Class	Adm No

Candidate Name: ____________________

millennia institute

2019 Preliminary Exams
Pre-University 3

H2 CHEMISTRY **9729/01**

Paper 1 Multiple Choice **24 Sept 2019**

1 hour

Additional materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not turn over this question paper until you are told to do so
Write in soft pencil.
Do not use staples, paper clips, glue or correction fluid.
Write your name, class and admission number in the spaces provided at the top of this page and on the Multiple Choice Answer Sheet provided.

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

Read the instructions on the Multiple Choice 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 question paper.
The use of an approved scientific calculator is expected, where appropriate.

FOR EXAMINER'S USE	
TOTAL (30 marks)	

This question paper consists of **15** printed pages and **1** blank page.

For each question there are four possible answers, **A**, **B**, **C**, and **D**. Choose the **one** you consider to be correct.

1 Which of the following contain one mole of the stated particles?

1 H^+ ions in 1 dm^3 of 0.5 mol dm^{-3} $H_2SO_4(aq)$
2 atoms in 6 dm^3 of $SO_3(g)$ at room temperature and pressure
3 electrons in 64.1 g of SO_2
4 neutrons in 1.6 g of $^{32}S_8$

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

2 Incomplete combustion of y dm^3 of propanol gas yielded a mixture of carbon dioxide and carbon monoxide in the ratio of 2:1, together with water vapour.
What is the volume of oxygen consumed?

A 3.5y dm^3 **B** 4y dm^3 **C** 4.5y dm^3 **D** 5y dm^3

3 The redox reaction between potassium manganate(VII) and $MnSO_4$ gives MnO_2 as the only manganese-containing product.
How many moles of $MnSO_4$ react with one mole of potassium manganate(VII) in this reaction?

A 0.5
B 1
C 1.5
D 2

4 The ion $\mathbf{Z}^{2+}$ has 12 electrons and 15 neutrons.

Which of the following statements is true?

A In an electric field, the ion $\mathbf{Z}^{2+}$ will be deflected at a smaller angle than that of Mg^{2+}.

B The first ionisation energy of element **Z** is lower than that of the Group 13 element in the same period as **Z**.

C The chloride of **Z** formed is expected to have a higher melting point than $MgCl_2$.

D Element **Z** is isoelectronic with neon.

5 Consider the following four compounds.

1 $CH_3CH_2CH_2CH_3$

2 $CH_3CH_2CH_2OH$

3 CH_3CH_2Cl

4 $(CH_3)_3CH$

What is the order of increasing boiling point of the compounds?

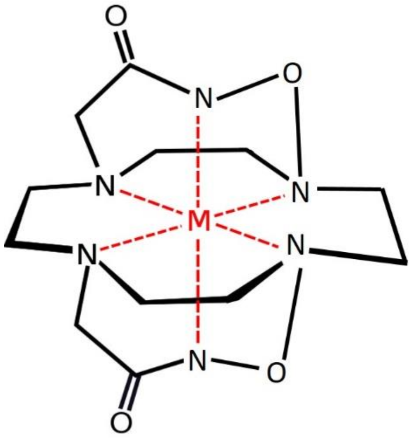
A 1 < 4 < 3 < 2

B 2 < 3 < 4 < 1

C 4 < 1 < 2 < 3

D 4 < 1 < 3 < 2

6 The research on metal complexes have achieved many international breakthrough developments, focusing on their properties and wide range of applications to tackle the challenges in human health and the environment.



Which of the following types of bonding can be found in the complex?

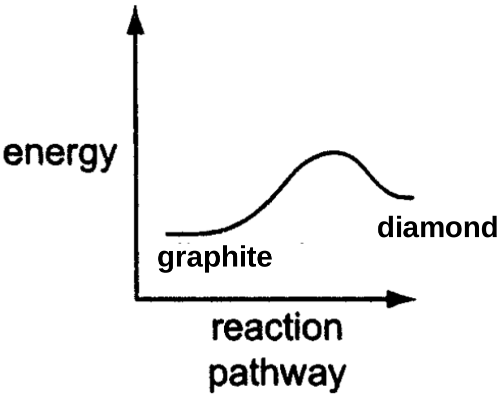
1 ionic bonding
2 dative bonding
3 hydrogen bonding
4 ion-dipole interactions

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

7 The conversion of graphite into diamond is endothermic and this reaction has an extremely small rate constant.

Which reaction pathway correctly represents this conversion?

A



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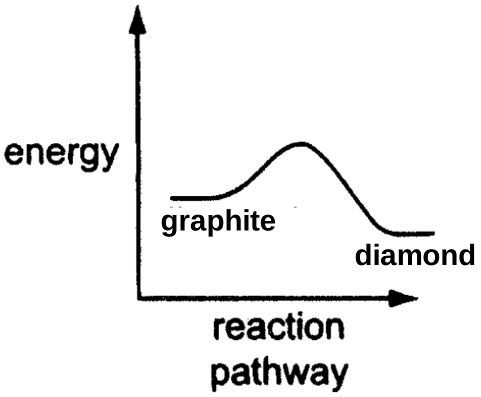

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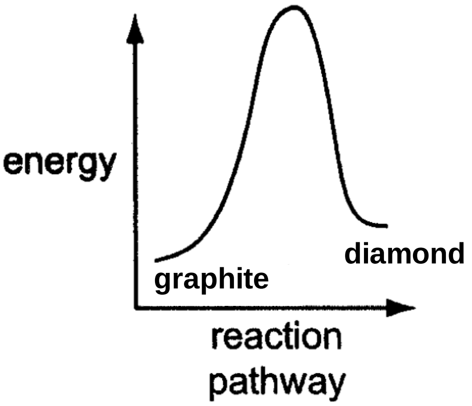

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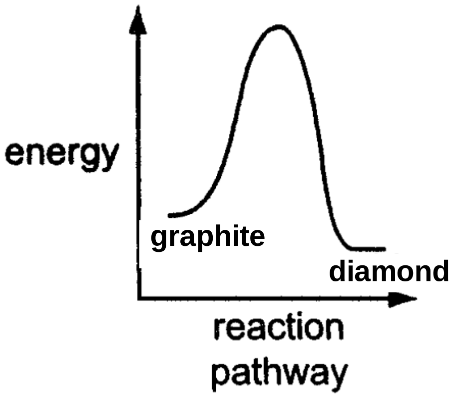


8

Reaction 1	Evaporation of ethanol
Reaction 2	Atomisation of magnesium
Reaction 3	Initiation step for the free radical substitution between chlorine and ethane

Which of the following statements about the reactions are correct?

1 ΔH is positive for all reactions.
2 ΔS is positive for all reactions.
3 ΔG is positive for all reactions.

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

9 When the temperature of a closed vessel containing a gas is increased by 273 °C, the pressure was found to increase by 20%.
What is the initial temperature of the closed vessel?

A 1092 °C **B** 1092 K **C** 1365°C **D** 1365 K

10 Which of the following two species are acting as an acid and a conjugate acid respectively in the following reaction?

$$H_2O + ClO^- \rightleftharpoons HOCl + OH^-$$

A H_2O and $HOCl$
B OH^- and H_2O
C OH^- and ClO^-
D $HOCl$ and ClO^-

11 The reaction for $A + 2B \rightarrow AB_2$ occurs by the following mechanism.

Step 1 $A + B \rightleftharpoons AB$ (fast)

Step 2 $AB + B \rightarrow AB_2$ (slow)

Which of the following represents the correct rate equation?

A Rate = k[A] **B** Rate = k[B] **C** Rate = k[AB][B] **D** Rate = $k[A][B]^2$

12 The following data was obtained during the first-order decomposition of the reaction:

$$2A(g) \rightarrow B(g) + C(s)$$

Time	Total pressure
10 min	300 Pa
After completion	200 Pa

Given that the reaction took place in a sealed container at constant temperature, what is the half-life of the reaction?

A 5 min

B 10 min

C 15 min

D 20 min

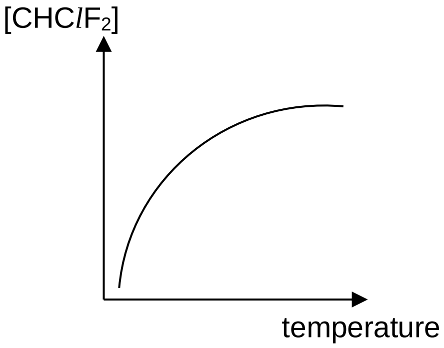
13 Chlorofluorocarbons (CFCs) are nontoxic, nonflammable chemicals containing atoms of carbon, chlorine, and fluorine. They are used in the manufacture of aerosol sprays, blowing agents for foams and packing materials, as solvents, and as refrigerants.

$$2CHClF_2\,(g) \rightleftharpoons CF_2{=}CF_2\,(g) + 2HCl\,(g)$$

Species	**Standard enthalpy change of formation / kJ mol^{-1}**
$CF_2{=}CF_2(g)$	–658.3
$HCl(g)$	–92.3
$CHClF_2(g)$	–485.2

Based on the data provided, which of the following describes how would the concentration of $CHClF_2(g)$ at equilibrium varies with temperature?

A



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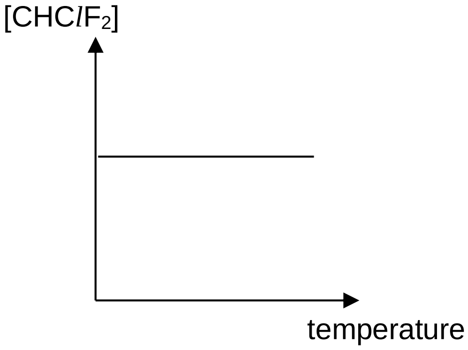

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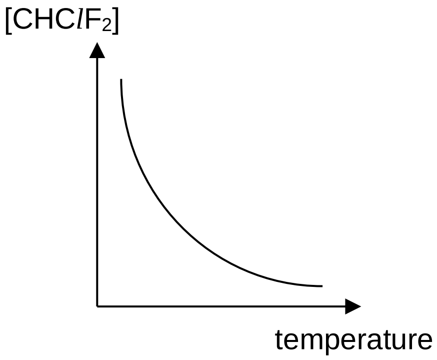

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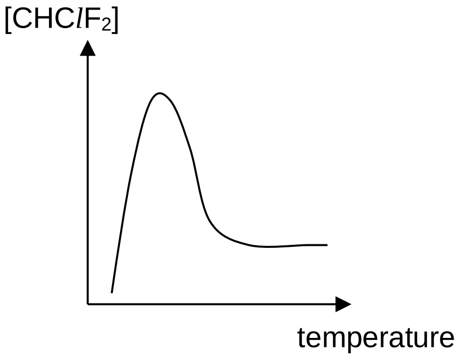


14 Which of the following mixtures will form a solution that resist pH changes when small quantites of acid or base is added?

A 500 cm^3 of 1 mol dm^{-3} aqueous Na*Cl* and 500 cm^3 of 1 mol dm^{-3} aqueous H*Cl*

B 750 cm^3 of 1 mol dm^{-3} aqueous CH_3COOH and 250 cm^3 of 1 mol dm^{-3} aqueous NaOH

C 600 cm^3 of 1 mol dm^{-3} aqueous NH_3 and 400 cm^3 of 1 mol dm^{-3} aqueous H_2SO_4

D 400 cm^3 of 1 mol dm^{-3} aqueous NaOH and 600cm^3 of 1 mol dm^{-3} aqueous H_2SO_4

15 What is the final pH of the solution formed by mixing equal volumes of two H_2SO_4 solutions, one of pH 2.0 and the other of pH 3.0?

A 1.96 **B** 2.26 **C** 2.50 **D** 2.78

16 **Q**, **R** and **S** are three elements found in Period 3 of the Periodic Table.

Among the elements in Period 3,

- the melting point of the oxide of **R** is the highest.
- the electrical conductivity of **Q** is the highest.
- the melting point of **S** is the lowest.

Which of the following elements is **not** represented by **Q**, **R** or **S**?

A Na **B** Mg **C** A*l* **D** Ar

17 Fluorine has anomalous properties in Group 17.

Which of the following statements is correct?

A HF is a strong acid.

B Fluorine is intensely coloured.

C The melting point of fluorine is high.

D The F–F bond is unusually weak.

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

Each galvanic cell is made up of two half-cells. E_1, E_2 and E_3 are the cell potentials of the three galvanic cells respectively.

Half-cell 1	Half-cell 2	E_{cell}
1 mol dm^{-3} Zn^{2+}(aq) and Zn	0.1 mol dm^{-3} Cu^{2+}(aq) and Cu(s)	E_1
1 mol dm^{-3} Zn^{2+}(aq) and Zn	1 mol dm^{-3} Cu^{2+}(aq)and Cu(s)	E_2
0.1 mol dm^{-3} Zn^{2+}(aq) and Zn	1 mol dm^{-3} Cu^{2+}(aq) and Cu(s)	E_3

Which of the following shows the correct sequence of E_{cell} arranged in decreasing order?

