of Roselle salt. The resulting solution contains a deep blue copper-containing complex ion,  $[\text{CuL}_2]^{2-}$ .

- (i) State what would you observe when Fehling's solution is added to glucose. Draw the structure of the organic product formed. [2]

However, the open structure made up a very small amount of the glucose molecules in aqueous solution. The glucose molecules are present predominantly in cyclic ring structures, namely  $\alpha$ -glucose and  $\beta$ -glucose, as shown in **Fig. 3.1**.



**Figure 3.1**

- (ii) This cyclic form of glucose exhibits both enantiomerism and cis-trans isomerism. One way of labelling the stereochemical configuration of  $\alpha$ -glucose is (trans, cis) while that of  $\beta$ -glucose is (trans, trans).

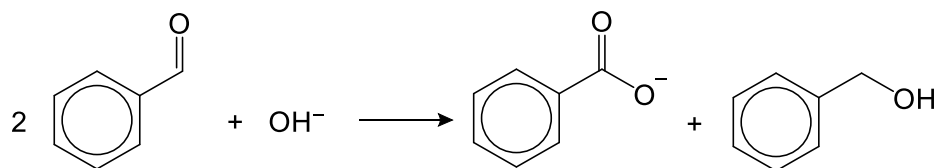
Explain why glucose can exhibit both enantiomerism and cis-trans isomerism. [2]

- (iii) A  $1.0 \text{ mol dm}^{-3}$   $\alpha$ -glucose solution has an optical rotation angle of  $+113.4^\circ$  while a  $1.0 \text{ mol dm}^{-3}$   $\beta$ -glucose solution has an optical rotation angle of  $+19.0^\circ$  at 298 K.

An equilibrium mixture containing both  $\alpha$ -glucose and  $\beta$ -glucose has an optical rotation angle of  $+52.2^\circ$ .

Determine the percentage of  $\alpha$ -glucose in the mixture. [2]

- (iv) On the other hand, the complex ion in Fehling's solution has no reaction with benzaldehyde, which is an aromatic aldehyde. This is because under the influence of the alkaline medium, benzaldehyde reacts according to the below equation.



Suggest the type of reaction that has occurred.

[1]

[Total: 17]

## Section B

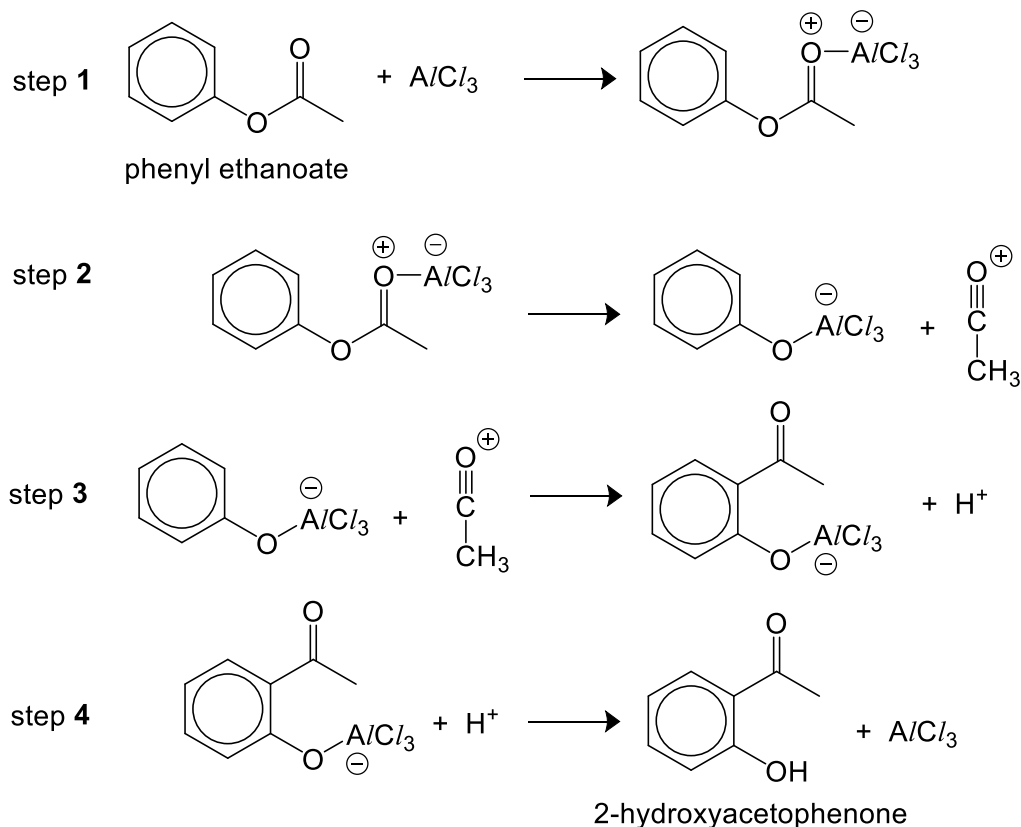
Answer **one** question from this section.

- 4 (a) There is said to be a 'diagonal relationship' between elements of the second and third periods of the Periodic Table, exemplified by lithium and magnesium, and by beryllium and aluminium. This relationship leads to diagonal pairs of elements having similar properties.
- (i) By considering the trends in electronegativity across the period and down the group, suggest why beryllium and aluminium have similar properties. [1]
- (ii) In terms of structure and bonding, explain why the boiling point of beryllium chloride is much lower than that of beryllium oxide. [2]
- (iii) Beryllium chloride dissolves in water to give  $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$ .  
Predict and explain the effect of adding beryllium chloride to a beaker of litmus solution. [2]
- (b) Beryllium oxide was heated with a mixture of potassium fluoride and hydrogen fluoride. An ionic compound was formed, which dissolved in water. When the resultant solution was added to aqueous lead(II) nitrate, a white precipitate, **A**, containing only beryllium, fluorine and lead was obtained. The white precipitate contained 3.08 % by mass of beryllium.
- (i) Given that the relative formula mass of **A** is approximately 290 and the empirical formula of **A** is  $\text{PbBe}_x\text{F}_y$ , determine the values of  $x$  and  $y$ .  
Shows all working clearly. [2]
- (ii) The anion in compound **A** is also formed when 1 mole of beryllium difluoride reacts with 2 moles of potassium fluoride.  
Draw a 'dot-and-cross' diagram of this anion, showing the outer shell electrons only. In your diagram, use the symbols '•' and 'x' to distinguish electrons from different atoms, and the symbol '□' for any additional electrons responsible for the overall negative charge. [1]



Aryl esters can be converted to aryl ketones by a reaction known as the Fries rearrangement.

In the presence of  $\text{AlCl}_3$ , the acetyl group,  $-\text{COCH}_3$ , is transferred to the 2-position to form 2-hydroxyacetophenone, depending on the reaction conditions used. A proposed mechanism for the Fries rearrangement of phenyl ethanoate is shown **Fig. 4.1**.



**Fig. 4.1**

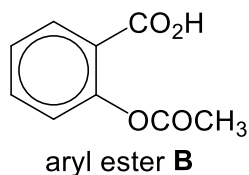
- (c) (i) Write an overall equation for the Fries rearrangement of phenyl ethanoate. [1]
- (ii) Considering the mechanism in **Fig. 4.1** and your overall equation in (c)(i), state and explain the roles of  $\text{AlCl}_3$  in Fries rearrangement. [2]
- (iii) Step 3 of the mechanism in **Fig. 4.1** occurs in two stages.
- In stage 1, benzene attacks the electron-deficient carbon atom of  $\text{CH}_3\text{CO}^+$  to form an intermediate with delocalised positive charge.
  - In stage 2, the loss of a proton restores the aromaticity of the compound.
- Using curly arrows to show the movement of electron pairs, complete the mechanism. Show all charges and relevant lone pairs. [3]
- (iv) Describe a simple chemical test to confirm that 2-hydroxyacetophenone is formed during the reaction. State what you would observe. [2]

- (v) 4-hydroxyacetophenone was also formed during the Fries rearrangement of phenyl ethanoate. However, 2-hydroxyacetophenone is likely to be formed in larger proportion than 4-hydroxyacetophenone due to the formation of favourable interactions between the ketone and alcohol functional groups.

Draw an appropriate diagram to illustrate the type of interactions formed, stating the interactions clearly.

[2]

- (d) Aryl ester **B** is an analog of phenyl ethanoate.



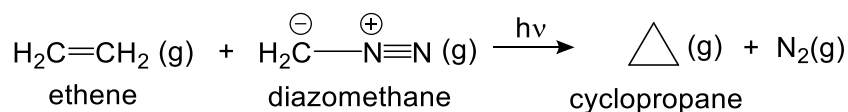
Considering the mechanism in (c)(iii), explain how the rate of Fries rearrangement might compare with phenyl ethanoate if aryl ester **B** was used instead.

[2]

[Total: 20]

5 (a) (i) Explain what is meant by the term *bond energy*. [1]

(ii) In the presence of light, diazomethane gas reacts with ethene to give cyclopropane.



Use relevant bond energies data from the *Data Booklet* to calculate the standard enthalpy change of the reaction between diazomethane gas and ethene. [2]

(iii) Other than average bond energies in the *Data Booklet*, suggest why the theoretical value calculated in (a)(ii) is likely to be *significantly* less exothermic than the actual value. [1]

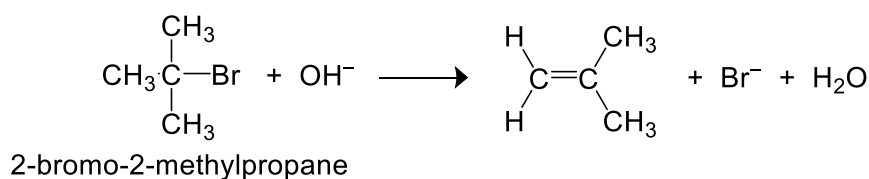
(b) Alkenes can be formed from alkyl halide, via elimination process, in the presence of a suitable base such as potassium hydroxide. Like nucleophilic substitution of alkyl halides, there are two possible mechanisms for the elimination reaction, namely E1 and E2.

E1 reaction is an unimolecular reaction which occurs via a two-step mechanism.

- In the first step which is also the rate-determining step, the alkyl halide undergoes a dissociation process to yield a carbocation and halide ion.
- The carbocation then reacts with hydroxide ion where a C–H bond is broken to give the alkene in the second step.

On the other hand, E2 reaction is a bimolecular elementary reaction.

Using 2-bromo-2-methylpropane as an example, **Fig. 5.1** shows the overall equation for the elimination reaction of alkyl halide.



**Fig. 5.1**

(i) Using 2-bromo-2-methylpropane as an example, write the rate equations for the E1 reaction **and** the E2 reaction. [2]

(ii) Using the information on E1 mechanism given above, outline the E1 mechanism for 2-bromo-2-methylpropane.

Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows. [3]

(iii) Explain how the rate of E1 reaction of 2-bromo-2-methylpropane would change if  $\text{CH}_3\text{CH}_2\text{O}^-$  is used as the base instead of  $\text{OH}^-$ . [2]

(c) Since both mechanisms proceed via the same carbocationic intermediate, there is usually competition between E1 reaction and S<sub>N</sub>1 reaction.