A $E_2 > E_3 > E_1$

B $E_3 > E_2 > E_1$

C $E_1 > E_2 > E_3$

D $E_1 > E_3 > E_2$

19 Electrolysis of a dilute aqueous NaC*l* solution was carried out by passing 0.1 A current through it.

What is the time required to liberate 0.01 mol of H_2 gas at the cathode?

A 9.65×10^3 s

B 1.93×10^4 s

C 2.90×10^4 s

D 3.86×10^4 s

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

In research laboratories, the standard calomel reference electrode and the AgC*l* / Ag reference electrodes are often used in place of the standard hydrogen electrode (SHE). Their standard reduction potentials with respect to the SHE are shown below.

Calomel electrode:	$\frac{1}{2}Hg_2Cl_2 + e^- \rightleftharpoons Hg + Cl^-$	$E^\ominus = +0.27$ V
AgC*l* / Ag electrode:	$AgCl + e^- \rightleftharpoons Ag + Cl^-$	$E^\ominus = +0.22$ V

A half–cell containing Au^+/Au has a reduction potential of +1.61 V with respect to AgC*l* / Ag electrode.

Which of the following statements is correct?

A The reduction potential of the Au^+/Au half–cell with respect to the SHE is +1.83 V.

B The reduction potential of the Au^+/Au half–cell with respect to the calomel electrode is +1.88 V.

C Ag is a stronger reducing agent than H_2.

D Hg_2Cl_2 is a weaker oxidising agent than AgC*l*.

21 Which of the following statements is **not** correct?

A Both Fe^{2+} and Fe^{3+} can catalyse the reaction between I^- and $S_2O_8^{2-}$.

B $[Fe(C_2O_4)_3]^{4-}$ has a coordination number of 6.

C $[Fe(H_2O)_6]^{3+}$ has a lower pK_a than $[Fe(H_2O)_6]^{2+}$.

D Aqueous solutions of Fe^{2+} appear green due to the absorption of green light.

22 Which of the following ions does **not** form coloured solutions?

A Co^{3+} **B** Cu^+ **C** Mn^{3+} **D** Ti^{2+}

23 Four different complexes can be obtained by reacting aqueous cobalt(III) chloride with ammonia under various conditions. Different proportions of chloride are precipitated when each complex is treated with aqueous silver nitrate.

	empirical formula	colour of solid	number of moles of Ag*Cl* precipitated per mole of complex
I	$CoCl_3(NH_3)_6$	orange	3
II	$CoCl_3(NH_3)_5$	violet	2
III	$CoCl_3(NH_3)_4$	violet	1
IV	$CoCl_3(NH_3)_4$	green	1

Which of the following statements are correct regarding the four different complexes?

1 Complex **I** is the only complex that is made up of only one type of ligand.
2 The cations of the four complexes have the same charge.
3 Complexes **III** and **IV** are stereoisomers.
4 All four complexes have the coordination number of 6.

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

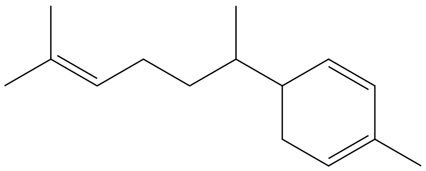
24 Which of the following compounds are arranged in increasing order of their solubility in water?

A $CH_3CH_2CO_2Na$, $CH_3CH_2CH_2OH$, $CH_3CH_2CH_2Cl$
B $CH_3CH_2CH_2Cl$, $CH_3CH_2CH_2OH$, $CH_3CH_2CO_2Na$
C $CH_3CH_2CH_2Cl$, $CH_3CH_2CO_2Na$, $CH_3CH_2CH_2OH$
D $CH_3CH_2CH_2OH$, $CH_3CH_2CO_2Na$, $CH_3CH_2CH_2Cl$

25 How many isomeric esters have the molecular formula $C_4H_8O_2$?

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

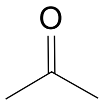
26 The flavour of ginger comes from zingiberene.



zingiberene

Which of the following compounds are produced from the reaction between zingiberene and hot concentrated acidified $KMnO_4$?

1



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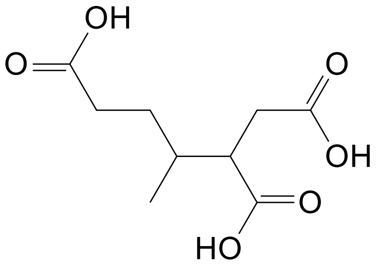
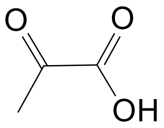


3 CO_2

4



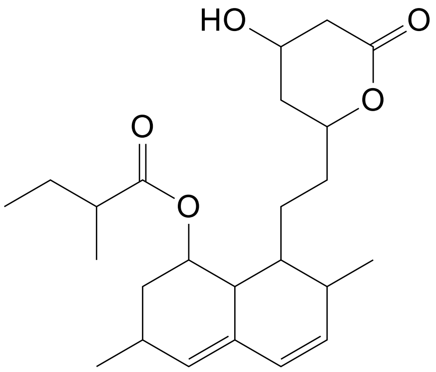
A 1 and 3 only **B** 2 and 4 only **C** 1, 2 and 4 only **D** 1, 3 and 4 only

27 Which of the following reactions would result in the formation of racemic mixture?

1 1-chloropropane ⟶ propan-1-ol
2 ethanal ⟶ cyanoethanol
3 but-2-ene ⟶ 2-chlorobutane

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

28 Statin is a class of lipid-lowering medication which is effective in lowering cholesterol and used for primary prevention in people at high risk of cardiovascular disease.



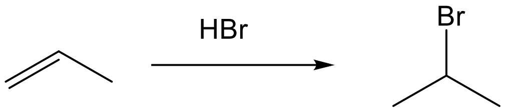
Statin

Which statement about statin is **not** correct?

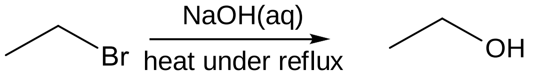
A When statin reacts with aqueous Br_2, the product contains chiral centres.
B When heated with ethanoic acid and concentrated sulfuric acid, statin forms an ester.
C When statin reacts with hot acidified $K_2Cr_2O_7$, one of the products contains three ketone groups.
D When 2,4-dinitrophenylhydrazine is added to statin, an orange precipitate is observed.

29 Which of the following reactions involves an organic intermediate which has a different charge from the other three reactions?

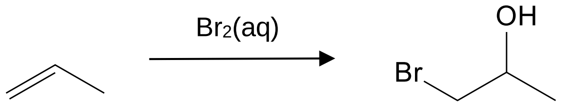
A



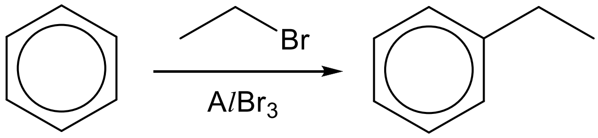
B



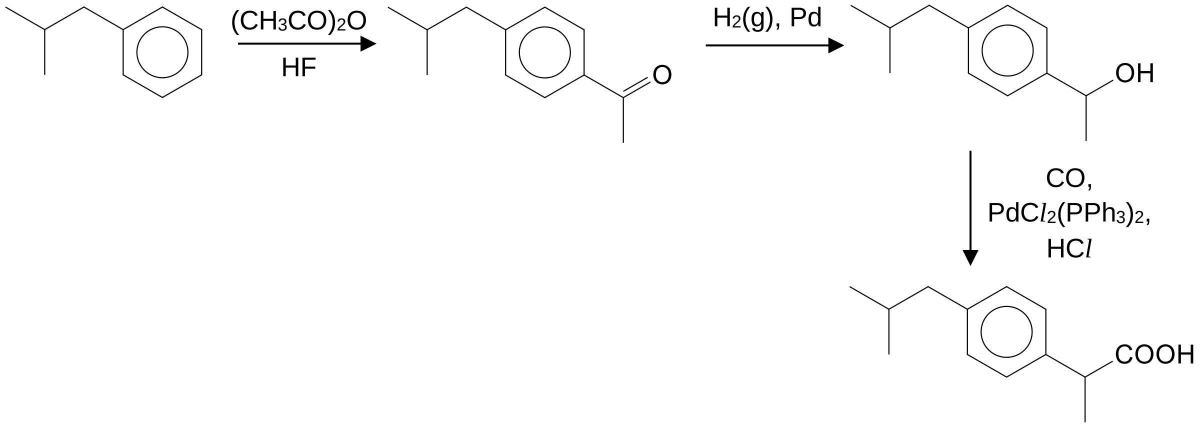
C



D



30 Ibuprofen is used to relieve pain from headache and to reduce fever. The synthesis of ibuprofen is shown below.



Ibuprofen

Which of the following type of reactions can be found in the synthetic route?

1 reduction
2 elimination
3 acidic hydrolysis
4 electrophilic substitution

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

END OF PAPER 1

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Q1 Option 1: Amount of H_2SO_4 = 0.5 x 1 = 0.5 mol

$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$

Amount of H^+ = 0.5 x 2 = 1 mol

Option 2: Amount of SO_3 molecules = 6 / 24 = 0.25 mol

1 SO_3 molecule has 4 atoms (1 S and 3 O atoms)

Amount of atoms = 0.25 x 4 = 1 mol

Option 3: Amount of SO_2 molecule = 64.1 / (32.1 + 16.0 x 2) = 1 mol

1 SO_2 molecule has 16 + 8 x 2 = 32 electrons

Amount of electrons = 1 x 32 = 32 mol

Option 4: Amount of S_8 molecule = 1.6 /(32.1 x 8) = 0.00623 mol

1 S_8 molecule has 16 x 8 = 128 neutrons

Amount of neutrons = 0.798 mol

Ans: 1 and 2 are correct => A

Q2 $CH_3CH_2CH_2OH + 4O_2 \rightarrow 2CO_2 + CO + 4H_2O$

Since mole ratio = volume ratio of gases,

Vol of O_2 consumed = 4y

Ans: B

Q3 [R] $MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2\,H_2O$

[O] $Mn^{2+} + 2H_2O \rightarrow MnO_2 + 4H^+ + 2e^-$

$2MnO_4^- + 3Mn^{2+} + 2H_2O \rightarrow 2MnO_2 + 3MnO_2 + 4H^+$

2 mol of MnO_4^- reacts with 3 mol of Mn^{2+}

1 mol of MnO_4^- reacts with 1.5 mol of Mn^{2+}

Ans: C

Q4 Z^{2+} has 12 electrons and 15 neutrons

Z has 14 electrons, 14 protons and 15 neutrons=> A_r = 14 + 25 = 39

Option A: angle of deflection $\propto \frac{\text{charge}}{\text{mass}}$

$\frac{\text{charge}}{\text{mass}}$ for Z^{2+} = $\frac{+2}{14+15}$ = $\frac{+2}{29}$

$\frac{\text{charge}}{\text{mass}}$ for Mg^{2+} = $\frac{+2}{24.3}$

$\frac{\text{charge}}{\text{mass}}$ for Mg^{2+} > $\frac{\text{charge}}{\text{mass}}$ for Z^{2+}

Angle of deflection for Mg^{2+} > Angle of deflection for Z^{2+}

Option A is correct

Option B: Based on the proton number, **Z** is referring to Silicon.

Si has a higher IE than Al (Group 13 element in the same period as Z) => You can check from Data Booklet or recall from the trend across the period.

Option C: $SiCl_4$ has a lower melting point than $MgCl_2$ as $SiCl_4$ has a simple molecular structure while $MgCl_2$ has a giant ionic structure. Larger amount of energy is needed to overcome the stronger electrostatic forces of attraction between Mg^{2+} and Cl^- than the weaker instantaneous dipole-induced dipole forces of attraction between $SiCl_4$ molecules.

Option D: Element **Z** has 14 electrons while neon has 10 electrons. Hence, they are not isoelectronic.

Q5 All options have simple molecular structures.

Option 1 and 4 have instantaneous dipole-induced dipole forces of attraction between molecules

Option 2 has hydrogen bonding between molecule

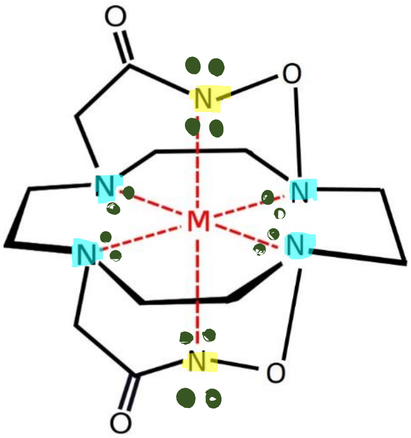
Option 3 has permanent dipole-permanent dipole forces of attraction between molecules.

Hence option 2 will be the highest followed by option 3

For option 1 and 4, the two molecules are isomers of each other. Thus, the surface area determines the boiling point. Since option 1 is a straight-chained molecule, it has a larger surface area between molecules which results in stronger instantaneous dipole-induced dipole forces of attraction than that of option 4 since option 4 is a branched-chain molecule. Hence option 4 as the lowest boiling point.

Boiling point: 4 < 1 < 3 < 2 => Option D is correct

Q6



The N highlighted in yellow has 6 electrons from N hence this N has a charge of -1.

The N highlighted in turquoise has 5 electrons from N hence thus N has no charge.

Since the complex has no overall charge, M has a charge of +2.

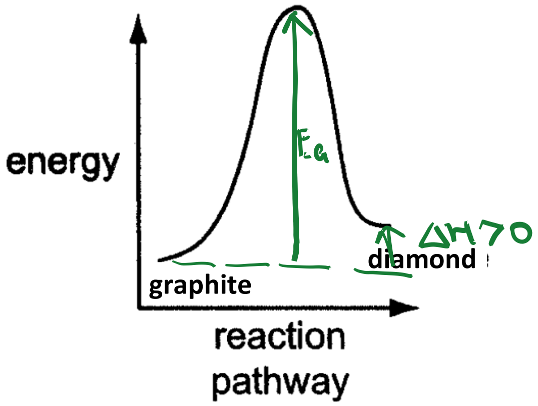
Bond between M^{2+} and N (in turquoise) is due to dative bond.

Bond between M^{2+} and N (in yellow) is due to ionic bond.

Ans: 1 and 2 => B is correct

Q7 Converting from graphite to diamond has ΔH > 0 and k is small refers to large E_a.

Thus C is the answer.



Q8 Reaction 1: Evaporation of ethanol: $C_2H_5OH(l) \rightarrow C_2H_5OH(g)$

ΔH > 0 => energy is taken in to overcome the hydrogen bonding between the molecules to convert liquid to gas.
Recall: Liquid is more closely packed than gas

ΔS > 0 => increase in number of gas molecules from zero to one.
More ways of arranging the particels. Entropy increases.

ΔG = 0 as it is an equilibrium reaction

Reaction 2: Atomisation of magnesium: $Mg(s) \rightarrow Mg(g)$
ΔH > 0 => energy is taken in to overcome the forces of attraction to convert solid to gas.
Recall: solid is more closely packed than gas

ΔS > 0 => increase in number of gas molecules from zero to one.
More ways of arranging the particels. Entropy increases.

Reaction 3: Initiation step for the free radical substitution between chlorine and ethane

$$Cl_2(g) \xrightarrow[uv]{} 2Cl\bullet_{(g)}$$

ΔH > 0 => energy is taken in to break the covalent bond between the Cl atoms

ΔS > 0 => increase in number of gas molecules from zero to one.
More ways of arranging the particels. Entropy increases.

ΔG > 0 as it is not a spontaneous reaction since uv light is supplied for the reaction to occur.
Option 1 and 2 are correct=> C

Q9 $pV = nRT$

Since nR and V are constant, $p=kT$

$\frac{p}{T} = k$

$\frac{p_1}{T_1} = \frac{p_2}{T_2}$

$\frac{p_1}{T_1} = \frac{1.2p_1}{T_1+273}$

$\frac{T_1+273}{T_1} = 1.2$

$0.2T_1 = 273$

$T_1 = 1365$ K

Ans: D

Q10 $H_2O + ClO^- \rightleftharpoons HOCl + OH^-$

Acid and its conjugate base is a difference of H^+

Hence H_2O is the acid and OH^- is its conjugate base

ClO^- is the base and HOCl is the conjugate acid.

Hence, option A is the correct answer

Q11 rate equation depends on the slow step and it **cannot include intermediate**.

To determine if the species is an intermediate, write the overall equation by summing up the steps in the mechanism. If the species appear on either side of the overall equation, it is not an intermediate.

Overall equation: $A + 2B \rightarrow AB_2$

Based on slow step, rate= k[AB][B]

Since AB is an intermediate, it has to be re-expressed by using K_C.

$K_c = \frac{[AB]}{[A][B]}$ => $[AB] = K_c[A][B]$

rate= $k[AB][B] = k\{K_c[A][B]\}[B] = k'[A][B]^2$

Ans: D

Q 12 [Rxt] 100% → 50% → 25% …

[Pdt] 0% → 50% → 25% …

	2A(g)	→	B(g)	+	C(s)
I	x		0		0
C	-x		+½x		-
F	0		½x		-

This is based on completion of reaction, hence A will be completely used up.

Hence ½x = 200 Pa x = 400 Pa

Note: pressure only applies to gas, hence carbon solid is ignored.

At the 1st half-life, 50% of A will be used up.

	2A(g)	→	B(g)	+	C(s)
I	x		0		0
C	-½x		+¼x		-
F	½x		¼x		-
	=200		=100		

At the 1st half-life, the total pressure = 200 + 100 = 300Pa

$t_{1/2}$ = 10 min => B is correct

13 $\Delta H_{rxn} = [-685.3 + 2(-92.3)] – [2(-485.3)] = +127.5 \text{ kJ mol}^{-1}$

As temperature increases, the system is disturbed. By LCP, the system will oppose the change by decreasing the temperature and favours the endothermic reaction to absorb the heat. Position of equilibrium shifts right and produces more products. Hence, [$CHClF_2$] decreases with increasing temperature.

Ans: C

14 Consider if there is a reaction from the mixtures and determine the resultant species left in the solution to decide if it is a buffer.

Recall that a buffer must contain either:

a weak acid and its conjugate base OR a weak base and its conjugate acid.

Option A is made up of a salt and acid which does not react.

resultant species: $NaCl$ and HCl => not a buffer as it contains a strong acid

Option B: a reaction will take place

$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

I	0.75	0.25	0	0
C	-0.25	-0.25	+0.25	+0.25
F	0.50	0	0.25	0.25

resultant species: CH_3COOH and CH_3COONa => a buffer since it contains a weak acid (CH_3COOH) and its conjugate base (CH_3COO^-)

Option B is correct

Option C: a reaction will take place

$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$

I	0.6	0.4	0
C	-0.6	-0.3	+0.3
F	0	0.1	0.3

resultant species: H_2SO_4 and $(NH_4)_2SO_4$ => not a buffer as it contains a strong acid

Option D: a reaction will take place.

$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$

I	0.4	0.6	0	0
C	- 0.4	-0.2	+0.2	+0.4
F	0	0.4	0.2	0.4

resultant species: H_2SO_4 and Na_2SO_4 => not a buffer as it contains a strong acid

Q15 $[H^+]$ from pH 2 = 10^{-2}

$[H^+]$ from pH 3 = 10^{-3}

When equal volumes are mixed, each concentration is halved.

$[H^+]_{\text{total after mixing}} = ½ [10^{-2} + 10^{-3}] = 0.00550$ mol dm^{-3}

pH = -log 0.00550 = 2.26

Ans: B

Q16 MgO has the highest melting point across Period 3 oxides. => **R** is Mg

Al has the highest electrical conductivity => **Q** is Al

Ar has the lowest melting point => **S** is Ar

Ans: Na is not represented. Option A is the answer.

Q17 HF is a weak acid

Fluorine is a pale yellow gas => not intensely coloured.

Melting point of fluorine is low as it has simple molecular structure.

F – F bond is unusually weak as observed from the trend. General trend of X –X bond decreases down the group due to increasing bond length. However, F –F bond is the weakest as seen from the values in Data Booklet. This is due to the repulsion as a result of the small atomic radius of F.

Bond	Bond energy
F-F	+158
Cl-Cl	+244
Br-Br	+193
I-I	+151

Ans: D

18 $Zn^{2+} + 2e^- \rightleftharpoons Zn$ $E^{\theta} = -0.76$ V

$Cu^{2+} + 2e^- \rightleftharpoons Cu$ $E^{\theta} = +0.34$V

Based on the standard electrode potential, Zn is the anode while Cu is the cathode.

[O] $Zn \rightarrow Zn^{2+} + 2e^-$ –(1)

[R] $Cu^{2+} + 2e^- \rightarrow Cu$ –(2)

E_2 is the reaction that happens at standard condition since the ions are 1 mol dm^{-3}

$E_2 = +0.34 - (-0.76) = +1.10$ V

For E_1 and E_3, the reactions are not at standard conditions.

For the reaction that is represented by E_1, $[Cu^{2+}]$ is lower than that of the standard condition. By LCP, the system will oppose the change by shifting the position of equilibrium (2) to the left to replenish the Cu^{2+}. This results in oxidation to be preferred and makes $E_{Cu2+/Cu}$ less positive.

$E_1 = E_{cathode} - E_{anode} = E_{Cu2+/Cu} - E_{Zn2+/Zn}$ => E_1 will be less positive than E_2

For the reaction that is represented by E_3, $[Zn^{2+}]$ is lower than that of the standard condition. By LCP, the system will oppose the change by shifting the position of equilibrium to the right (1) to replenish the Zn^{2+}. This results in oxidation to be preferred and makes $E_{Zn2+/Zn}$ less positive.

$E_1 = E_{cathode} - E_{anode} = E_{Cu2+/Cu} - E_{Zn2+/Zn}$ => E_3 will be more positive than E_2

Hence $E_3 > E_2 > E_1$ => Ans: B

19 [R] $2H_2O + 2e^- \rightarrow H_2 + OH^-$

$n_e = 0.01 \times 2 = 0.02$

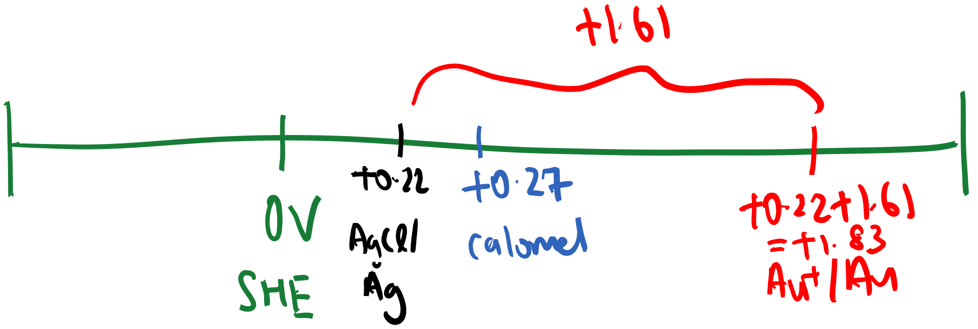
$Q = n_eF = It$

$0.02 \times 96500 = 0.1t$

t= 19300 s

Ans: B

20



Option A is correct as observed from the number line. Hence E(Au^+/Au) is +1.83 V wrt SHE

Option B: E(Au^+/Au) wrt calomel = +1.83 – (+0.27) = +1.56V

Option C: $E_{AgCl/Ag}$ is more positive than $E_{H+/H2}$ => Hence H_2 is more likely to be oxidised than Ag. Thus, H_2 is a stronger reducing agent.

Option D: $E_{HgCl2/Hg}$ is more positive than $E_{AgCl/Ag}$ => Hence $HgCl_2$ is more likely to be reduced than AgCl. Thus, $HgCl_2$ is a stronger oxidising agent.

21 Option A is correct:

When Fe^{2+} is the catalyst,

$2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$

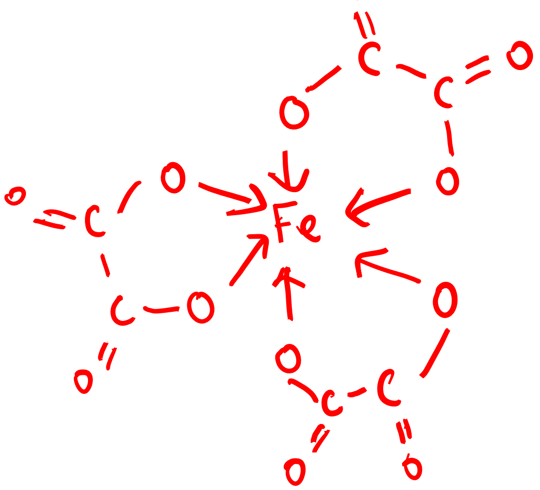
$2Fe^{3+} + 2I^- \rightarrow I_2 + 2Fe^{2+}$

When Fe^{3+} is the catalyst,

$2Fe^{3+} + 2I^- \rightarrow I_2 + 2Fe^{2+}$

$2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$

Option B: coordination number is denoted by the number of dative bonds formed around the central metal and not via the number of ligands. Coordination no = 6



Option C: $[Fe(H_2O)_6]^{3+}$ forms a more acidic solution than $[Fe(H_2O)_6]^{2+}$ due to the higher charge density of Fe^{3+} which has a stronger polarizing power and thus distorts the O-H bond to a larger extent, releasing H^+. Thus, $[Fe(H_2O)_6]^{3+}$ has a lower pK_a.