(i) Write a balanced chemical equation for the nucleophilic reaction of 2-bromo-2-methylpropane with potassium hydroxide. [1]

(ii) Considering the equation in **Fig. 5.1** and your answer in (c)(i), explain, in thermodynamic terms, why E1 reaction predominates over S<sub>N</sub>1 reaction when a higher temperature was used. [2]

(iii) When benzyl bromide, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Br, is reacted with potassium hydroxide, it was found that it does not undergo elimination reaction. Also, benzyl bromide undergoes substitution via S<sub>N</sub>1 instead of the usual S<sub>N</sub>2 mechanism, typical for a primary alkyl halide.

Explain the above observations. [3]

(iv) In comparing the reactivity between different alkyl halides towards nucleophilic substitution, there are two main factors at work: the strength of C–X bond and the stability of the leaving group X<sup>–</sup>.

One way of measuring the stability of the leaving group X<sup>–</sup> ion is to use the pK<sub>a</sub> values of HX acids in **Table 5.2**.

**Table 5.2**

HX	HF	HCl	HBr	HI
pK <sub>a</sub> of HX	+3	–7	–9	–10

By relating the pK<sub>a</sub> values given in **Table 5.2** to the position of equilibrium and the stability of X<sup>–</sup> ion, explain how the reactivity of alkyl halide towards nucleophilic substitution vary from fluorine to iodine. [3]

[Total: 20]



**JURONG PIONEER JUNIOR COLLEGE**  
**2019 JC2 H2 CHEMISTRY (9729)**  
**Preliminary Examination Paper 3**  
**(Suggested Answers)**

- 1 (a) For HI, violet fumes is observed.

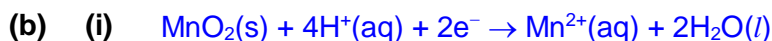
$$E(\text{H-Cl}) = +431 \text{ kJ mol}^{-1}; E(\text{H-I}) = +299 \text{ kJ mol}^{-1}$$

Since  $E(\text{H-I}) < E(\text{H-Cl})$ , H-I bond is weaker and is more easily broken than H-Cl bond. Hence, HI is less thermally stable and decomposes more readily (*i.e.* HI decomposes upon contact with the hot wire).

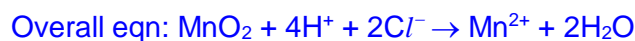
OR

radius of Cl = 0.099 nm; radius of I = 0.133 nm

Since I has a larger radius than Cl, H-I bond is longer and weaker so it is more easily broken than H-Cl bond. Hence, HI is less thermally stable and decomposes more readily (*i.e.* HI decomposes upon contact with the hot wire).



(ii)  $E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}} (+1.23) - (+1.36) = -0.13 \text{ V} < 0$  (not energetically feasible)



$$\Delta G = -zFE_{\text{cell}} \text{ where } z = \text{total number of electrons transferred per overall eqn}$$
$$= -(2)(96500)(-0.13) = +25090 \text{ J mol}^{-1} = +25.1 \text{ kJ mol}^{-1}$$

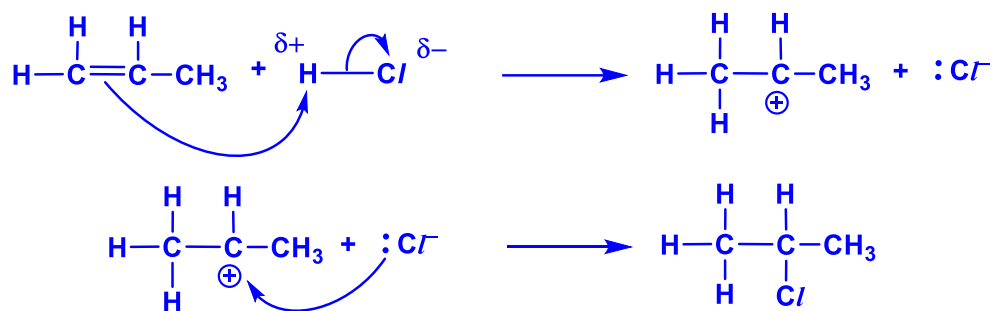
Since  $\Delta G > 0$ , the reaction is not energetically feasible (or not spontaneous) and thus unlikely to occur.

- (iii) When concentrated HCl is used,  $[\text{H}^+]$  is high and this causes the position of equilibrium of  $\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Mn}^{2+} + 2\text{H}_2\text{O}$  to shift right so as to react away some  $\text{H}^+$  ions. This makes  $E(\text{MnO}_2/\text{Mn}^{2+})$  becomes more positive than +1.23 V such that the  $E_{\text{cell}}$  becomes positive and  $\therefore$  energetically feasible.

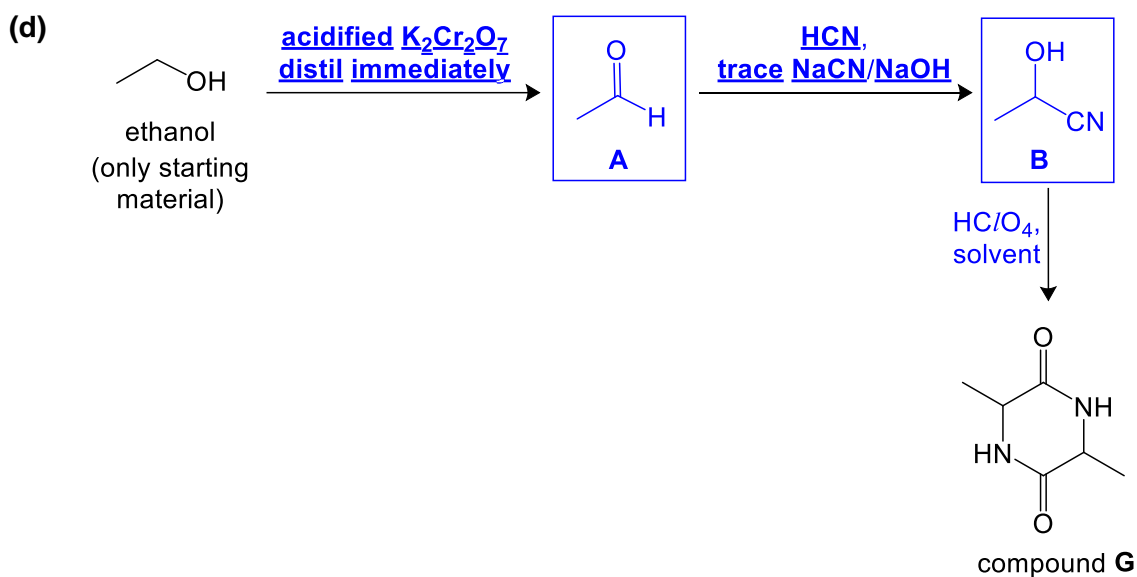
When concentrated HCl is used,  $[\text{Cl}^-]$  is high and this causes the position of equilibrium of  $\text{Cl}_2 + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-$  to shift left so as to react away some  $\text{Cl}^-$  ions. This makes  $E(\text{Cl}_2/\text{Cl}^-)$  becomes more negative (or less positive) than +1.36 V such that the  $E_{\text{cell}}$  becomes positive and  $\therefore$  energetically feasible.

The continuous removal of  $\text{Cl}_2$  gas from the reaction mixture as it is evolved shifts the position of equilibrium of  $\text{Cl}_2 + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-$  to the left to form back some  $\text{Cl}_2$ . This makes  $E(\text{Cl}_2/\text{Cl}^-)$  becomes more negative (or less positive) than +1.36 V such that the  $E_{\text{cell}}$  becomes positive and  $\therefore$  energetically feasible.

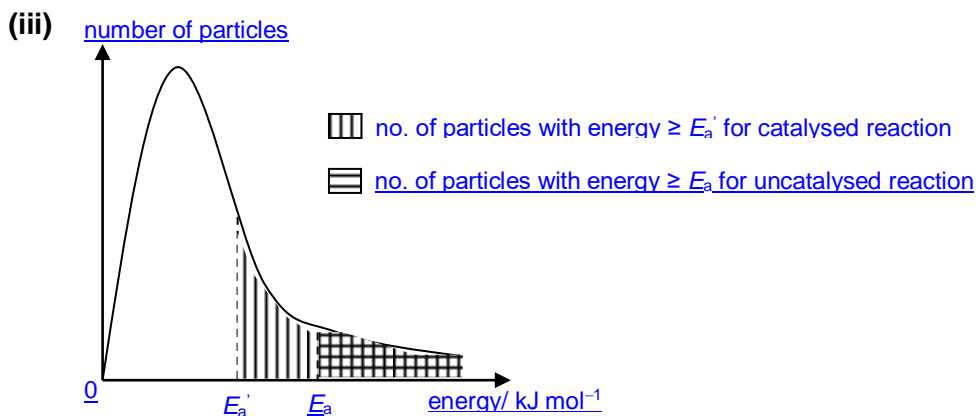
- (c) (i) Type of mechanism: electrophilic addition



- (ii) Propene can use its two  $\pi$  electrons to form a dative bond with  $\text{H}^+$  (or to accept a  $\text{H}^+$ ).
- (iii) Nucleophilic substitution
- (iv) p-p orbital overlap results in the delocalisation of lone pair on O of C=O into the  $\pi$  electron cloud of C=O, forming a partial double bond character in the C-O bond. This strengthens the C-O bond in  $-\text{CO}_2\text{H}$ , making it difficult to break. Hence, carboxylic acid is unreactive towards  $\text{HCl}$ .

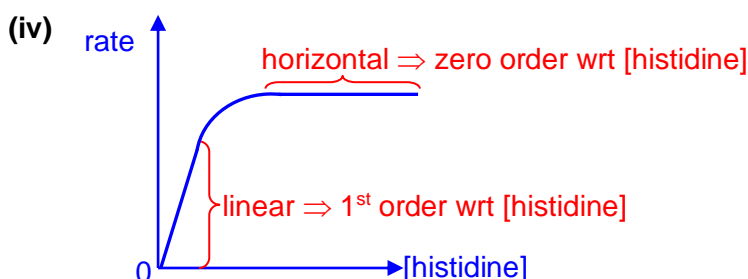


- (e) (i) val-ala-val-ser-gly-arg-asn-leu-gly-val  
or leu-gly-val- val-ala-val-ser-gly-arg-asn  
or ser-gly-arg-asn-leu-gly-val- ala-val-ser
- (ii) The lone pair on  $\text{N}_a$  is in the hybridised  $\text{sp}^2$  orbital which is perpendicular to the p-orbitals of adjacent  $\text{C}=\text{C}$  and  $=\text{C}-\text{N}$  bonds. Hence, the lone pair on  $\text{N}_a$  is not delocalised and is available for protonation.
- or
- The lone pair on  $\text{N}_b$  is in the unhybridised p orbital which is parallel to the p-orbitals of adjacent  $\text{C}=\text{N}$  and  $\text{C}=\text{C}$ . Hence, the lone pair on  $\text{N}_b$  is delocalised and less/not available for protonation.



When enzyme is used in the decarboxylation reaction, it provides an alternative reaction pathway with lower activation energy,  $E_a'$ . This increases the number of reacting particles with energy  $\geq E_a'$ .

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



- 2 (a) For ideal gas, the volume of gas particles is negligible compared to the volume of gas/container.

For ideal gas, there is no/negligible forces of attractions between the gas particles.

For ideal gas, the collision between the gas particle is perfectly elastic.

(b) (i)  $K_p = \frac{p_{\text{O}_3}^2}{p_{\text{O}_2}^3}$

- (ii) Using  $pV = nRT$  where  $V$  is in  $\text{m}^3$ ,

$$c = \frac{n}{V} \text{ mol m}^{-3} = \frac{p}{RT} \text{ mol m}^{-3} = \frac{p}{1000RT} \text{ mol dm}^{-3}$$

$$K_c = \frac{[\text{O}_2]^2}{[\text{O}_3]^3} = \left(\frac{p_{\text{O}_2}}{1000RT}\right)^2 \times \left(\frac{1000RT}{p_{\text{O}_3}}\right)^3$$

$$= K_p \times 1000RT$$

$$= (6.1 \times 10^{-62})(1000)(8.31)(273+25) = 1.5 \times 10^{-55} \text{ Pa}^{-1} \text{ (shown)}$$

- (iii) Since  $K_p \ll 1$ , it implies that the position of equilibrium  $3\text{O}_2 \rightleftharpoons 2\text{O}_3$  lies on the far left and hence, the forward reaction hardly occurs and there are much less products than reactants at equilibrium.

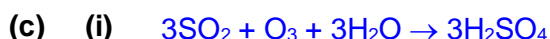
(iv)	$3\text{O}_2(\text{g})$	$\ll$	$2\text{O}_3(\text{g})$
initial conc. / mol dm <sup>-3</sup>	$10.0 \div 4 = 2.50$		0
change	$-1.5x$		$+x$
eqm conc. / mol dm <sup>-3</sup>	$2.50 - 1.5x$		$x$

$$K_c = \frac{[\text{O}_3]^2}{[\text{O}_2]^3} = \frac{x^2}{(2.50 - 1.5x)^3}$$

Since  $K_c \ll 1$ , we can assume that  $x \ll 2.50$  such that

$$1.5 \times 10^{-55} \approx \frac{x^2}{2.50^3}$$

equilibrium  $[\text{O}_2]$ ,  $x = 1.53 \times 10^{-27}$  mol dm<sup>-3</sup>



- (ii) More energy is required to remove  $\text{H}^+$  from negatively charged ion  $\text{HSO}_4^-$  than from electrically neutral  $\text{H}_2\text{SO}_4$  due to greater electrostatic force of attraction. Hence,  $\text{HSO}_4^-$  is a weaker acid than  $\text{H}_2\text{SO}_4$ .

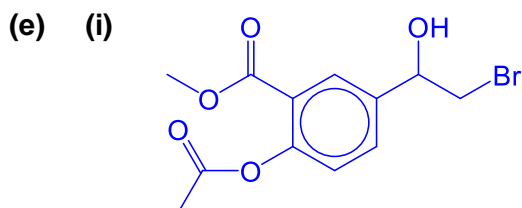
(iii)	$\text{SO}_4^{2-}$	+	$\text{H}^+$	$\rightarrow$	$\text{HSO}_4^-$
initial amt	$0.200 \times \frac{10}{1000}$ $= 0.002$		$0.100 \times \frac{5}{1000}$ $= 0.0005$		0
change	$-0.0005$		$-0.0005$		$+0.0005$
final amt / mol	0.0015		0		0.0005

System: acidic buffer (mixture contain weak acid  $\text{HSO}_4^-$  and its salt  $\text{SO}_4^{2-}$ )

$$\text{pH} = \text{p}K_a + \lg \frac{[\text{salt}]}{[\text{acid}]} = [-\lg(0.012)] + \lg \left( \frac{0.0015}{0.0005} \right) = 2.40$$

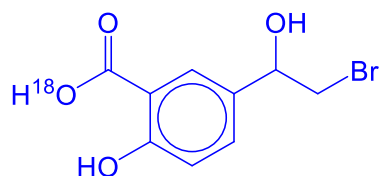
- (d) p-p orbital overlap results in the delocalisation of lone pair of electrons on O of phenol into benzene ring, making the lone pair less available for donation. Hence, phenol is a weaker nucleophile than alcohol (or less reactive towards nucleophilic reaction).

Reagent and condition: (1)  $\text{NaOH}(\text{aq})$ , room temperature  
(2),  $\text{CH}_3\text{COCl}(\text{l})$ , room temperature





(ii)

(iii) excess  $(\text{CH}_3)_3\text{NH}_2$ , ethanol, heat in sealed tube

(iv) If step 2 is carried out first, the phenolic group can undergo electrophilic substitution.

(v) The N of salbutamol still possesses a lone pair and can function as a nucleophile for further substitution to occur.

3 (a) (i)  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$ 

(ii) The maximum oxidation state is determined by the total number of 4s electrons and unpaired 3d electrons.

Since the total number of 4s and unpaired 3d electrons increases from Sc to Mn and decreases from Mn to Zn, the maximum oxidation state increases from Sc to Mn then decreases from Mn to Zn.

(iii)  $\text{Sc}^{3+}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6$  $\text{Fe}^{3+}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$ 

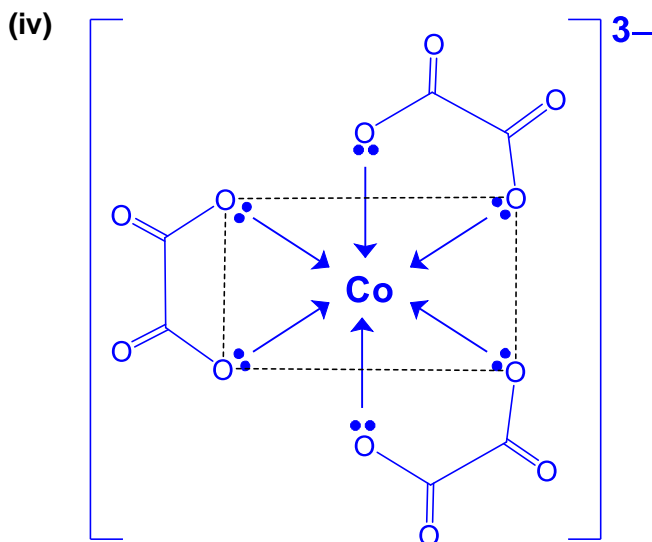
Iron(III) salt are usually coloured due to d–d transition.

The presence of ligands causes the d orbitals to split into 2 different energy levels with relatively small energy difference,  $\Delta E$ .

Radiation from the visible light region of the electromagnetic spectrum, corresponding to  $\Delta E$ , is absorbed when an electron transits from a d orbital of lower energy to partially filled d orbital of higher energy.

Hence, iron(III) salts are coloured and the colour observed is the complement of the colours absorbed.

On the other hand,  $\text{Sc}^{3+}$  has no 3d electron and hence electron transition between d orbitals is not possible and radiation from visible light region is not absorbed.

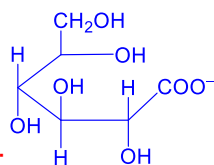


$\text{Cu}^{2+}$  undergoes redox reaction with Cu foil to form a stable colourless  $[\text{CuCl}_2]^-$  complex in the presence of  $\text{Cl}^-$  due to ligand exchange reaction.

The evaporation/removal of water due to heating causes the concentration of all aqueous species to increase while  $[\text{H}_2\text{O}]$  remains relatively constant. This causes the position of equilibrium (1) to shift to the right side which has less concentration terms of aqueous species (excludes  $[\text{H}_2\text{O}]$ ).



(c) (i) Red-brown ppt of  $\text{Cu}_2\text{O}$  formed.



Structure of organic product:

(ii) Since glucose has chiral carbons and has no plane of symmetry, it can exhibit enantiomerism.

Since there is restricted rotation around the C–C bond of the ring structure, it can exhibit cis–trans isomerism.

(iii) Let the percentage of  $\alpha$ -glucose in the mixture be  $x\%$  and that of  $\beta$ -glucose is  $(100-x)\%$ .

$$\left[ (+113.4) \times \frac{x}{100} \right] + \left[ (+19.0) \times \frac{100-x}{100} \right] = +52.2$$

% of  $\alpha$ -glucose in the mixture,  $x = 35.2\%$

(iv) Disproportionation

- 4 (a) (i) Electronegativity increases across the period and decreases down the group. Hence, beryllium and aluminium have similar electronegativity and have similar properties.

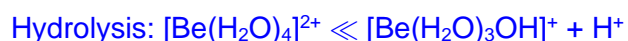
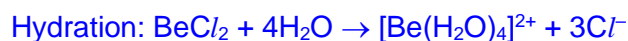
- (ii)  $\text{BeCl}_2$  has simple covalent/molecular structure while  $\text{BeO}$  has a giant ionic structure.

Less energy is required to overcome the weaker instantaneous dipole–induced dipole attraction between  $\text{BeCl}_2$  molecules than that required for the stronger ionic bonds between  $\text{Be}^{2+}$  and  $\text{O}^{2-}$ .

Hence, the boiling point of  $\text{BeCl}_2$  is lower than that of  $\text{BeO}$ .

- (iii)  $\text{BeCl}_2$  dissolves in water to give  $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$  which hydrolyses (or react with water) to give an acidic solution. Due to the high charge density of  $\text{Be}^{2+}$ , it can polarise and weaken the O–H bond in the coordinated  $\text{H}_2\text{O}$  molecules, releasing  $\text{H}^+$  into the solution.

Hence, a weakly acidic solution is formed and causes a beaker of litmus solution to change from purple to red.



- (b) (i) Since the  $A_r$  of Pb is 207.2, compound A can only contain 1 Pb.

$$\% \text{ by mass of Pb in A} = \frac{207.2}{290} \times 100 \% = 71.45 \%$$

$$\% \text{ by mass of F in A} = 100 - 71.45 - 3.08 = 25.47 \%$$

element	Pb	Be	F
mass in 100 g / g	71.45	3.08	25.47
amount / mol	$\frac{71.45}{207.2} = 0.3448$	$\frac{3.08}{9.0} = 0.3422$	$\frac{25.47}{19.0} = 1.341$
simple ratio	1	1	4

Hence, the empirical formula of A is  $\text{PbBeF}_4$  and thus,  $x = 1$  and  $y = 4$ .

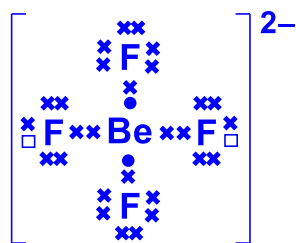
or

$$\text{mass of Be in one mol of } \text{PbBe}_x\text{F}_y = \frac{3.08}{100} \times 290 = 8.932 \text{ g}$$

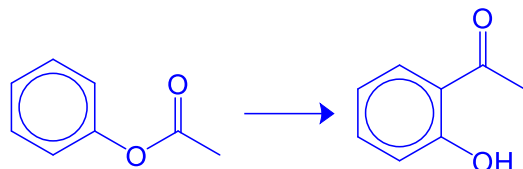
$$\text{mass of F in one mol of } \text{PbBe}_x\text{F}_y = 290 - 207.2 - 8.932 = 73.868 \text{ g}$$

element	Pb	Be	F
mass in 100 g / g	207.2	8.932	73.868
amount / mol	$\frac{207.2}{207.2} = 1$	$\frac{8.932}{9.0} = 0.9924$	$\frac{73.868}{19.0} = 3.888$
simple ratio	1	1	4

Hence, the empirical formula of A is  $\text{PbBeF}_4$  and thus,  $x = 1$  and  $y = 4$ .