Option D: The appearance of the colour of solution is complementary to the colour absorbed. Thus the green solution observed is due to the absorption of red light. This statement is not correct.

22 Co^{3+}: [Ar]$3d^6$

Cu^{+}: [Ar]$3d^{10}$

Mn^{3+}: [Ar]$3d^4$

Ti^{2+}: [Ar]$3d^2$

Ans: B since there is no d-d transition which can take place as the d-orbitals are fully filled. The other options have partially filled d-orbitals which result in d-d transition.

23 The number of moles of AgCl represents the no of free Cl^- found outside of the complex.

Complex **I**: Since there are 3 moles of AgCl, there are 3 free Cl^- outside of the complex. Complex formula: $[Co(NH_3)_6]^{3+}$

Complex **II**: Since there are 2 moles of AgCl, there are 2 free Cl^- outside of the complex. Complex formula: $[Co(NH_3)_5Cl]^{2+}\ 2Cl^- \bullet NH_3$

Complex **III**: Since there is 1 mole of AgCl, there is 1 free Cl^- outside of the complex. Complex formula: $[Co(NH_3)_4Cl_2]^+\ Cl^- \bullet 2NH_3$

Complex **IV**: Since there is 1 mole of AgCl, there is 1 free Cl^- outside of the complex. Complex formula: $[Co(NH_3)_4Cl_2]^+\ Cl^- \bullet 2NH_3$

Option 1 is correct as complex **I** only contains NH_3 ligand.

Option 2 is incorrect as the charge are different for the complexes.

Option 3 is correct as complexes **III** and **IV** can form cis-trans isomers.

Option 4 is correct.

Ans: D

24 $CH_3CH_2CO_2Na$: forms ion-dipole interaction with water

$CH_3CH_2CH_2OH$: forms hydrogen bonding with water

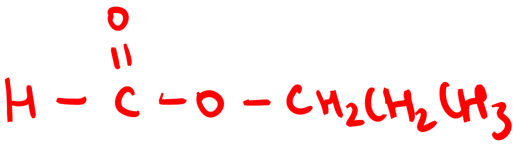
$CH_3CH_2CH_2Cl$: forms permanent dipole- permanent dipole with water

Strength: ion-dipole interaction> hydrogen bonding > permanent dipole- permanent dipole

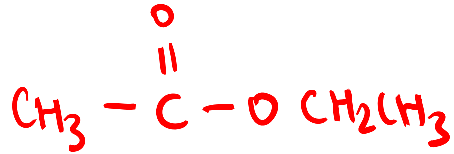
Increasing order: $CH_3CH_2CH_2Cl$, $CH_3CH_2CH_2OH$, $CH_3CH_2CO_2Na$,

Ans: B

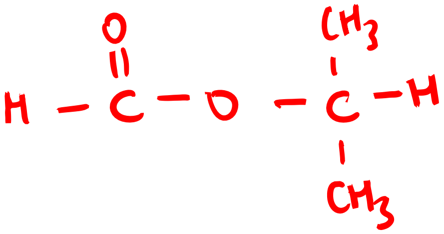
25



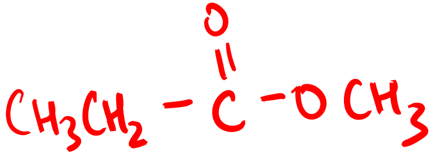
$HCOOCH_2CH_2CH_3$



$CH_3COOCH_2CH_3$

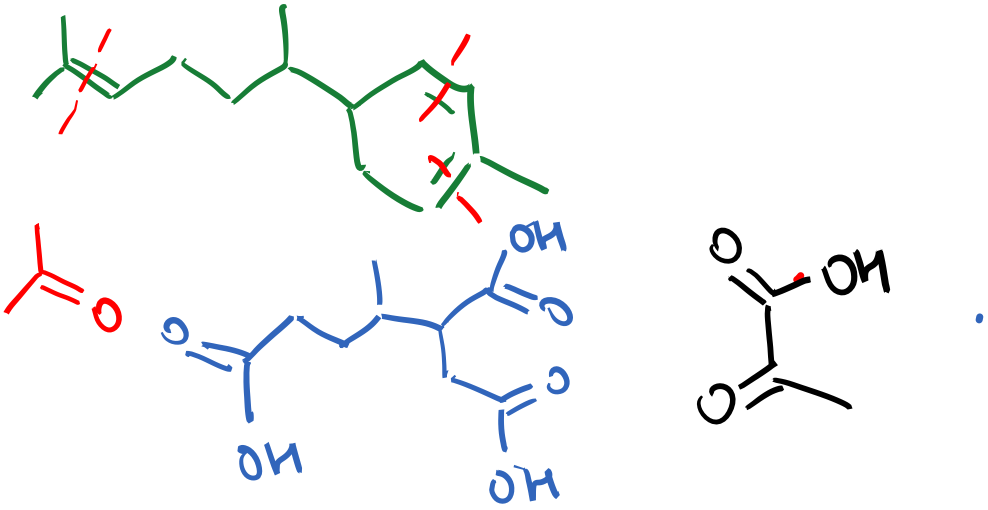


$HCOOCH(CH_3)_2$



$CH_3CH_2COOCH_3$

26

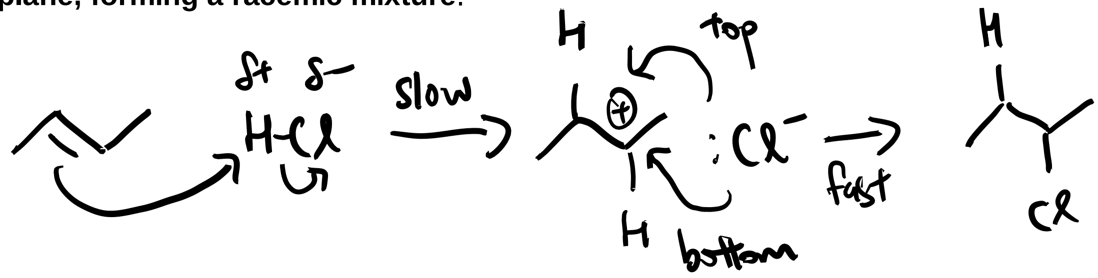


Ans: 1,2 and 4=> Option C

27 Option 1: 1-chloropropane undergoes S_N2 nucleophilic substitution to form propan-1-ol which will result in the inversion of configuration.

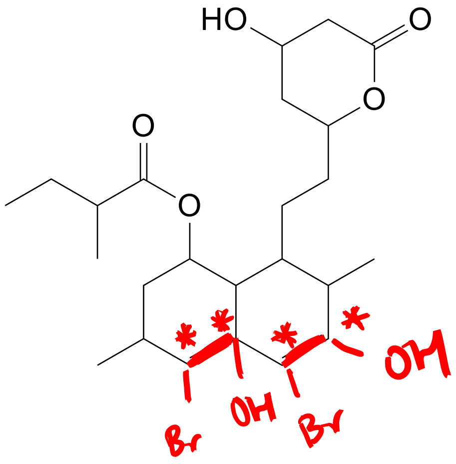
Option 2: A racemic mixture is formed as the reactive C in ethanal is trigonal planar in shape, hence the CN^- nucleophile can attack from the top or bottom of the plane, forming a racemic mixture.

Option 3: A racemic mixture is formed as the intermediate is trigonal planar in shape, hence the nucleophile can attack from the top or bottom of the plane, forming a racemic mixture.



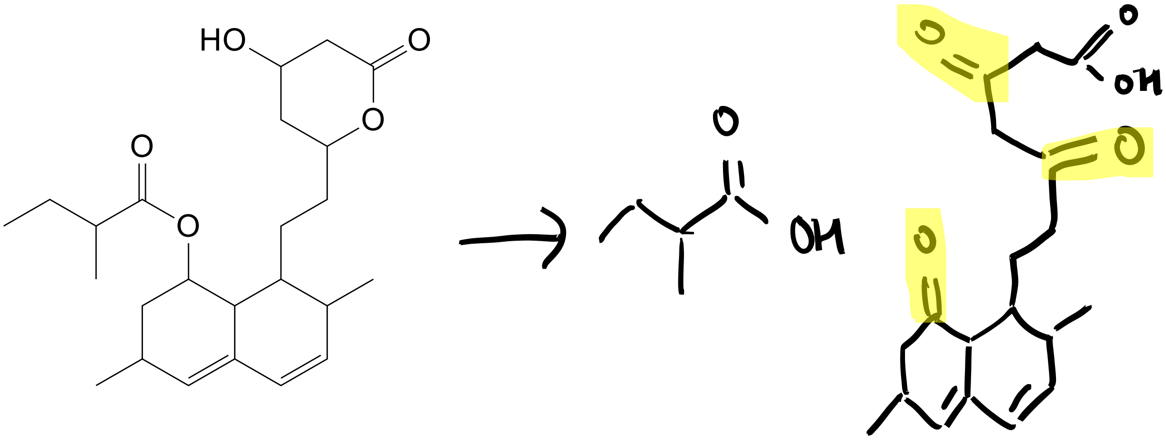
Ans: C

28 Option A is correct:



Option B is correct as the secondary alcohol will react with ethanoic acid to form ester in the presence of conc H_2SO_4.

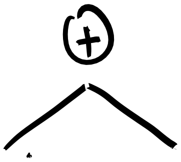
Option C is correct as secondary alcohol undergoes oxidation and acidic hydrolysis takes place for ester.



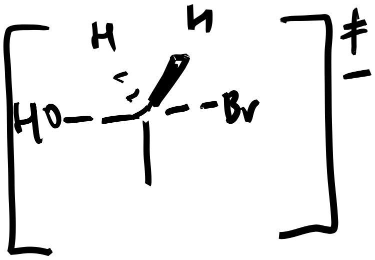
Option D: There is no carbonyl group present, thus no orange precipitate will be observed.

29

A

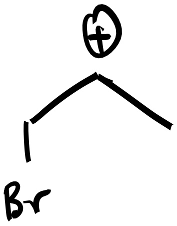


B

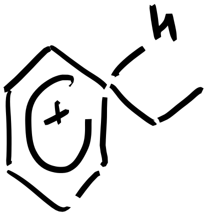


(no intermediate)

C

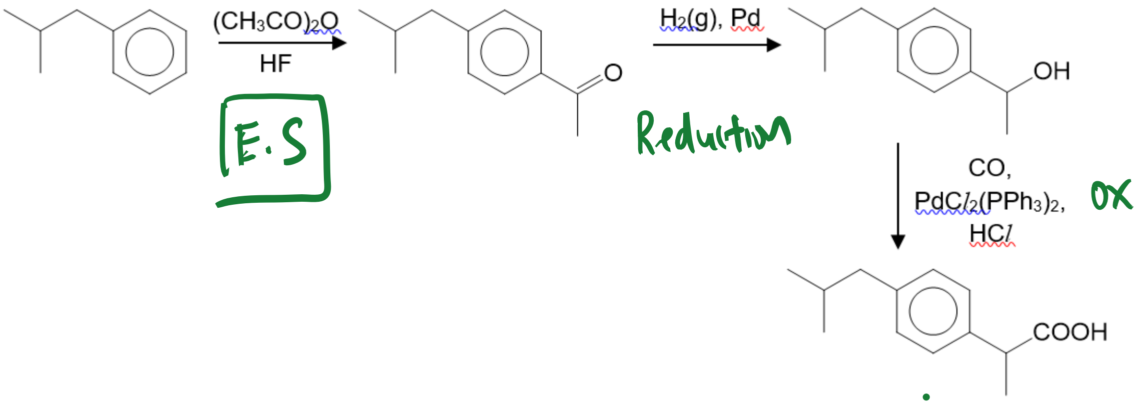


D



Ans: B

30



E.S

Reduction

oxidation

Ibuprofen

Ans: B

Class Adm No

Candidate Name: ____________________

Class	Adm No

millennia institute

2019 Preliminary Exams
Pre-University 3

H2 CHEMISTRY **9729/02**

Paper 2 Structured Questions **16 Sept 2019**

2 hours

Candidates answer on the Question paper.

Additional materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not turn over this question paper until you are told to do so

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

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

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

Answer **all** questions.

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.

Question	**1**	**2**	**3**	**4**	**5**	Total
Marks	**7**	**23**	**16**	**14**	**15**	**75**

1 **(a)** Zinc-air batteries worked by oxidising zinc with oxygen from the air. At the cathode, oxygen converts to hydroxide ions. At the anode, zinc reacts with the hydroxide ions to form zincate, $[Zn(OH)_4]^{2-}$.