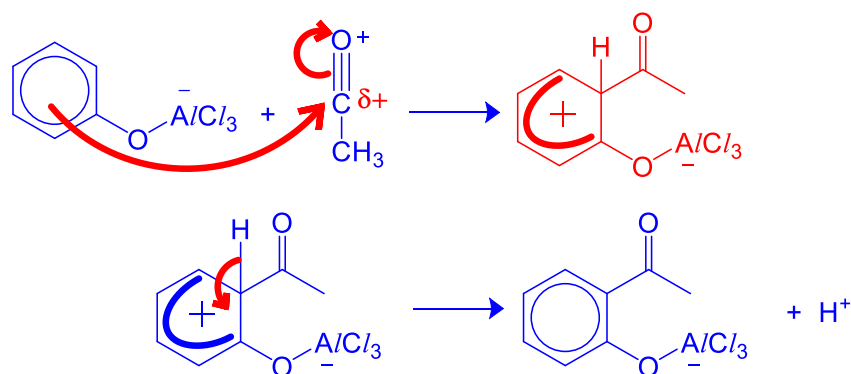
(c) (i)



(ii)  $\text{AlCl}_3$  is acting as a catalyst since it reacted in step 1 and was regenerated in step 4.

$\text{AlCl}_3$  is also acting as a Lewis acid since it accepted a lone pair of electrons from O atom of phenyl ethanoate via dative-bond formation.

(iii)



(iv) Test: Add neutral  $\text{FeCl}_3(\text{aq})$  to the reaction mixture.

Obs: If 2-hydroxyacetophenone is formed, violet coloration is formed.

or

Test: Add  $\text{Br}_2(\text{aq})$  to the reaction mixture.

Obs: If 2-hydroxyacetophenone is formed, orange  $\text{Br}_2$  decolourised.

or

Test: Add 2,4-DNPH to the reaction mixture.

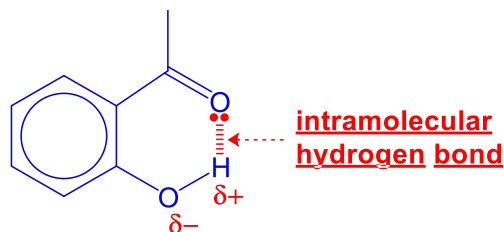
Obs: If 2-hydroxyacetophenone is formed, orange ppt is formed.

or

Test: Add alkaline  $\text{I}_2(\text{aq})$  to the reaction mixture and heat.

Obs: If 2-hydroxyacetophenone is formed, pale yellow ppt is formed.

(v)

Checklist for hydrogen bonding:

- $\delta+$  on H and  $\delta-$  on O of O–H
- lone pair on O of C=O
- dotted line to represent hydrogen bond
- label “intramolecular hydrogen bond”

2-hydroxyacetophenone can form intramolecular hydrogen bond due to the close proximity of C=O and –OH groups, stabilising it and hence, 2-hydroxyacetophenone is likely to form in larger proportion.

- (d) Electron-withdrawing  $-\text{CO}_2\text{H}$  reduces the electron density of benzene and makes the benzene ring less electron-rich, causing phenyl ethanoate to be less reactive toward electrophilic attack. Hence, the rate of Fries rearrangement is slower for B compared to phenyl ethanoate.

- 5 (a) (i) *Bond energy* is the heat energy required when 1 mole of covalent bond in gaseous phase is broken into gaseous atoms.

(ii)

Bonds broken		Bonds formed	
C=C	+610	3C–C	3(+350)
C–N	+305		
Total	+915	Total	+1050

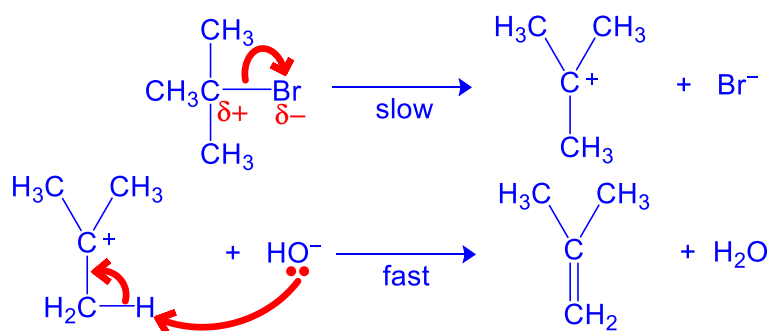
$$\Delta H_r = (+915) - (+1050) = -135 \text{ kJ mol}^{-1}$$

- (iii) The ring strain in cyclopropane (or angle strain due to the rigid 3-membered ring structure of cyclopropane) weakens the C–C bond.

- (b) (i) Since E1 is a unimolecular reaction, it implies that the rate-determining step involves only one unit of a chemical species. From the description of E1 given, the first step is the rate-determining step and hence, the rate equation for E1 is  $\text{rate} = k[(\text{CH}_3)_3\text{CBr}]$ .

Since E2 is a bimolecular elementary reaction, it implies that it is one step mechanism (*i.e.* mechanism is the same as overall equation). Hence, the rate equation for E2 is  $\text{rate} = k[(\text{CH}_3)_3\text{CBr}][\text{OH}^-]$ .

(ii)



- (iii) Since the rate-determining step does not involve the base (or zero order w.r.t the base or only  $(\text{CH}_3)_3\text{CBr}$  is involved), changing  $\text{CH}_3\text{CH}_2\text{O}^-$  to  $(\text{CH}_3)_3\text{CO}^-$  would not change the rate of the E1 reaction.
- (c) (i)  $\text{CH}_3\text{CHBr}(\text{CH}_3)_2 + \text{OH}^- \rightarrow \text{CH}_3\text{CH}(\text{OH})(\text{CH}_3)_2 + \text{Br}^-$
- (ii) E1 proceeds with an increase in entropy/disorderliness in the system since the number of particles increases from 2 mol to 3 mol but no change for  $\text{S}_{\text{N}}1$ . Hence,  $\Delta G$  of E1 becomes more negative with increasing temperature.
- (iii) Benzyl chloride does not have adjacent C–H for elimination to occur.  
p–p orbital overlap results in the delocalisation of the positive charge on  $\text{C}^+$  into benzene ring, dispersing the positive charge and stabilising the carbocation.
- (iv) Since the  $\text{p}K_{\text{a}}$  decreases from HF to HI, it implies that the position of equilibrium of  $\text{HX} \ll \text{H}^+ + \text{X}^-$  lies increasingly more to the right.  
Hence, the stability of leaving group  $\text{X}^-$  increases from  $\text{F}^-$  to  $\text{I}^-$  and the reactivity towards nucleophilic substitution increases from alkyl fluoride to alkyl iodide.

NAME \_\_\_\_\_

CLASS **18S** \_\_\_\_\_**JURONG PIONEER JUNIOR COLLEGE**  
**JC2 PRELIMINARY EXAMINATION 2019****CHEMISTRY****9729/04****Higher 2****26 August 2019**

Paper 4 Practical

**2 hours 30 minutes****Candidates answer on the Question paper.**

Additional Materials: As listed in the Confidential Instructions

**READ THESE INSTRUCTIONS FIRST**

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

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

The use of an approved scientific calculator is expected, where appropriate.  
You may lose marks if you do not show your working or if you do not use appropriate units.  
Qualitative Analysis Notes are printed on pages 23 and 24.

At the end of the examination, fasten all your work securely together.

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

Shift	
Laboratory	
For Examiner's Use	
1	
2	
3	
4	
Total	

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

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

For  
Examiner's  
Use

# 1 Determination of the identity of the halogen, X, in $\text{CH}_2\text{XCO}_2\text{H}$

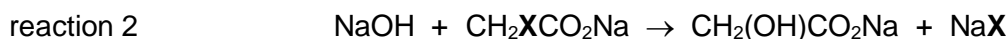
Compound **W** is a halogenoethanoic acid,  $\text{CH}_2\text{XCO}_2\text{H}$ , where **X** is a halogen.

A halogenoethanoic acid reacts with aqueous sodium hydroxide in two reactions.

The alkali neutralises the carboxylic acid.



The halogenoalkyl group then undergoes a substitution reaction.



4 g of **W** were heated for one minute with 250 cm<sup>3</sup> of 0.40 mol dm<sup>-3</sup> aqueous sodium hydroxide in a beaker. Some of the sodium hydroxide reacted with compound **W** as shown by equations 1 and 2. The solution that remained contains unreacted sodium hydroxide. This solution is **FA 1**.

In **1(a)**, you will perform a dilution and by titrating **FA 1** with the diluted sulfuric acid, you will determine the identity of **X** in  $\text{CH}_2\text{XCO}_2\text{H}$ .

**FA 1** is aqueous sodium hydroxide after reaction with **W**.

**FA 2** is 2.00 mol dm<sup>-3</sup> sulfuric acid,  $\text{H}_2\text{SO}_4$ .

methyl orange indicator

## (a) (i) Dilution of FA 2

1. Use a pipette to transfer 10.0 cm<sup>3</sup> of **FA 2** into a 250 cm<sup>3</sup> volumetric flask.
2. Make up the contents of the flask to the 250 cm<sup>3</sup> mark with deionised water.
3. Place the stopper in the flask and mix the contents thoroughly by slowly inverting the flask a number of times.
4. Label this diluted solution of sulfuric acid as **FA 3**.

## (ii) Titration of FA 1 against FA 3

1. Fill the burette labelled **FA 3**, with **FA 3**.
2. Use a pipette to transfer 25.0 cm<sup>3</sup> of **FA 1** into the conical flask.
3. Add a few drops of methyl orange indicator.
4. Run **FA 3** from the burette into the conical flask. The end-point is reached when the yellow solution becomes orange.
5. Record your titration results, to an appropriate level of precision, in the space provided on Page 3.
6. Repeat points 2 to 5 as necessary until consistent results are obtained.



## Titration results

For  
Examiner's  
Use

[3]

- (iii) From your titrations, obtain a suitable volume of **FA 3**,  $V_{\text{FA3}}$ , to be used in your calculations. Show clearly how you obtained this volume.

$V_{\text{FA3}} = \dots\dots\dots$  [3]

- (b) (i) Calculate the concentration of sulfuric acid in **FA 3** that you have prepared.

$[\text{H}_2\text{SO}_4]$  in **FA 3** =  $\dots\dots\dots$  [1]

- (ii) Calculate the amount of sodium hydroxide present in  $25.0 \text{ cm}^3$  of **FA 1**.

amount of NaOH in  $25.0 \text{ cm}^3$  of **FA 1** =  $\dots\dots\dots$  [1]

- (iii) Calculate the amount of sodium hydroxide in  $250\text{ cm}^3$  of **FA 1** and hence, calculate the amount of sodium hydroxide that reacted with **W**.

amount of NaOH that reacted with **W** = ..... [2]

- (iv) Use your answer to (b)(iii) to calculate the  $M_r$  of **W**,  $\text{CH}_2\text{XCO}_2\text{H}$ .

Hence, deduce the identity of **X** in  $\text{CH}_2\text{XCO}_2\text{H}$ .

[ $A_r$ : C, 12.0; O, 16.0; H, 1.0; F, 19.0; Cl, 35.5; Br, 79.9; I, 126.9]

**X** is ..... [2]

- (c) (i) The maximum error in any single burette reading is  $\pm 0.05\text{ cm}^3$ .

Calculate the maximum percentage error in the volume of **FA 3** used in 1(a)(iii).

maximum percentage error in the volume of **FA 3** used = ..... [1]

- (ii) Apart from the inaccuracies in reading the volumes of solutions, suggest a significant source of error in this experiment.

Explain how you could minimise this error.

.....

..... [1]

[Total: 14]

*For  
Examiner's  
Use*

## 2 An experiment to investigate the behaviour of acids and bases in aqueous solutions

**FA 4** is  $1.00 \text{ mol dm}^{-3}$  sodium hydrogencarbonate,  $\text{NaHCO}_3$ .

**FA 5** is aqueous sodium hydroxide.

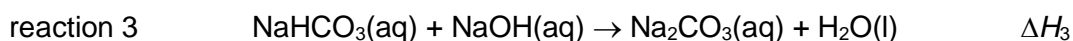
You will need access to the **FA 2** solution you used earlier.

According to Arrhenius theory of acids and bases, an acid produces  $\text{H}^+$  ions and a base produces  $\text{OH}^-$  ions, in aqueous solution. An acid–base reaction involves reacting together these two ions to produce water molecules as shown in the following equation.



This experiment involves two different acid-base reactions.

The first reaction is between sodium hydrogencarbonate, **FA 4**, and sodium hydroxide, **FA 5**.



The molar enthalpy change for reaction 3,  $\Delta H_3$ , is the enthalpy change when  $1.00 \text{ mol}$  of  $\text{NaHCO}_3$  reacts completely with  $\text{NaOH}$ .

Instead of using an indicator to determine the end–point, you will perform a thermometric titration to determine the equivalence point of the reaction. You will add portions of **FA 5** progressively to a known volume of **FA 4**. You will continue adding **FA 5** until the equivalence point is reached and passed. Throughout the experiment you will note and record the temperature of the mixture after each addition.

You will then analyse your results graphically to determine the

- titration volume at the equivalence point,  $V_{\text{equivalence}}$ ,
- maximum temperature change,  $\Delta T_{\text{max}}$ ,
- molar enthalpy change,  $\Delta H_3$ , for reaction 3.

**(a) Determination of the enthalpy change of reaction between FA 4 and FA 5**

In this experiment you will need to record the maximum temperature of the reaction mixture when specified volumes of **FA 5** have been added. It is important that the volume of **FA 5** recorded is the total volume you have added up to that point when the temperature reading was made.

Note: If you overshoot on an addition, record the **actual** total volume of **FA 5** added up to that point.

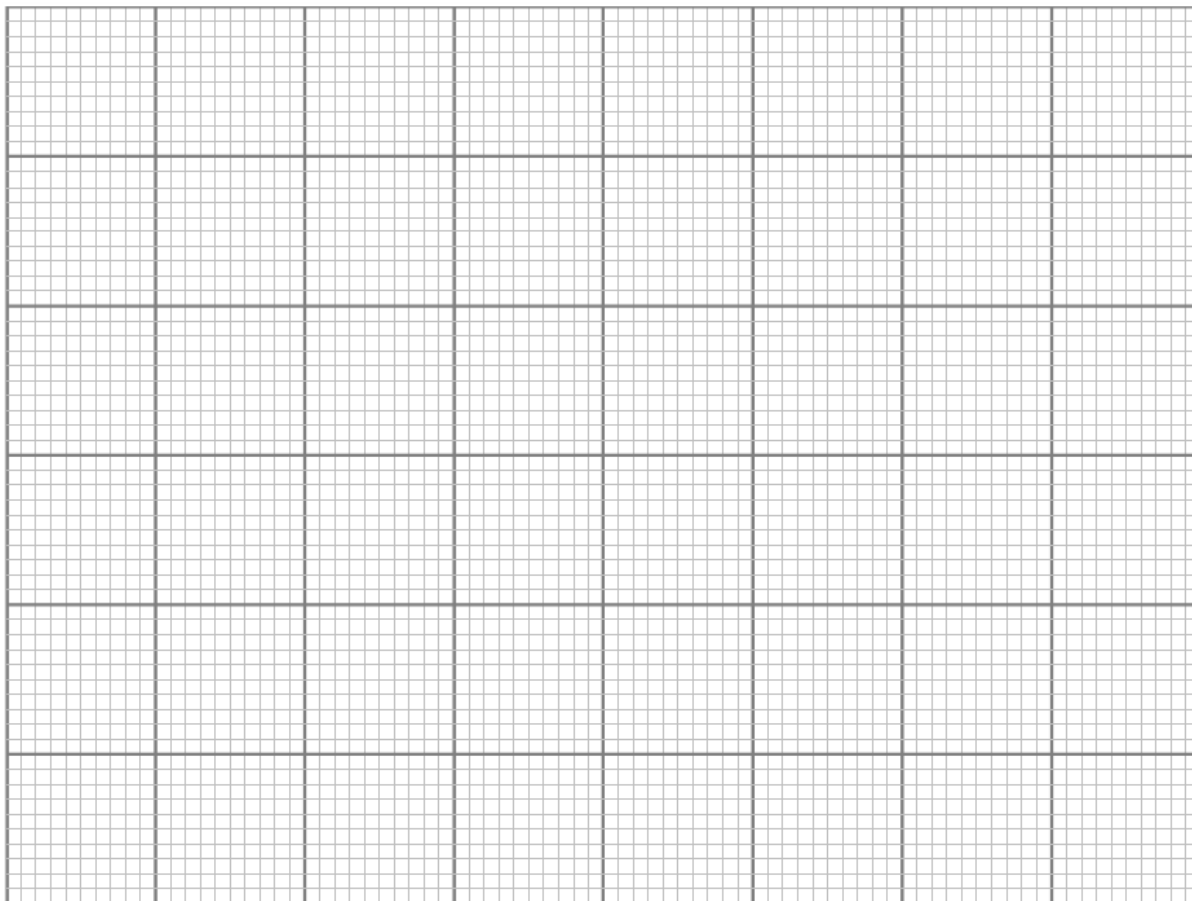
In an appropriate format in the space provided below, record all values of temperature,  $T$ , and each total volume of **FA 5** added.

1. Fill a burette with **FA 5**.
2. Place a Styrofoam cup inside a second Styrofoam cup which is held in a glass beaker to prevent it tipping over.
3. Using a pipette, transfer  $25.0\text{ cm}^3$  of **FA 4** into the first Styrofoam cup.
4. Stir the **FA 4** solution in the cup with the thermometer. Read and record its temperature. Tilt the cup if necessary to ensure the thermometer bulb is fully immersed.
5. From the burette, add  $2.00\text{ cm}^3$  of **FA 5** to the cup and stir the mixture thoroughly.
6. Read and record the maximum temperature of the mixture,  $T$ , and the volume of **FA 5** added.
7. Repeat points **5** and **6** until a total of  $30.00\text{ cm}^3$  of **FA 5** has been added. After each addition of **FA 5**, record the maximum temperature of the mixture and the total volume of **FA 5** added up to that point.

**Results**

[2]

- (b) (i) On the grid below, plot a graph of temperature,  $T$  on the  $y$ -axis against volume of **FA 5** added on the  $x$ -axis.



[3]

- (ii) Draw **two** smooth lines of best fit.

- The first best-fit curve or straight line should be drawn using the plotted points where the temperature is **rising**.
- The second best-fit curve or straight line should be drawn using the plotted points where the temperature is **falling**.
- Extrapolate these lines until they cross.

- (iii) Determine from your graph

- the maximum temperature reacted,  $T_{\max}$ ,
- the maximum temperature change,  $\Delta T_{\max}$ , and
- the volume,  $V_{\text{equivalence}}$ , of **FA 5** needed to completely react with  $25.0 \text{ cm}^3$  of **FA 4**.

Show on your graph how you obtained these values.  
Record these values in the spaces provided below.

Maximum temperature reached,  $T_{\max} = \dots\dots\dots$

Maximum temperature change,  $\Delta T_{\max} = \dots\dots\dots$

Volume of **FA 5** required,  $V_{\text{equivalence}} = \dots\dots\dots$

[3]

- (iv) Calculate the concentration of sodium hydroxide, [NaOH], in **FA 5**.

[NaOH], in **FA 5** = ..... [1]

- (v) Calculate the heat change,  $q$ , for your experiment in (a) and hence determine a value for the molar enthalpy change for reaction 3,  $\Delta H_3$ .

You should assume that the:

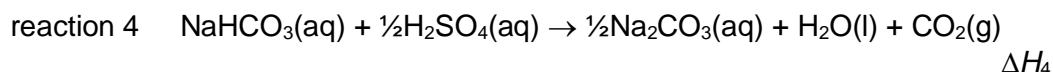
- Specific heat capacity of the mixture is  $4.18 \text{ J g}^{-1} \text{ K}^{-1}$ ;
- Density of the mixture is  $1.00 \text{ g cm}^{-3}$ .

$\Delta H_3$  = ..... [2]

**Question 2 continues on the next page.**

**(c) The reaction between FA 4 and FA 2**

The second acid–base reaction is between sodium hydrogencarbonate, **FA 4**, and sulfuric acid, **FA 2**.



The molar enthalpy change for reaction 4,  $\Delta H_4$ , is the enthalpy change when 1.00 mol of  $\text{NaHCO}_3$  reacts completely with  $\text{H}_2\text{SO}_4$ .

A student carried out an experiment to determine the molar enthalpy change for reaction 4,  $\Delta H_4$ , using a known volume of **FA 4** that reacts with excess **FA 2**.

The student carried out the experiment according to the following instructions.

1. Using a measuring cylinder, transfer 40.0 cm<sup>3</sup> of **FA 4** into a Styrofoam cup, which is placed in a 250 cm<sup>3</sup> glass beaker.
2. Stir and measure the temperature of this **FA 4**,  $T_{\text{FA 4}}$ .
3. Using another measuring cylinder, measure 15.0 cm<sup>3</sup> of **FA 2**.
4. Stir and measure the temperature of this **FA 2**,  $T_{\text{FA 2}}$ .
5. Carefully add the **FA 2** from the measuring cylinder to the **FA 4** in the Styrofoam cup in small portions to avoid too much frothing.
6. Using the thermometer, stir the mixture continuously. Measure and record the lowest temperature,  $T_{\text{min}}$ , of the mixture.

The results are shown in the table in Table 2.1.