(i) Construct an ion-electron equation for the reaction that takes place at each electrode under alkaline conditions. [2]

Cathode: ……………………………………………………………………………………

Anode: ……………………………………………………………………………………

(ii) At 298K, the standard electrode potential of the $[Zn(OH)_4]^{2-}(aq)|Zn(s)$ half-cell is -1.25 V. Calculate the cell voltage using relevant data from the *Data Booklet*. [1]

(iii) Using relevant data from the *Data Booklet*, deduce if oxygen gas can be replaced with chlorine gas. [2]

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(b) Another type of battery known as the nickel-cadmium battery is a type of rechargeable battery using nickel oxide hydroxide and metallic cadmium as electrodes. The electrode reaction equations for the **discharging** process under alkaline conditions is given below.

Cathode: $Cd + 2OH^- \rightarrow Cd(OH)_2 + 2e^-$
Anode: $2NiO(OH) + 2H_2O + 2e^- \rightarrow 2Ni(OH)_2 + 2OH^-$

(i) Construct the overall equation for the reaction that takes place during **charging**. [1]

……………………………………………………………………………………………

(ii) Suggest a disadvantage of using nickel-cadmium battery. [1]

………

………

[Total: 7]

[Turn over

2 Paramagnetism and diamagnetism are different forms of magnetism. Paramagnetic materials are weakly attracted by an externally applied magnetic field and form magnetic fields in the direction of the applied magnetic field. In contrast, diamagnetic materials are repelled from magnetic fields and form magnetic fields in the direction opposite to that of the applied magnetic field.

Transition metals are mostly paramagnetic or diamagnetic. The magnetic property is characterised by the presence of unpaired electrons in paramagnetic compounds and absence of unpaired electrons in diamagnetic compounds.

The table below shows the magnetic property of metal complexes.

Formula of complex	**Magnetic property of complex**
$Fe(CO)_5$	Paramagnetic
$[Fe(H_2O)_6]^{2+}$	Paramagnetic
$[Fe(H_2O)_6]^{3+}$	Paramagnetic
$[ZnCl_4]^{2-}$	Diamagnetic
$[V(H_2O)_6]^{3+}$	
$[Sc(H_2O)_3(OH)_3]$	

(a) **(i)** Write the electronic configurations of V in $[V(H_2O)_6]^{3+}$ and Sc in $[Sc(H_2O)_3(OH)_3]$. [2]

V in $[V(H_2O)_6]^{3+}$: ....

Sc in $[Sc(H_2O)_3(OH)_3]$: ....

(ii) State the magnetic property of $[V(H_2O)_6]^{3+}$ and $[Sc(H_2O)_3(OH)_3]$ in the above table. [1]

(iii) Draw labelled diagrams to show the shapes of the d orbitals of the metal ion in $[V(H_2O)_6]^{3+}$. Include the relative energy of the d-orbitals in the complex. [3]

d-orbitals of lower energy:……………………………………………………………………..

d-orbitals of higher energy: ……………………………………………………………………..

(iv) Explain why transition metal can show variable oxidation states. [1]

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(b) Sodium reacts with iron pentacarbonyl to produce a salt known as sodium tetracarbonylferrate, $Na_2Fe(CO)_4$.

$$2Na + Fe(CO)_5 \longrightarrow Na_2Fe(CO)_4 + CO \text{ ------- eqn (1)}$$

(i) Explain what is meant by the coordination number of a complex using $Fe(CO)_5$ as an example. [1]

…………………………………………………………………………………………………

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(ii) Draw the structure of $Fe(CO)_5$ and state its shape. [2]

Shape: …………………………………………………………………………………………...

(iii) Deduce the oxidising and reducing agent in eqn (1). [2]

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(iv) Explain why carbon monoxide, CO, is poisonous. [2]

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(v) The tetracarbonylferrate dianion acts as a nucleophile and react with alkyl halide by the S_N2 mechanism to form a new C-Fe bond.

$$[Fe(CO)_4]^{2-} + CH_3Br \longrightarrow [Fe(CH_3)(CO)_4]^{-} + Br^{-} \quad \text{------- eqn (2)}$$

Suggest a mechanism between $Fe(CO)_4^{2-}$ and CH_3Br. State clearly any intermediates that may be formed and use curly arrows to indicate the movement of electron pairs. [3]

(vi) State the rate equation for the reaction in eqn (2). [1]

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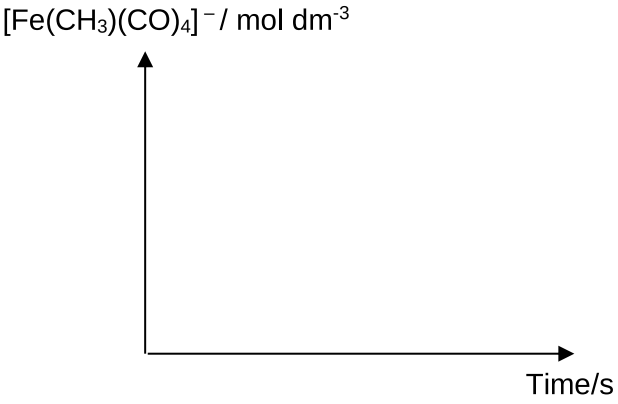
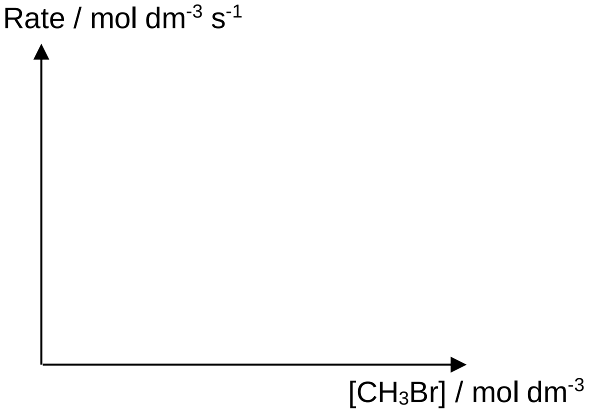
(vii) **I** Sketch the graph of $[Fe(CH_3)(CO)_4]^-$ against time.



II Sketch the graph of rate against $[CH_3Br]$ given that $[Fe(CO)_4]^{2-}$ is in excess.



[2]

(c) The melting point of sodium tetracarbonylferrate, $Na_2Fe(CO)_4$ is lower than that of sodium oxide. With reference to the structure and bonding, explain the difference in melting point.[3]

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……………………………………………………………………………………………………

[Total: 23]

[Turn over

3 **(a)** Phosgene, $COCl_2$, is essential in the manufacturing of everyday products, including medical products and footwear. Phosgene is produced by combining carbon monoxide and chlorine with a catalyst.

$$CO(g) + Cl_2(g) \rightarrow COCl_2(g)$$

(i) Draw a 'dot-and-cross' diagram of $COCl_2$ and state the bond angle about the central atom. [2]

Bond angle: ………………………..

(ii) Using relevant data from the *Data Booklet*, construct a fully labelled energy level diagram to calculate the enthalpy change of the above reaction. [3]

(iii) Explain what is meant by the term entropy of a chemical system. [1]

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(iv) Predict, with reasons, the sign of the entropy change of the reaction between CO(g) and Cl_2(g) to form $COCl_2$. [2]

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(v) Hence, state and explain the significance of the sign of the standard Gibbs free energy change when temperature is low. [2]

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(b) Above 200°C, a 2.0 dm^3 cylinder containing gaseous phosgene decomposes to carbon monoxide and chlorine in a dynamic equilibrium according to the following equation:

$$COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$$

(i) Predict and explain the effect of a catalyst on the position of the above equilibrium. [1]

…………………………………………………………………………………………………

…………………………………………………………………………………………………

(ii) At 350°C, the percentage dissociation of $COCl_2$ is found to be 45% and the total pressure at equilibrium is 3.5 atm. Calculate the value of K_p at 350 °C. [3]

(iii) Calculate the mass of the carbon monoxide gas that exists inside the cylinder at 350°C. [2]

[Total: 16]

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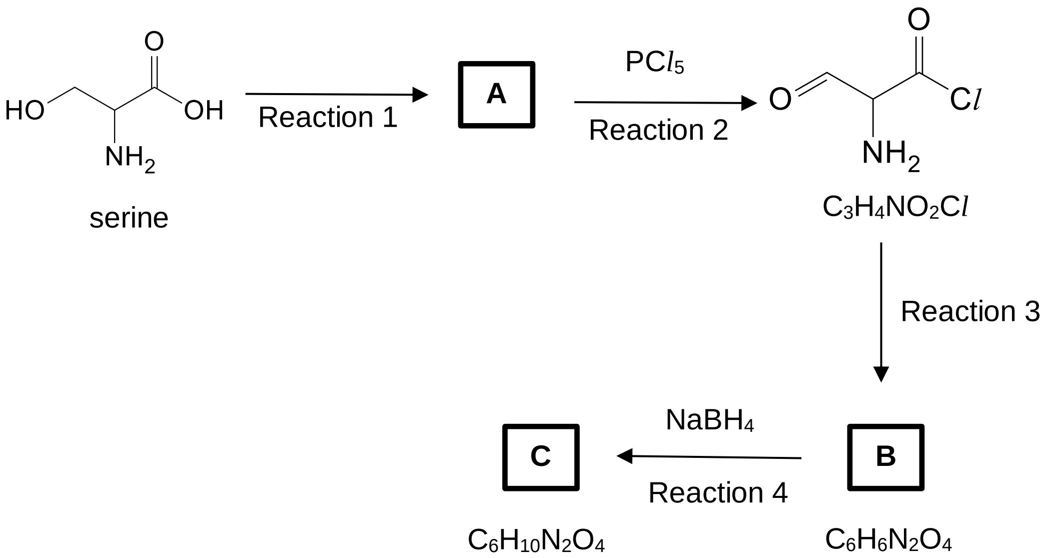
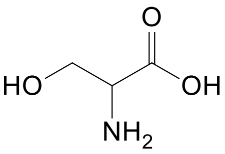
4 Spider silk is a protein fibre. Major amino acids in the silk protein are alanine, serine and glycine.

The following reaction scheme involves serine as a starting material.



(a) Explain what is meant by a chiral centre.

Label with an asterisk (*) for any chiral centre that is present in serine. [2]



....

....

....

(b) Name the functional group common to compounds **B** and **C**. [1]

....

(c) Draw the structure of compound **A** and state the reagents and conditions for reaction 1. [2]

A

Reagent and conditions: ……………………………………………………………………………..

(d) Name the type of reaction for reactions 2, 3 and 4. [3]

Reaction 2: ………………………………………………………………………………………...

Reaction 3: ………………………………………………………………………………………...

Reaction 4: ………………………………………………………………………………………...

(e) Draw the structures of compound **B** and **C**. [2]

B **C**

(f) The following table contains the pK_a values of different compounds.

Compound	**pK_a**
Serine	2.21
Propanoic acid	4.87
Phenol	9.95

(i) Suggest a reason why pK_a of propanoic acid is higher than serine. [2]

....

....

....

....

(ii) Suggest a reason why pK_a of propanoic acid is lower than phenol. [2]

....

....

....

....

....

[Total: 14]

5 **(a)** **X** and **Y** are two different elements in Period 3. The following are some of their properties:

- Oxide of **X** is insoluble in water while the aqueous solution of chloride of **X** is weakly acidic.
- Element **Y** conducts electricity and has a lower melting point than element **X**.
- The first ionisation energy of element **X** is lower than that of element **Y**.

(i) Identify the elements, **X** and **Y**. [2]

X: ……………………………………………………………………………………………

Y: ……………………………………………………………………………………………

(ii) Write the balanced equation(s) for the reaction when chloride of **X** dissolves in water and state the pH of the solution. [2]

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(iii) Explain why oxide of **X** is insoluble in water. [1]

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(iv) Explain why element **Y** has a lower melting point than element **X**. [2]

……………………………………………………………………………………………………

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(v) Explain why the first ionisation energy of element **X** is lower than that of element **Y**. [2]

………………………………………………………………………………………………

………………………………………………………………………………………………

(b) Sulfur is another period 3 element with a relative atomic mass of 32.09.

There are three naturally occurring isotopes. The relative abundances of the isotopes of sulfur are found to be the following.

Isotope	**% Abundance**
^{32}S	95.0
^{33}S	a
^{34}S	b

(i) Define the term *relative atomic mass*. [1]

………………………………………………………………………………………………

………………………………………………………………………………………………

(ii) Calculate the percentage abundances of isotopes ^{33}S and ^{34}S. [2]

(c) A 2.00 g sample of food additive containing magnesium carbonate is allowed to react with 50 cm^3 of 0.200 mol dm^{-3} aqueous hydrochloric acid. The excess acid required 19.30 cm^3 of 0.100 mol dm^{-3} aqueous potassium hydroxide for complete reaction.