$T_{\text{FA 4}} / ^\circ\text{C}$	28.6
$T_{\text{FA 2}} / ^\circ\text{C}$	28.9
$T_{\text{min}} / ^\circ\text{C}$	28.2

**Table 2.1**



- (d) Calculate the molar enthalpy change for reaction 4,  $\Delta H_4$ . For this experiment, the weighted average initial temperature,  $T_{\text{average}}$ , of **FA 4** and **FA 2** may be calculated using the formula below.

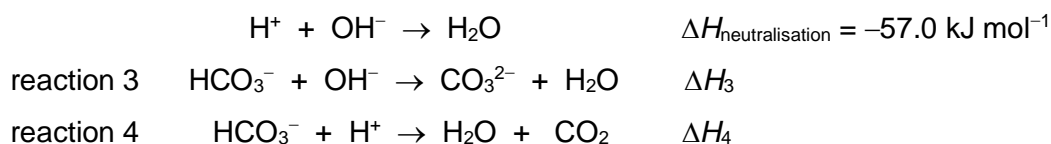
$$T_{\text{average}} = \frac{(V_{\text{FA2}} \times T_{\text{FA2}}) + (V_{\text{FA4}} \times T_{\text{FA4}})}{(V_{\text{FA2}} + V_{\text{FA4}})}$$

You should assume that the:

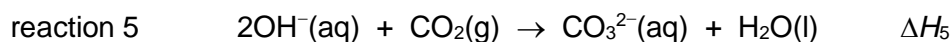
- Specific heat capacity of the mixture is  $4.18 \text{ J g}^{-1} \text{ K}^{-1}$ ;
- Density of the mixture is  $1.00 \text{ g cm}^{-3}$

$$\Delta H_4 = \dots\dots\dots [2]$$

- (e) Ionic equations for neutralisation, reaction 3 and reaction 4 are shown below.



Carbon dioxide may be removed from stale air by bubbling the air through aqueous alkali. An equation for this reaction is given below.



Use your answers to **2(b)(v)** and **2(d)**, together with the molar enthalpy change of neutralisation,  $\Delta H_{\text{neutralisation}}$ , to determine a value for the molar enthalpy change for this reaction,  $\Delta H_5$ .

$$\Delta H_5 = \dots\dots\dots [4]$$

- (g) An alternative definition of acid-base behavior was proposed by Brønsted and Lowry.

In terms of the Brønsted–Lowry theory of acids and bases, suggest the role of hydrogencarbonate ions,  $\text{HCO}_3^-$ , in reaction 3 and in reaction 4. Explain your answer.

**reaction 3**

role of  $\text{HCO}_3^-$  ions .....

explanation .....

**reaction 4**

role of  $\text{HCO}_3^-$  ions .....

explanation ..... [2]

[Total: 19]

**[BLANK PAGE]**

**3 Investigation of some reactions involving transition element ions.**

Manganese containing compounds are often used in redox reactions in the laboratory.

In aqueous solution,  $\text{MnO}_4^-$ (aq) ions are stable. However,  $\text{MnO}_4^{2-}$ (aq) ions, which has a characteristic green colour, are unstable as they spontaneously undergo a redox reaction.

Both  $\text{MnO}_4^-$  and  $\text{MnO}_4^{2-}$  solid compounds are stable.

**FA 6** is solid potassium manganate(VII),  $\text{KMnO}_4$ .

**FA 8** is a hydrocarbon compound.

Perform the tests described in Table 3.1, and record your observations in the table. Test and identify any gases evolved. If there is no observable change, write **no observable change**.

**Table 3.1**

		tests	observations
(a)	(i)	<p>Add one spatula of <b>FA 6</b> to a hard-glass test-tube.</p> <p>Heat gently for about 10s and then strongly for about 20s.</p> <p>Leave the test-tube and residue to cool completely. Keep the residue for use in <b>3(a)(ii)</b>.</p> <p><b>While waiting, you can start on 3(d).</b></p>	
	(ii)	<p>Add deionised water to a small beaker until it is about half full. Place the beaker on a white tile.</p> <p>Pour the cooled residue from <b>3(a)(i)</b> <b>slowly</b> into the deionised water in the beaker.</p> <p><b>Observe the solution closely.</b></p> <p>Swirl the solution and filter a small portion of this solution into a clean test-tube. The filtrate is <b>FA 7</b>.</p>	
	(iii)	<p>Add 1 cm depth of <b>FA 7</b> to a test-tube. Add <math>\text{Fe}^{2+}</math>(aq), slowly with shaking, until no further change is seen.</p>	

[3]

- (b) Table 3.2 gives some standard electrode potential values involving manganese containing ions.

Table 3.2

electrode reaction	$E / V$
$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \ll \text{Mn}^{2+} + 4\text{H}_2\text{O}$	+1.52
$\text{MnO}_4^- + \text{e}^- \ll \text{MnO}_4^{2-}$	+0.56
$\text{MnO}_4^{2-} + 4\text{H}^+ + 2\text{e}^- \ll \text{MnO}_2 + 2\text{H}_2\text{O}$	+2.26

Consider your observations when deionised water was added to the residue in **3(a)(ii)**, together with those you made in **3(a)(iii)** and the information in Table 3.2.

- (i) Use data from Table 3.2 to explain what happens to manganese during this reaction.

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

- (ii) State the type of reaction that has occurred in **3(a)(ii)**.

..... [1]

- (c) The decomposition reaction in **3(a)(i)** also produces  $\text{MnO}_2$  as one of the products. Write a balanced equation for the decomposition reaction occurring in **3(a)(i)** using your observations in Table 3.1.

..... [1]

**Question 3 continues on the next page.**

(d) Before starting this question, ensure your Bunsen burner is turned off.

Hot water is provided for the hot water bath required in this question.

Perform the tests described in Table 3.3, and record your observations in the table. Test and identify any gases evolved. If there is no observable change, write **no observable change**.

Table 3.3

	tests	observations
(i)	Add 2 cm depth of aqueous sodium hydroxide in a test-tube.  Add 5 drops of <b>FA 8</b> to this test-tube.  Add a few drops of aqueous potassium manganate(VII).	
(ii)	Add 2 cm depth of aqueous sulfuric acid in a test-tube.  Add 5 drop of <b>FA 8</b> to this test-tube.  Add a few drops of aqueous potassium manganate(VII).  Place the mixture in the hot water bath for a few minutes.	
(iii)	Add 5 cm depth of deionised water in a test-tube.  Add 1 drop of <b>FA 8</b> to this test-tube.  Add aqueous bromine slowly, with shaking, until no further change is seen.	Yellow aqueous bromine decolourises

[1]

(e) When **FA 8** reacts with aqueous potassium managanate(VII) under alkaline conditions in **3(d)(i)**, compound **Z** is the main organic product formed.

The molecular formula of **Z** is  $C_6H_{12}O_2$ .

(i) Deduce the molecular formula of **FA 8**.

Explain your deduction. Your explanation should be supported by evidence from your observations in **3(d)(i)**.

molecular formula of **FA 8** .....

[2]

explanation .....

.....

- (ii) Draw possible structures of **FA 8** and compound **Z**.

FA 8	compound Z

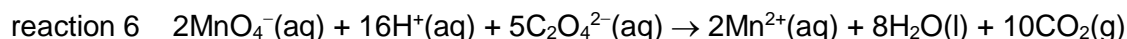
[1]

[Total: 10]

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#### 4 Planning

In acidic solution, potassium manganate(VII) undergoes a redox reaction with ethanedioate ions,  $\text{C}_2\text{O}_4^{2-}$  as shown in reaction 6.



As the initial reaction between potassium manganate(VII) and ethanedioate ions is slow, a small amount of  $\text{Mn}^{2+}$  is added to the reaction mixture to speed up the reaction. The order of the reaction with respect to the concentration of potassium manganate(VII) may be determined by performing a number of experiments and measuring the time taken,  $t$ , for a fixed volume of  $\text{CO}_2$  to be produced in each of these experiments.

A teacher demonstrated one of the experiments as follows.

She prepared a mixture containing  $50 \text{ cm}^3$  of potassium manganate(VII),  $50 \text{ cm}^3$  of sulfuric acid and  $1 \text{ cm}^3$  of aqueous manganese(II) sulfate.

$50 \text{ cm}^3$  of sodium ethanedioate was added to the mixture and,  $40 \text{ cm}^3$  of gas was collected after 12 seconds.

The order of reaction can be graphically determined by plotting the common logarithm of  $1/t$ ,  $\lg(1/t)$  against the common logarithm of the volume of  $\text{KMnO}_4$  used,  $\lg(V_{\text{KMnO}_4})$ .

(a) Write a plan for such a series of experiments.

You may assume that you are provided with:

- $0.02 \text{ mol dm}^{-3}$  potassium manganate(VII),  $\text{KMnO}_4$ ,
- $0.2 \text{ mol dm}^{-3}$  sodium ethanedioate,  $\text{Na}_2\text{C}_2\text{O}_4$ ,
- $1.0 \text{ mol dm}^{-3}$  dilute sulfuric acid,  $\text{H}_2\text{SO}_4$ ,
- aqueous manganese(II) sulfate solution,
- deionised water,
- the apparatus normally found in a school or college laboratory.

Your plan should include details of:

- a clearly labelled diagram of the experimental set-up used for gas collection,
- the quantities of reactants and the apparatus to be used,
- the procedure that you would follow,
- the measurements you would make to allow a suitable graph to be drawn.



*Diagram of the experimental set-up:*

*For  
Examiner's  
Use*

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9729/04/J2 PRELIMINARY EXAM/2019

- (b) Sketch, on Fig. 4.1, the graph you would expect to obtain.  
Explain your answer.

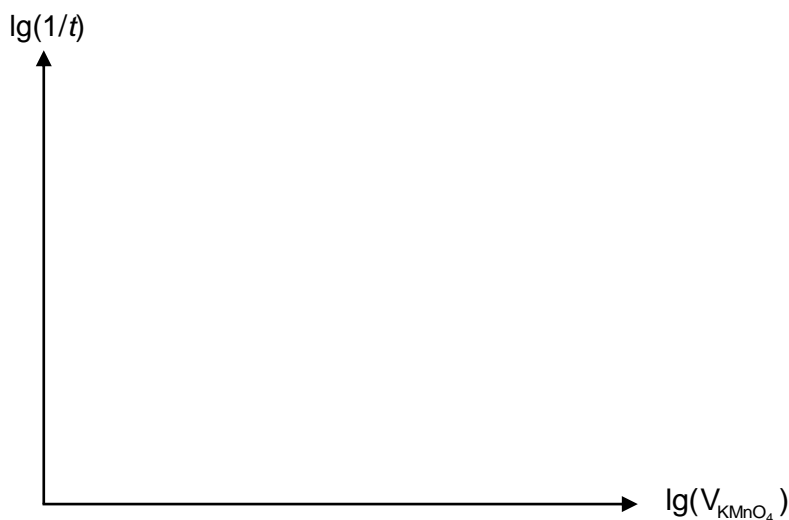


Fig 4.1

explanation .....

.....

.....

.....

.....

[3]

- (c) Describe how you would use your graph to determine the order of reaction with respect to the concentration of potassium manganate(VII).

.....

[1]

- (d) (i) Suggest why the initial reaction between manganate(VII) ions and ethanedioate ions is slow.