Calculate the percentage of magnesium carbonate that is present in the food additive. [3]

[Total: 15]

END OF PAPER 2

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Class	Adm No

Candidate Name: ____________________

millennia institute

2019 Preliminary Exams

Pre-University 3

H2 CHEMISTRY **9729/02**

Paper 2 Structured Questions **16 Sept 2019**

2 hours

Candidates answer on the Question paper.

Additional materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not turn over this question paper until you are told to do so

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

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

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

Answer **all** questions.

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.

Question	**1**	**2**	**3**	**4**	**5**	Total
Marks	**7**	**23**	**16**	**14**	**15**	**75**

This question paper consists of 11 printed pages and 1 blank page.

1	**(a)**	Zinc-air batteries worked by oxidising zinc with oxygen from the air. At the cathode, oxygen converts to hydroxide ions. At the anode, zinc reacts with the hydroxide ions to form zincate, $[Zn(OH)_4]^{2-}$.		
		(i)	Construct an ion-electron equation for the reaction that takes place at each electrode under alkaline conditions. [2]	
			Cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ Anode: $Zn + 4OH^- \rightarrow [Zn(OH)_4]^{2-} + 2e^-$	
		(ii)	At 298K, the standard electrode potential of the $[Zn(OH)_4]^{2-}(aq)\|Zn(s)$ half-cell is -1.25 V. Calculate the cell voltage using relevant data from the *Data Booklet*. [1]	
			$E_{cell} = 0.40 – (-1.25) = +1.65$ V	
		(iii)	Using relevant data from the *Data Booklet*, deduce if oxygen gas can be replaced with chlorine gas. [2]	
			$E_{cell} = 1.36 – (-1.25) = +2.61$ V Since the E_{cell} value is more positive when oxygen gas is replaced with chlorine gas, the reaction is feasible.	
	(b)	Another type of battery known as the nickel-cadmium battery is a type of rechargeable battery using nickel oxide hydroxide and metallic cadmium as electrodes. The electrode reaction equations for the **discharging** process under alkaline conditions is given below. Cathode: $Cd + 2OH^- \rightarrow Cd(OH)_2 + 2e^-$ Anode: $2NiO(OH) + 2H_2O + 2e^- \rightarrow 2Ni(OH)_2 + 2OH^-$		
		(i)	Construct the overall equation for the reaction that takes place during **charging**. [1]	
			$2Ni(OH)_2 + Cd(OH)_2 \rightarrow 2NiO(OH) + Cd + 2H_2O$	
		(ii)	Suggest a disadvantage of using nickel-cadmium battery. [1]	
			Cadmium is a toxic heavy metal which can result in pollution if discarded in landfill or incinerated.	
			[Total: 7]	

2 Paramagnetism and diamagnetism are different forms of magnetism. Paramagnetic materials are weakly attracted by an externally applied magnetic field and form magnetic fields in the direction of the applied magnetic field. In contrast, diamagnetic materials are repelled from magnetic fields and form magnetic fields in the direction opposite to that of the applied magnetic field.

Transition metals are mostly paramagnetic or diamagnetic. The magnetic property is characterised by the presence of unpaired electrons in paramagnetic compounds and absence of unpaired electrons in diamagnetic compounds.

The table below shows the magnetic property of metal complexes.

Formula of complex	**Magnetic property of complex**
$Fe(CO)_5$	Paramagnetic
$[Fe(H_2O)_6]^{2+}$	Paramagnetic
$[Fe(H_2O)_6]^{3+}$	Paramagnetic
$[ZnCl_4]^{2-}$	Diamagnetic
$[V(H_2O)_6]^{3+}$	
$[Sc(H_2O)_3(OH)_3]$	

(a) **(i)** Write the electronic configurations of V in $[V(H_2O)_6]^{3+}$ and Sc in $[Sc(H_2O)_3(OH)_3]$. [2]

Sc^{3+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

V^{3+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2$

(ii) State the magnetic property of $[V(H_2O)_6]^{3+}$ and $[Sc(H_2O)_3(OH)_3]$ in the above table. [1]

$[V(H_2O)_6]^{3+}$: paramagnetic

$[Sc(H_2O)_3(OH)_3]$: diamagnetic

(iii) Draw labelled diagrams to show the shapes of the d orbitals of the metal ion in $[V(H_2O)_6]^{3+}$. Include the relative energy of the d-orbitals in the complex. [3]

Draw d_{xy}, d_{xz} and d_{yz}, stating that it is of lower energy and d_{x2-y2} and d_{z2} at higher energy

(iv) Explain why transition metal can show variable oxidation states. [1]

The electrons in the 3d and 4s subshells are similar in energy, thus different number of these electrons are available for use in bond formation / ions formed by using different number of electrons for bonding are of similar stability.

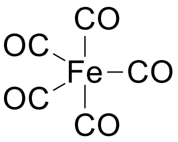
(b) Sodium reacts with iron pentacarbonyl to produce a salt known as sodium tetracarbonylferrate, $Na_2Fe(CO)_4$.

$$2Na + Fe(CO)_5 \longrightarrow Na_2Fe(CO)_4 + CO \text{ ------- eqn (1)}$$

(i) Explain what is meant by the coordination number of a complex using $Fe(CO)_5$ as an example. [1]

Co–ordination number is the number of dative bonds attached to the central atom or ion in a complex. In the case of $Fe(CO)_5$, there are 5 dative bonds formed between Fe atom and C of CO, thus, the coordination number of $Fe(CO)_5$ is 5.

(ii) Draw the structure of $Fe(CO)_5$ and state its shape. [2]



Shape: trigonal bipyramidal

(iii) Deduce the oxidising and reducing agent in eqn (1). [2]

Na is the reducing agent since itself is oxidised from Na to Na^+ in $Na_2Fe(CO)_4$, with an increase in oxidation number from 0 to +1.

$Fe(CO)_5$ is the oxidising agent since Fe is reduced with a decrease in oxidation number from 0 in $Fe(CO)_5$ to -2 in $Na_2Fe(CO)_4$.

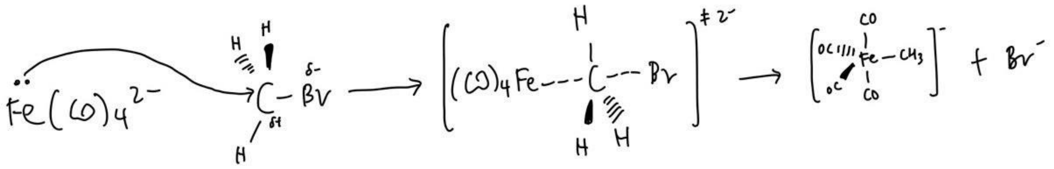
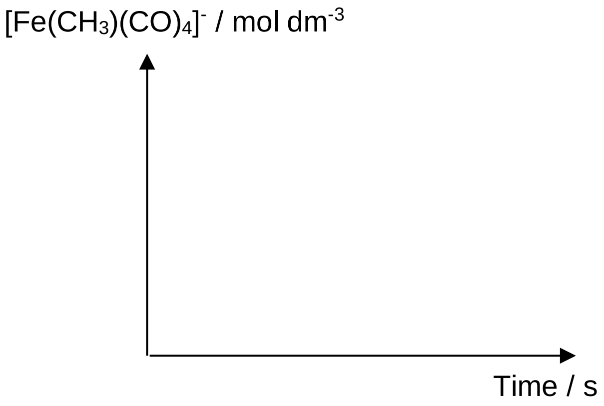
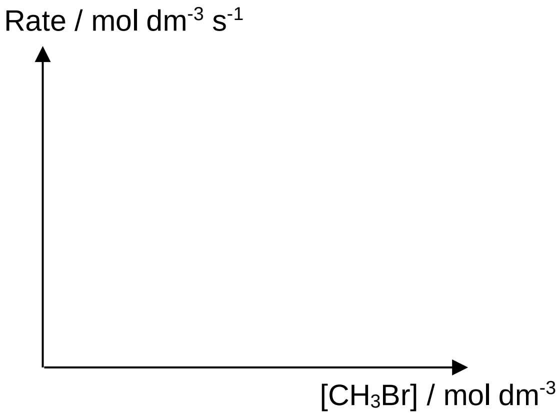
(iv) Explain why carbon monoxide, CO, is poisonous. [2]

CO competes with O_2 for bonding with haemoglobin as it enters into the bloodstream. Being a stronger ligand than O_2, CO will displace the weaker O_2 ligand in oxyhaemoglobin by forming a stronger dative bond with iron in haemoglobin, resulting in a more stable carboxyhaemoglobin complex. The formation of carboxyhaemoglobin complex is not readily reversible due to its stability, and this reduces the availability of haemoglobin for oxygen transport. Deprivation of oxygen causes damage to living organs and tissues, resulting in death. Hence, Co is poisonous.

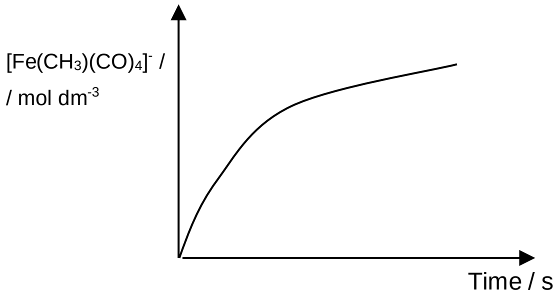
(v) The tetracarbonylferrate dianion acts as a nucleophile and react with alkyl halide by the S_N2 mechanism to form a new C-Fe bond.

$$[Fe(CO)_4]^{2-} + CH_3Br \longrightarrow [Fe(CH_3)(CO)_4]^- + Br^- \text{ ------- eqn (2)}$$

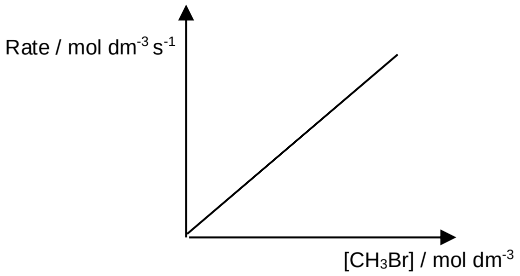
Suggest a mechanism between $Fe(CO)_4^{2-}$ and CH_3Br. State clearly any intermediates that may be formed and use curly arrows to indicate the movement of electron pairs. [3]

			S_N2 Nucleophilic Substitution (not included in marking point as question already states S_N2) 
		(vi)	State the rate equation for the reaction in eqn 2. [1]
			Rate = k $[CH_3Br][Fe(CO)_4{}^{2-}]$
		(vii)	**I** Sketch the graph of $[Fe(CH_3)(CO)_4]^-$ against time.  **II** Sketch the graph of rate against $[CH_3Br]$ given that $[Fe(CO)_4]^{2-}$ is in excess.  [2]

I:



II:



(c) The melting point of sodium tetracarbonylferrate, $Na_2Fe(CO)_4$ is lower than that of sodium oxide. With reference to the structure and bonding, explain the difference in melting point.[3]

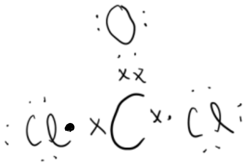
Both sodium oxide and $Na_2Fe(CO)_4$ have giant ionic lattice structure with strong electrostatic forces of attraction between oppositely charged ions. Both compounds have Na^+ as the cation. Since L.E$\propto\left|\frac{q^+q^-}{r^++r^-}\right|$ and $[Fe(CO)_4]^{2-}$ anion is larger than O^{2-} anion, the lattice energy of Na_2O is more exothermic than that of $Na_2Fe(CO)_4$. Thus, more energy is needed to overcome the stronger ionic bonds in Na_2O than $Na_2Fe(CO)_4$, thus $Na_2Fe(CO)_4$ has a lower melting point.

[Total: 23]

3 **(a)** Phosgene, $COCl_2$, is essential in the manufacturing of everyday products, including medical products and footwear. Phosgene is produced by combining carbon monoxide and chlorine with a catalyst.