.....

.....

[1]

- (ii) A small amount of  $\text{Mn}^{2+}$  is added to catalyse the reaction.  
State the type of catalyst involved in the reaction. Explain your answer.

[1]

- (iii) Using the information given in **4(d)(ii)** and reaction 6, sketch, on Fig. 4.2, the graph you would expect to obtain if the experiment was conducted without the addition of  $\text{Mn}^{2+}(\text{aq})$  solution.

For  
Examiner's  
Use

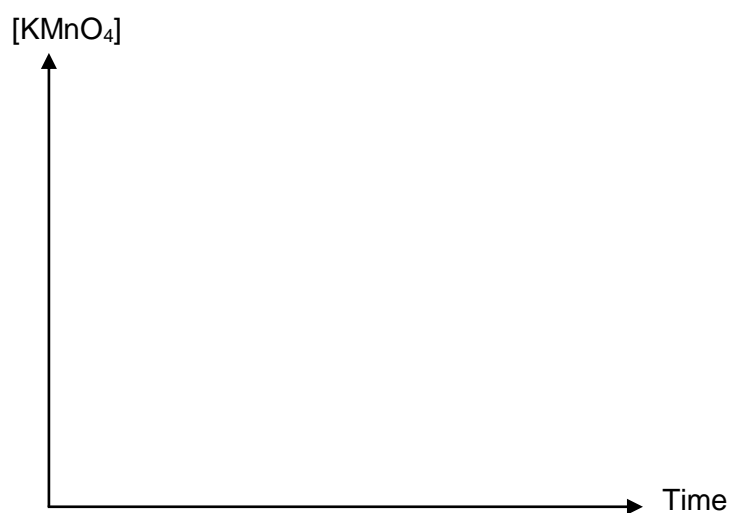


Fig 4.2

[1]

[Total: 12]

### Qualitative Analysis Notes

[ppt. = precipitate]

#### (a) Reactions of Aqueous Cations

<b>cation</b>	<b>Reaction with</b>	
	NaOH(aq)	NH <sub>3</sub> (aq)
aluminium, Al <sup>3+</sup> (aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH <sub>4</sub> <sup>+</sup> (aq)	ammonia produced on heating	–
barium, Ba <sup>2+</sup> (aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca <sup>2+</sup> (aq)	white ppt. with high [Ca <sup>2+</sup> (aq)]	no. ppt.
chromium(III), Cr <sup>3+</sup> (aq)	grey–green ppt. soluble in excess giving dark green solution	grey–green ppt. insoluble in excess
copper(II), Cu <sup>2+</sup> (aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess

		giving dark blue solution
iron(II), $\text{Fe}^{2+}(\text{aq})$	green ppt. turning brown on contact with air insoluble in excess	green ppt. turning brown on contact with air insoluble in excess
iron(III), $\text{Fe}^{3+}(\text{aq})$	red–brown ppt. insoluble in excess	red–brown ppt. insoluble in excess
magnesium, $\text{Mg}^{2+}(\text{aq})$	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), $\text{Mn}^{2+}(\text{aq})$	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, $\text{Zn}^{2+}(\text{aq})$	white ppt. soluble in excess	white ppt. soluble in excess

**(b) Reactions of Aqueous Anions**

<b>Anion</b>	<b>Reaction</b>
carbonate, $\text{CO}_3^{2-}$	$\text{CO}_2$ liberated by dilute acids
chloride, $\text{Cl}^-(\text{aq})$	gives white ppt. with $\text{Ag}^+(\text{aq})$ (soluble in $\text{NH}_3(\text{aq})$ );
bromide, $\text{Br}^-(\text{aq})$	gives pale cream ppt. with $\text{Ag}^+(\text{aq})$ (partially soluble in $\text{NH}_3(\text{aq})$ );
iodide, $\text{I}^-(\text{aq})$	gives yellow ppt. with $\text{Ag}^+(\text{aq})$ (insoluble in $\text{NH}_3(\text{aq})$ );
nitrate, $\text{NO}_3^-(\text{aq})$	$\text{NH}_3$ liberated on heating with $\text{OH}^-(\text{aq})$ and Al foil
nitrite, $\text{NO}_2^-(\text{aq})$	$\text{NH}_3$ liberated on heating with $\text{OH}^-(\text{aq})$ and Al foil; $\text{NO}$ liberated by dilute acids (colourless $\text{NO} \rightarrow$ (pale) brown $\text{NO}_2$ in air)
sulfate, $\text{SO}_4^{2-}(\text{aq})$	gives white ppt. with $\text{Ba}^{2+}(\text{aq})$ (insoluble in excess dilute strong acids)
sulfite, $\text{SO}_3^{2-}(\text{aq})$	$\text{SO}_2$ liberated on warming with dilute acids; gives white ppt. with $\text{Ba}^{2+}(\text{aq})$ (soluble in excess dilute strong acids)

**(c) Tests for Gases**

<b>gas</b>	<b>Test and test results</b>
ammonia, $\text{NH}_3$	turns damp red litmus paper blue
carbon dioxide, $\text{CO}_2$	gives a white ppt. with limewater (ppt. dissolves with excess $\text{CO}_2$ )
chlorine, $\text{Cl}_2$	bleaches damp litmus paper
hydrogen, $\text{H}_2$	"pops" with a lighted splint
oxygen, $\text{O}_2$	relights a glowing splint
sulfur dioxide, $\text{SO}_2$	turns acidified aqueous potassium manganate(VII) from purple to colourless

**(d) Colour of halogens**

<b>halogen</b>	<b>colour of element</b>	<b>colour in aqueous solution</b>	<b>colour in hexane</b>
chlorine, $\text{Cl}_2$	greenish yellow gas	pale yellow	pale yellow
bromine, $\text{Br}_2$	reddish brown gas/liquid	orange	orange-red
iodine, $\text{I}_2$	black solid/purple gas	brown	purple



**JURONG PIONEER JUNIOR COLLEGE**  
**2019 JC2 H2 CHEMISTRY (9729)**  
**Preliminary Examination Paper 4**  
**(Suggested Answers)**

**1 Determination of the identity of the halogen, X, in  $\text{CH}_2\text{XCO}_2\text{H}$**

**(a) (ii) Titration results**

Titration number	1	2
Final burette reading / $\text{cm}^3$	24.90	34.95
Initial burette reading / $\text{cm}^3$	0.00	10.00
Volume of FA3 used / $\text{cm}^3$	24.90	24.95
	✓	✓

**(iii)** average volume of **FA 3** used,  $V_{\text{FA3}} = \frac{24.90 + 24.95}{2} = 24.93 \text{ cm}^3$

**(b) (i)**  $n(\text{H}_2\text{SO}_4)$  in  $10.0 \text{ cm}^3$  of **FA 2**  $= 2.00 \times \frac{10.0}{1000} = 0.0200 \text{ mol}$   
 $= n(\text{H}_2\text{SO}_4)$  in  $250 \text{ cm}^3$  **FA 3**

$[\text{H}_2\text{SO}_4]$  in **FA 3**  $= 0.020 \div \frac{250}{1000} = 0.0800 \text{ mol dm}^{-3}$

or

Using  $c_1V_1 = c_2V_2$ ,

$[\text{H}_2\text{SO}_4]$  in **FA 3**  $= \frac{2.00 \times 10.0}{250} = 0.0800 \text{ mol dm}^{-3}$

**(ii)**  $n(\text{H}_2\text{SO}_4)$  reacted in titration  $= \frac{24.93}{1000} \times 0.0800 = 0.001996 \text{ mol}$

Since  $1\text{H}_2\text{SO}_4 \equiv 2 \text{ NaOH}$ ,

$n(\text{NaOH})$  in  $25.0 \text{ cm}^3$  of **FA 1**  $= 0.001992 \times 2 = 0.00399 \text{ mol}$

**(iii)**  $n(\text{NaOH})$  in  $250 \text{ cm}^3$  of **FA 1**

$= 0.00399 \times \frac{250}{25.0} = 0.0399 \text{ mol}$

$= n(\text{NaOH})$  left unreacted after reaction with **W**

$n(\text{NaOH})$  added to **W**  $= 0.40 = 0.100 \text{ mol}$

$n(\text{NaOH})$  reacted with **W**  $= 0.100 - 0.0399 = 0.0601 \text{ mol}$



- (iv) From equation 1 and 2, since  $1W \equiv 2NaOH$ ,  
 $n(W)$  in 4 g =  $\frac{1}{2} \times 0.0601 = 0.03004$  mol  
 $M_r$  of W =  $4 \div 0.03004 = 133.2 \approx 133$  (no units)  
 $A_r$  of X =  $133.2 - 59 = 74.2$  (no units)  
 X is bromine/ Br

(c) (i) max. % error in volume of FA3 used =  $\frac{2(\pm 0.05)}{24.95} \times 100 = \pm 0.401\%$

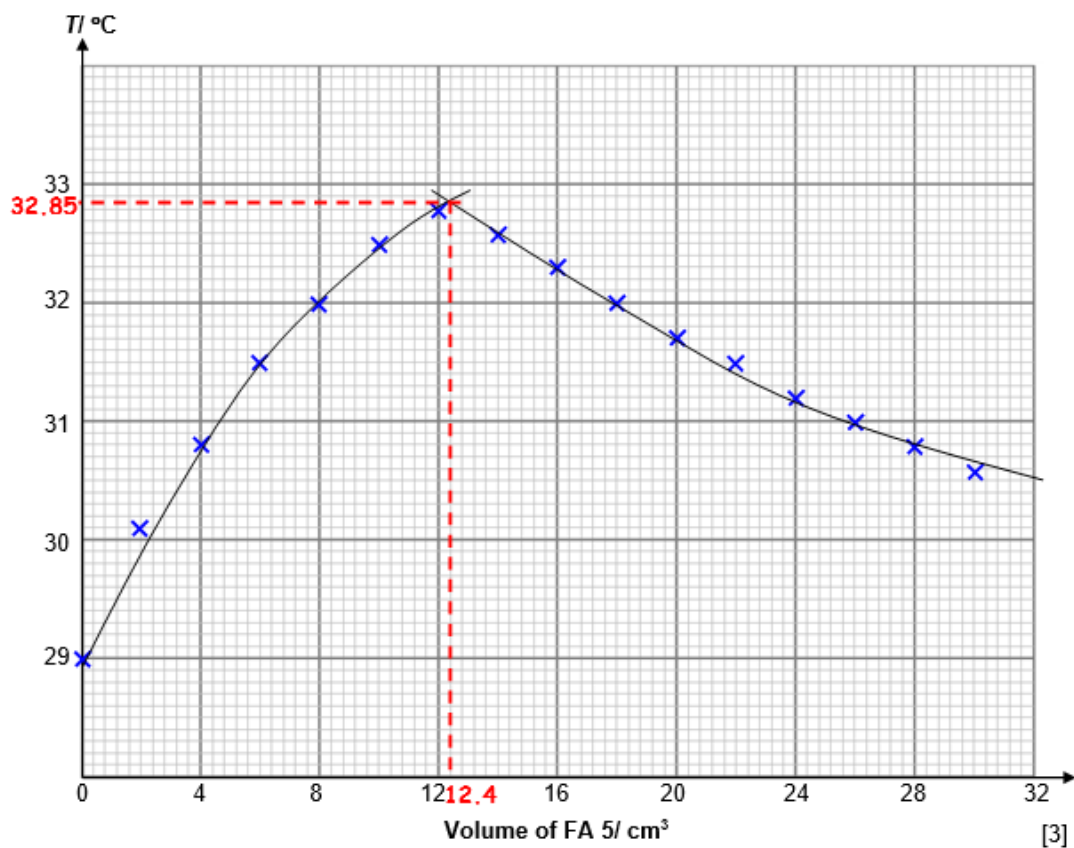
- (ii) Error : Mass measurement of W was not precise as the mass was given to nearest g.  
 Modification : Use a more precise weighing balance that can measure to 3.d.p.  
 or  
 Error : Substitution of halogeno group may be incomplete.  
 Modification : Heat W with NaOH for a longer period of time.  
 or  
 Error : Loss of product through heating.  
 Modification : Heat the reaction mixture under reflux

## 2 An experiment to investigate the behaviour of acids and bases in aqueous solutions

### (a) Determination of the enthalpy change of reaction between FA 4 and FA 5

Total volume of FA 5 added/ cm <sup>3</sup>	Maximum temperature/ °C
0.00	29.0
2.00	30.1
4.00	30.8
6.00	31.5
8.00	32.0
10.00	32.5
12.00	32.8
14.00	32.6
16.00	32.3
18.00	32.0
20.00	31.7
22.00	31.5
24.00	31.2
26.00	31.0
28.00	30.8
30.00	30.6

(b) (i)



- (ii) correctly reads  $T_{\max}$  to  $\pm \frac{1}{2}$  small square + correctly calculates  $\Delta T_{\max}$  + correctly reads  $V_{\text{equivalence}}$  to  $\pm \frac{1}{2}$  small square.  
&  
(iii)

(iv)  $n(\text{NaHCO}_3) \text{ used} = \frac{25.0}{1000} \times 1.00 = 0.0250 \text{ mol} = n(\text{NaOH}) \text{ reacted}$

$$[\text{NaOH}] \text{ in FA 5} = 0.0250 \div \frac{12.4}{1000} = 2.02 \text{ mol dm}^{-3}$$

- (v) From the graph,  $V_{\text{equivalence}} = 12.4 \text{ cm}^3$ .  
heat evolved,  $q = (25.0 + 12.4)(4.18)(3.85) = 603 \text{ J}$   
 $\Delta H_3 = -(603 \times 10^{-3}) \div 0.0250 = -24.1 \text{ kJ mol}^{-1}$

(c) The reaction between FA 4 and FA 2

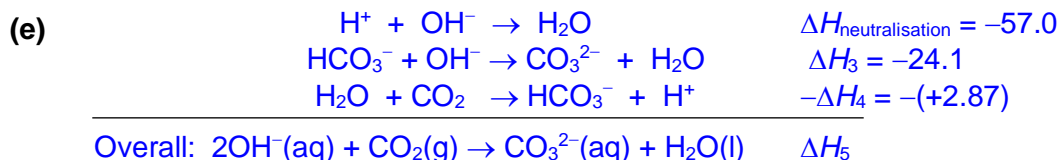
(d)  $T_{\text{average}} = \frac{(40.0 \times 28.6) + (15.0 \times 28.9)}{(40.0 + 15.0)} = 28.7 \text{ }^\circ\text{C}$

heat absorbed,  $q = (40.0 + 15.0)(4.18)(28.7 - 28.2) = 115 \text{ J}$

$$n(\text{NaHCO}_3) \text{ used} = 1.00 \times \frac{40.0}{1000} = 0.0400 \text{ mol}$$

Since  $\text{NaHCO}_3$  is the limiting reagent,

$$\Delta H_4 = +(115 \times 10^{-3}) \div 0.0400 = +2.87 \text{ kJ mol}^{-1}$$



$$\Delta H_5 = (-57.0) + (-24.1) - (+2.87) = -84.0 \text{ kJ mol}^{-1}$$

(g) **reaction 3**

role of  $\text{HCO}_3^-$  ions Bronsted acid

explanation  $\text{HCO}_3^-$  is a proton donor (or loses a proton).

**reaction 4**

role of  $\text{HCO}_3^-$  ions Bronsted base

explanation  $\text{HCO}_3^-$  is a proton acceptor (or gains a proton).

### 3 Investigation of some reactions involving transition element ions.

		tests	observations
(a)	(i)	Add one spatula of <b>FA 6</b> to a hard-glass test-tube. Heat gently for about 10s and then strongly for about 20s.  Leave the test-tube and residue to cool completely. Keep the residue for use in <b>3(a)(ii)</b> . <b>While waiting, you can start on 3(d).</b>	$\text{O}_2$ gas relights glowing splint. Black residue obtained.
	(ii)	Add deionised water to a small beaker until it is about half full. Place the beaker on a white tile. Pour the cooled residue from <b>3(a)(i)</b> <b>slowly</b> into the deionised water in the beaker. <b>Observe the solution closely.</b>  Swirl the solution and filter a small portion of this solution into a clean test-tube. The filtrate is <b>FA 7</b> .	Solid dissolves to form green solution which then turns purple.  Purple filtrate obtained. Dark brown residue obtained.
	(iii)	Add 1 cm depth of <b>FA 7</b> to a test-tube. Add $\text{Fe}^{2+}(\text{aq})$ , slowly with shaking, until no further change is seen.	Purple <b>FA 7</b> turns yellow/orange/ brown and then pale green/ colourless.

(b) (i) The green solution obtained immediately when water is added to the residue is  $\text{MnO}_4^{2-}$ .

$$E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}} = (+2.26) - (+0.56)$$

$$= +1.70 \text{ V} > 0 \text{ (energetically feasible)}$$


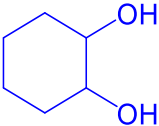
Green  $\text{MnO}_4^{2-}$  is oxidised to purple  $\text{MnO}_4^-$  and reduced to brown  $\text{MnO}_2$  ppt.

(ii) **disproportionation**



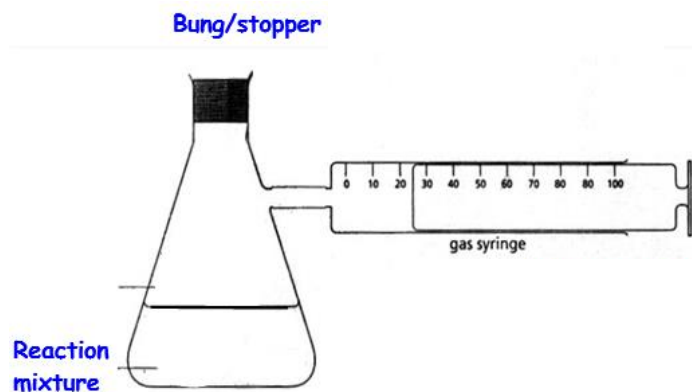
(d)	tests	observations
(i)	Add 2 cm depth of aqueous sodium hydroxide in a test-tube. Add 5 drops of <b>FA 8</b> to this test-tube. Add a few drops of aqueous potassium manganate(VII).	Solution turns green. Green solution then turns brown/brown ppt. formed.
(ii)	Add 2 cm depth of aqueous sulfuric acid in a test-tube. Add 5 drop of <b>FA 8</b> to this test-tube. Add a few drops of aqueous potassium manganate(VII). Place the mixture in the hot water bath for a few minutes.	Purple FA 9 decolourises.
(iii)	Add 5 cm depth of deionised water in a test-tube. Add 1 drop of <b>FA 8</b> to this test-tube. Add aqueous bromine slowly, with shaking, until no further change is seen.	Yellow aqueous bromine decolourises

- (e) (i) molecular formula of **FA 8**  $\text{C}_6\text{H}_{10}$   
 explanation **FA 8** undergoes oxidation from alkene to give diol.

(ii)	<b>FA 8</b>	compound <b>Z</b>
		

## 4 Planning

(a)



1. Use a burette to transfer 50.00 cm<sup>3</sup> of KMnO<sub>4</sub> into a conical flask.
2. Using a 50.0 cm<sup>3</sup> measuring cylinder, transfer 50.0 cm<sup>3</sup> of H<sub>2</sub>SO<sub>4</sub> into the same conical flask. Using a dropper, add 1 cm<sup>3</sup> of MnSO<sub>4</sub>(aq) to the conical flask.
3. Using a 50.0 cm<sup>3</sup> measuring cylinder, measure 50.0 cm<sup>3</sup> of Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>.
4. Transfer the Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> to the conical flask and quickly insert the bung into the conical flask. Immediately start the stopwatch and swirl the conical flask.
5. Record time taken using stopwatch when 40 cm<sup>3</sup> of gas is collected in the gas syringe.
6. Repeat steps 1 to 5 for 4 other experiments, using the volumes as shown in the table below. Measure deionised water using a measuring cylinder.

Expt	Vol KMnO <sub>4</sub> /cm <sup>3</sup>	Vol deionised water/cm <sup>3</sup>	Vol H <sub>2</sub> SO <sub>4</sub> /cm <sup>3</sup>	Vol Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub> /cm <sup>3</sup>	Vol Mn <sup>2+</sup> /cm <sup>3</sup>	t/s
1	50.00	0.0	50.0	50.0	1	
2	40.00	10.0	50.0	50.0	1	
3	30.00	20.0	50.0	50.0	1	
4	20.00	30.0	50.0	50.0	1	
5	10.00	40.0	50.0	50.0	1	

(b)

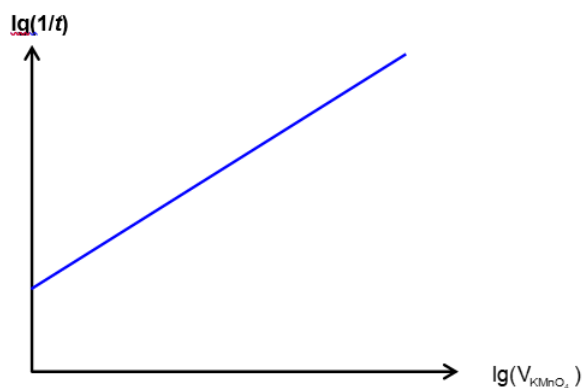


Fig 4.1

$$\text{Rate} = k[\text{KMnO}_4]^a$$

Since rate  $\propto 1/t$  and  $[\text{KMnO}_4] \propto V_{\text{KMnO}_4}$  since total volume is kept constant,

$$1/t = k(V_{\text{KMnO}_4})^a$$

$$\lg(1/t) = \lg k' + a \lg(V_{\text{KMnO}_4})$$

$\lg(1/t) = a \lg(V_{\text{KMnO}_4}) + \lg k'$  which is similar to a  $y = mx + c$  straight line graph

(c) Gradient of the line = order of reaction

(d) (i) The reaction is slow as it has high activation energy due to the repulsion between both the negatively charged  $\text{MnO}_4^-$  and  $\text{C}_2\text{O}_4^{2-}$ .

(ii) Homogenous catalyst since  $\text{Mn}^{2+}(\text{aq})$  is in the same phase as the reactants.