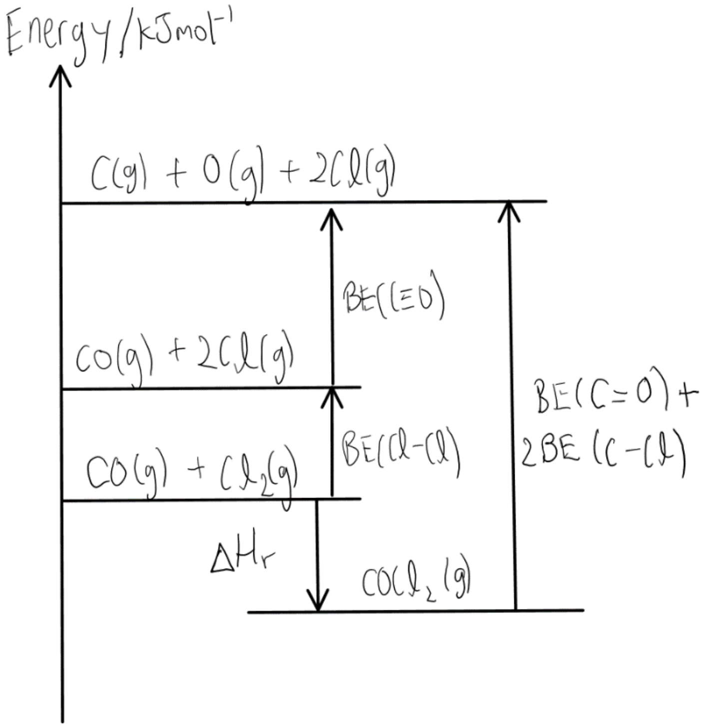
$$CO(g) + Cl_2(g) \rightarrow COCl_2(g)$$

(i) Draw a 'dot-and-cross' diagram of $COCl_2$ and state the bond angle about the central atom. [2]



Bond angle: 120°

(ii) Using relevant data from the *Data Booklet*, construct a fully labelled energy level diagram to calculate the enthalpy change of the above reaction. [3]



ΔH_r = 244 + 1077 – (740 + 2(340)) = -99 kJ mol^{-1}

(iii) Explain what is meant by the term entropy of a chemical system. [1]

Entropy measures the amount of disorderliness in a system.

3 **(iv)** Predict, with reasons, the sign of the entropy change of the reaction between CO(g) and Cl_2(g) to form $COCl_2$. [2]

Entropy change of the reaction should be negative, as the number of moles of gas decreases from 2 moles to 1 mole, there are less ways of arranging the particles, hence the system decreases in disorderness.

(v) Hence, state and explain the significance of the sign of the standard Gibbs free energy change when temperature is low. [2]

$\Delta G = \Delta H - T\Delta S$, standard Gibbs free energy change should be negative at low temperature, since the enthalpy change is negative, and entropy change is negative. $|T\Delta S| < |\Delta H|$. Thus, the reaction is spontaneous at low temperature.

(b) Above 200°C, a 2.0 dm^3 cylinder containing gaseous phosgene decomposes to carbon monoxide and chlorine in a dynamic equilibrium according to the following equation:

$$COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$$

(i) Predict and explain the effect of a catalyst on the position of the above equilibrium. [1]

No change in the position of equilibrium since the catalyst increases the rate of both the forward and backward reaction to the same extent.

(ii) At 350°C, the percentage dissociation of $COCl_2$ is found to be 45% and the total pressure at equilibrium is 3.5 atm. Calculate the value of K_p at 350 °C. [3]

	$COCl_2(g)$	$\rightleftharpoons$	$CO(g)$	+	$Cl_2(g)$
Initial pressure/ atm	a		0		0
Change in pressure / atm	-0.45a		+0.45a		+0.45a
Equilibrium pressure / atm	0.55a		0.45a		0.45a

0.55a + 0.45a + 0.45a = 3.5 atm

a = 2.414

$K_p = \frac{(2.414\times0.45)^2}{(2.414\times0.55)} = 0.889$ atm

(iii) Calculate the mass of the carbon monoxide gas that exists inside the cylinder at 350°C. [2]

pV = m/Mr RT

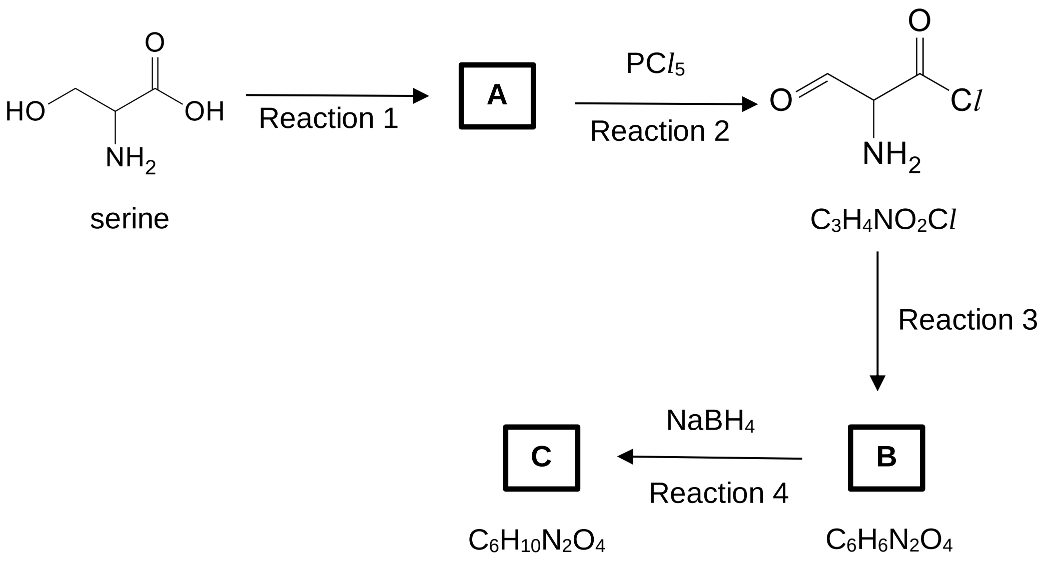
$(2.41 \times 0.45) \times 101325 \times 2.0 \times 10^{-3} = (m / 28)(8.31)(350 + 273)$

M = 1.19 g

[Total: 16]

4 Spider silk is a protein fibre. Major amino acids in the silk protein are alanine, serine and glycine.

The following reaction scheme involves serine as a starting material.

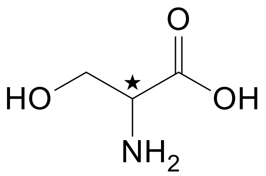


(a) Explain what is meant by a chiral centre.

Label with an asterisk (*) for any chiral centre that is present in serine. [2]

A chiral centre exists when a molecule has at least one asymmetric carbon atom where the carbon atom is bonded to 4 different substituents.

Serine has a chiral carbon.

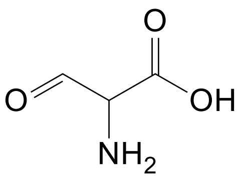


(b) Name the functional group common to compounds **B** and **C**. [1]

Secondary Amide

(c) Draw the structure of compound **A** in the box and state the reagents and conditions for reaction 1. [2]

A:



Dilute $K_2Cr_2O_7$, $H_2SO_4(aq)$, heat with immediate distillation

(d) Name the type of reaction for reactions 2, 3 and 4. [3]

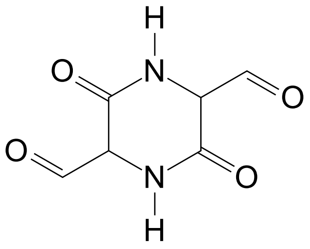
Reaction 2: nucleophilic substitution

Reaction 3: condensation / nucleophilic substitution

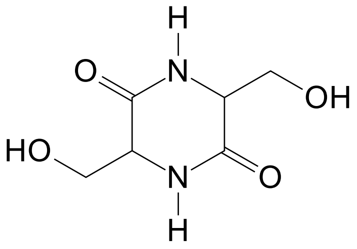
Reaction 4: Reduction

(e) Draw the structures of compound **B** and **C** in the box. [2]

B:



C:



(f) The following table contains the pK_a values of different compounds.

Compound	**pK_a**
Serine	2.21
Propanoic acid	4.87
Phenol	9.95

(i) Suggest a reason why pK_a of propanoic acid is higher than serine. [2]

The NH_2 group in serine exerts an electron-withdrawing effect, pulling electrons away from the O atom of the carboxylate salt, dispersing the negative charge and making the carboxylate ion more stable. Thus, serine is more acidic than propanoic acid and has a lower pK_a value.

(ii) Suggest a reason why pK_a of propanoic acid is lower than phenol. [2]

For the propanoate ion, there is a delocalisation of the negative charge over the two oxygen atoms. This disperses the negative charge and stabilises the anion. For the phenoxide ion, the p-orbital of oxygen overlaps with the π orbital of the benzene ring and this delocalises the negative charge on the oxygen atom into the benzene ring. However, this delocalisation is not as effective as that of the carboxylate ion as the carbon atoms are not very electronegative compared to oxygen atoms. Hence phenol is less acidic than propanoic acid.

[Total: 14]

5	**(a)**		**X** and **Y** are two different elements in Period 3. The following are some of their properties: - Oxide of **X** is insoluble in water while the aqueous solution of chloride of **X** is weakly acidic. - Element **Y** conducts electricity and has a lower melting point than element **X**. - The first ionisation energy of element **X** is lower than that of element **Y**.
		(i)	Identify the elements, **X** and **Y**. [2]
			X: aluminium Y: Magnesium
		(ii)	Write the balanced equation(s) for the reaction when chloride of **X** dissolves in water and state the pH of the solution. [2]
			$AlCl_3\,(s) + 6\,H_2O(l) \rightarrow [Al(H_2O)_6]^{3+}\,(aq) + 3Cl^-\,(aq)$ $[Al(H_2O)_6]^{3+}(aq) \rightarrow [Al(H_2O)_5(OH)]^{2+}\,(aq) + H^+\,(aq)$ pH = 3
		(iii)	Explain why oxide of **X** is insoluble in water. [1]
			Energy released from the ion-dipole interaction between Al^{3+} and O^{2-} and water is insufficient to overcome the high strong electrostatic forces of attraction between oppositely charged ions in Al_2O_3.
		(iv)	Explain why element **Y** has a lower melting point than element **X**. [2]
			Both X and Y has giant metallic lattice structure with strong electrostatic forces of attraction between the positively charged ions and sea of delocalised electrons. Since Al has more delocalised electrons than Mg (or Al^{3+} has a higher charge density than Mg^{2+}), more energy is needed to overome the stronger electrostatic forces of attraction in Al than in Mg. Thus, Mg (element Y) has a lower melting point.
		(v)	Explain why the first ionisation energy of element **X** is lower than that of element **Y**. [2]
			Less energy is required to remove an electron from the 3p orbital in Al than to remove an electron from the 3s orbital in Mg as the 3p electron is further away from the nucleus and experiences greater screening than 3s electron.

(b) Sulfur is another period 3 element with a relative atomic mass of 32.09.

There are three naturally occurring isotopes. The relative abundances of the isotopes of sulfur are found to be the following.

Isotope	**% Abundance**
^{32}S	95.0
^{33}S	*a*
^{34}S	*b*

(i) Define the term *relative atomic mass*. [1]

Relative atomic mass (A_r) is defined as the weighted average mass of the isotopes of an element compared to $\frac{1}{12}$ of the mass of one atom of ^{12}C.

(ii) Calculate the percentage abundances of isotopes ^{33}S and ^{34}S. [2]

32.09 = 0.95(32) + 33(a/100) + 34(100-95-a/100)

a = 1.0 %

b = 4.0 %

(c) A 2.00 g sample of food additive containing magnesium carbonate is allowed to react with 50 cm^3 of 0.200 mol dm^{-3} aqueous hydrochloric acid. The excess acid required 19.30 cm^3 of 0.100 mol dm^{-3} aqueous potassium hydroxide for complete reaction.

Calculate the percentage of magnesium carbonate that is present in the food additive. [3]

$MgCO_3 + 2HCl \rightarrow MgCl_2 + H_2O + CO_2$

$KOH + HCl \rightarrow NaCl + H_2O$

Amount of initial HCl = 50/1000 x 0.2 = 0.01 mol

Amount of HCl in excess = 19.3/1000 x 0.1 = 0.00193 mol

Amount of reacted HCl = 0.01 - 0.00193 = 0.00807 mol

Amount of $MgCO_3$ = 0.00807/2 = 0.004035 mol

Mass of $MgCO_3$ = 0.004035 x (24.3 + 12 + 48) = 0.340 g

Percentage of magnesium carbonate = 0.34/2 x 100 = 17.0 %

[Total: 15]

END OF PAPER 2

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Class	Adm No

Candidate Name: ____________________

H

millennia institute

2019 Preliminary Exams

Pre-University 3

H2 CHEMISTRY **9729/03**

Paper 3 Free Response **20 Sept 2019**

2 hours

Candidates answer on separate paper.

Additional materials: Answer Paper
Data Booklet
Graph Paper

READ THESE INSTRUCTIONS FIRST

Do not turn over this question paper until you are told to do so

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

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

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

Section A
Answer **all** questions.

Section B
Answer **one** question.

A Data Booklet is provided.

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

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

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.

Question	**Section A**			**Section B**		Total
	1	**2**	**3**	**4**	**5**	
Marks	**19**	**19**	**22**	**20**	**20**	**80**

This question paper consists of **9** printed pages and **1** blank page.

Section A

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

1 **(a)** 3–chloropropanoic acid, $CH_2ClCH_2CO_2H$, is a weak Brønsted acid. A 0.100 mol dm^{-3} solution of $CH_2ClCH_2CO_2H$ has a pH of 2.49.

(i) Calculate the pK_a of 3–chloropropanoic acid. [3]

(ii) State and explain the differences in the relative acid strength between 3–chloropropanoic acid and propanoic acid. [2]

(iii) 3-chloropropanoyl bromide is the acid derivative of 3–chloropropanoic acid. Propose a 3-step synthetic route for the formation of 3-chloropropanoyl bromide, using 3-hydroxypropanal as the starting reagent. State clearly the reagents and conditions used for each step. [5]

(b) A student investigated the rate of reaction between 3–chloropropanoic acid and aqueous sodium carbonate. The rate of the reaction may be determined by measuring how long it takes for the gas to be completely released.

A series of experiments were carried out to study the order of reaction with respect to 3–chloropropanoic acid and sodium carbonate. The following results were obtained.

Experiment Number	Volume / cm^3			Time / s
	3–chloropropanoic acid	Na_2CO_3	H_2O	
1	20.0	40.0	40.0	78
2	20.0	30.0	50.0	100
3	5.0	20.0	25.0	75

(i) Write an equation, including state symbols, for the reaction between sodium carbonate and 3–chloropropanoic acid. [1]

(ii) State the relationship between time and rate. [1]

(iii) Determine the order of the reaction with respect to 3–chloropropanoic acid and sodium carbonate. [2]

(iv) Hence, write the rate equation, stating the units of k. [2]

(v) With the aid of an appropriate diagram, explain how the addition of a catalyst can increase the rate of a reaction between 3–chloropropanoic acid and sodium carbonate. [3]

[Total: 19]

2 **(a)** Using only the elements C, H and O, draw the structural formulae of **two** different **organic** compounds, each containing a **single** carbon atom, with an oxidation state of 0 and +2 respectively. [2]

(b) A symmetrical organic compound **A**, $C_2H_4N_2O_2$, upon reacting with hot dilute NaOH(aq) produces a colourless, pungent gas that turns moist red litmus paper blue.

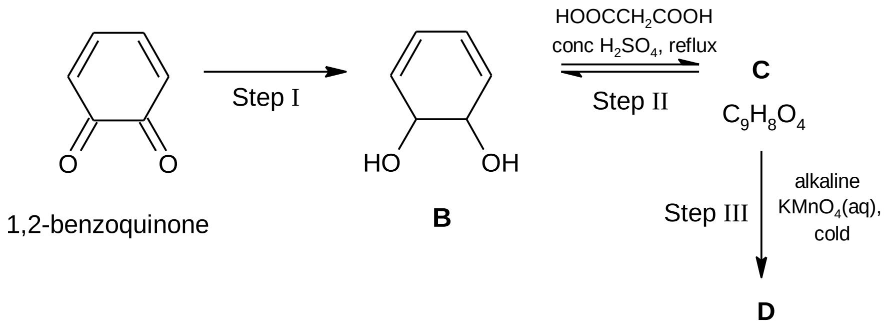
(i) Draw the structure of compound **A** and state the functional group present. [2]

(ii) The functional group present in compound **A** can be reduced by lithium aluminium hydride, $LiA\mathit{l}H_4$. Draw the dot-and-cross diagram for $LiA\mathit{l}H_4$. [1]

(iii) Other than $LiA\mathit{l}H_4$, $NaBH_4$ can also be used for the reduction of certain functional groups. $LiA\mathit{l}H_4$ is able to produce hydride ion, H^- more readily than $NaBH_4$. Suggest why $LiA\mathit{l}H_4$ is a more powerful reducing agent than $NaBH_4$. [1]

(c) Quinones are used in photography as a reducing agent. Quinone compounds are multifunctional as they exhibit properties of both ketones and alkenes.

The following scheme involves 1, 2-benzoquinone, where step I involves the use of $LiA\mathit{l}H_4$.

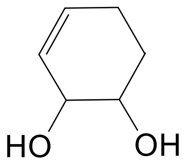


(i) Draw the structures of **C** and **D**. [2]

(ii) Identify the chiral centres on **B**. Hence, explain why it does not display optical activity.[2]

(iii) Using a simple chemical test, suggest how 1,2-benzoquinone can be distinguished from compound **B**. In your answer, state all reagents and conditions used and the expected observations. [2]

(iv) When compound **B** undergoes partial hydrogenation, it forms compound **E**.



E

Describe the mechanism of the reaction when compound **E** reacts with Br_2 in CCl_4 in the dark. In your answer, show all relevant charges and movement of electrons clearly. [3]

(d) $K_2Cr_2O_7$ and $KMnO_4$ are common oxidising agents used in organic synthesis where $KMnO_4$ is the more powerful of the two. Compound **F**, C_4H_8O, reacted with $K_2Cr_2O_7$ and $KMnO_4$ separately to yield different products as shown in the reactions below.

$$\underset{\textbf{F}}{C_4H_8O} \xrightarrow[K_2Cr_2O_7/H_2SO_4]{} \underset{\textbf{G}}{C_4H_6O_2}$$

$$\underset{\textbf{F}}{C_4H_8O} \xrightarrow[KMnO_4/H_2SO_4]{} \underset{\textbf{H}}{C_2H_4O_2}$$

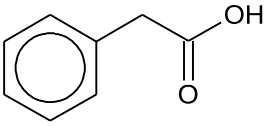
Given the following information,

- All three compounds, **F**, **G** and **H** react with sodium metal.
- **G** and **H** react with Na_2CO_3, but **F** does not.
- **F** and **G** decolourise aqueous bromine.

Suggest the structures of compounds **F**, **G** and **H**, explaining the chemistry involved. [4]

[Total: 19]

3 **(a)** Phenylethanoic acid is used as a treatment for hyperammonemia, a condition where there is an accumulation of ammonia in the human body.



phenylethanoic acid

(i) In an experiment, 60 cm^3 of 0.10 mol dm^{-3} of sodium hydroxide was added to 20 cm^3 of 0.20 mol dm^{-3} of phenylethanoic acid in a conical flask. Calculate the pH of the final solution when all 60 cm^3 of sodium hydroxide was added to the flask. [3]

(ii) 2-amino-2-phenylethanoic acid can be synthesised from phenylethanoic acid through a series of substitution reactions.

Draw the displayed formula of 2-amino-2-phenylethanoic acid. [1]

(iii) Write two equations to show how an aqueous solution of 2-amino-2-phenylethanoic acid is able to resist the change in pH upon addition of small amounts of acid and base. [2]

(iv) Draw the structure of the predominant form when 2-amino-2-phenylethanoic acid is in an aqueous solution of pH 10. [1]

(b) **(i)** Predict and explain whether phenylethanoyl chloride or phenylethanoic acid has a higher reactivity towards nucleophilic reagents. [2]

(ii) Given that phenylethanoyl chloride has a boiling point of 95 °C and phenylethanoic acid has a boiling point of 266 °C, explain this difference in terms of structure and bonding. [2]

(iii) State the number of sp^2 and sp^3 hybridised carbon atoms found in one molecule of phenylethanoic acid. [1]

(iv) State the number of sigma and pi bonds in one molecule of phenylethanoic acid. [1]

(c) Acid chloride reacts instantly with cold water. The reaction is very exothermic in which steamy white fumes of hydrogen chloride gas are released and the carboxylic acid is formed. The mechanism of the reaction takes place in two stages as described below.

First stage

- The lone pair on the oxygen atom of water molecule attacks the electron deficient carbon atom of the acid chloride, causing the π bond of the C=O bond to break.

Second stage

- The carbon-oxygen double bond reforms and a chloride ion is released.
- As a result, a hydrogen ion is removed by the chloride ion to give the carboxylic acid and hydrogen chloride.

(i) Using ethanoyl chloride as an example, illustrate the mechanism of the reaction when ethanoyl chloride reacts with cold water. [3]

(ii) State the type of reaction occurring in the first stage of the mechanism. [1]

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

Suggest the structures of compounds **Y** and **Z**. Explain your answers. [5]

[Total: 22]

Section B

Answer **one** question from this section.

4 **(a)** Nickel is a transition metal and can exhibit variable oxidation states. The reducing power of Ni can be determined through its oxidation to Ni^{2+}.

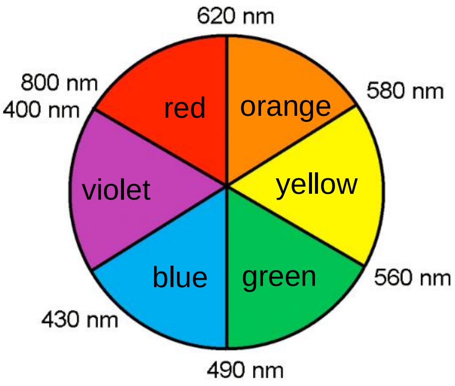
(i) Define the term *standard electrode potential*. [1]

(ii) Draw a fully labelled diagram of the electrochemical cell that you would set up in order to measure the standard reduction potential of Ni^{2+}/Ni under standard conditions. [3]

(iii) Hence or otherwise, suggest what happens to the value of the voltmeter reading when a more concentrated nickel(II) solution is used in part **(ii)**. [1]

(iv) An electrolytic cell contains $Ni(NO_3)_2$ and $Mn(NO_3)_2$ in an aqueous electrolyte uses graphite as the electrodes. Determine the products discharged at the cathode and anode and write the overall balanced equation for the electrolytic cell. [3]

(b) Aqueous nickel salts are coloured. $[Ni(NH_3)_6]^{2+}$ ions absorb at 600 nm, whereas $[NiCl_4]^{2-}$ ions absorbed at 420 nm. The colour and the respective wavelengths are given in the colour wheel below.



(i) State the oxidation number of nickel in $[NiCl_4]^{2-}$. [1]

(ii) Suggest the colour of:
I: $[Ni(NH_3)_6]^{2+}$
II: $[NiCl_4]^{2-}$ [2]

(iii) Explain why the two complexes are coloured. [3]

(c) The stability of complexes can be determined by the stability constant of the complexes. Consider the formation of $[Ni(NH_3)_6]^{2+}$ from $[Ni(H_2O)_6]^{2+}$. The stability constant, K_{stab}, is given by

$$K_{stab} = \frac{[[Ni(NH_3)_6]^{2+}]}{[[Ni(H_2O)_6]^{2+}][NH_3]^6}$$

Complex	Stability constant
$Ni(H_2O)_6]^{2+} + 6NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+} + 6H_2O$	4.8×10^7
$Ni(H_2O)_6]^{2+} + 3\ en \rightleftharpoons [Ni(en)_3]^{2+} + 6H_2O$	2.0×10^{18}

State and explain if the en ligand will replace the NH_3 ligand for the nickel complexes. [2]

(d) **(i)** The coordination compound $NiCl_2(H_2O)_4$ has an octahedral geometry. Draw and identify the type of isomerism present in the compound. [2]

(ii) Explain why $[Ni(en)_3]Cl_2$ can dissolve in water. [2]

[Total: 20]

5 **(a)** **(i)** State the structure and describe the bonding present in the chlorides of sodium and aluminium respectively. [2]

(ii) Construct a fully labelled energy level diagram for the formation of sodium chloride using the following values and relevant values from the *Data Booklet* and calculate the standard enthalpy change of formation of sodium chloride. [3]

Thermochemical term	**ΔH / kJ mol^{-1}**
Lattice energy of NaC*l*(s)	-788
Enthalpy change of atomisation of Na(s)	+108
First electron affinity of Cl(g)	-349

(iii) Describe what happens when the chlorides of aluminium and silicon are dissolved in water. Write the relevant equations and state the observation when Universal Indicator is added. [4]

(b) The reactions of different halogens with hydrogen differ due to their reactivity.
Explain the relative stability of the hydrogen halides with reference to the Data Booklet. [3]

(c) The iodine clock reaction involves 2 reactions.
First reaction involves peroxydisulfate ($S_2O_8^{2-}$) and excess iodide ions. The second reaction involves thiosulfate ($S_2O_3^{2-}$) ion reacting with the iodine produced.

(i) Write the equations for the two reactions of the clock reaction. [2]

(ii) If 30 cm^3 of 0.002 mol dm^{-3} of $S_2O_3^{2-}$ is used in the reaction, determine the mass of potassium peroxydisulfate needed for the first step. [2]

(iii) Iron(II) ions are sometimes added to the reaction between peroxydisulfate and iodide. Write the equations to show how iron(II) ions aid in speeding up the rate of reaction. [2]

(d) Iron is also used in other reactions, such as the Haber Process.
State the role of iron in the Haber Process and explain why iron is suitable for this role. [2]

[Total: 20]

END OF PAPER 3

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Class Adm No

Candidate Name: ____________________

H

millennia institute

2019 Preliminary Exams

Pre-University 3

H2 CHEMISTRY **9729/03**

Paper 3 Free Response **20 Sept 2019**

2 hours

Candidates answer on separate paper.

Additional materials: Answer Paper
Data Booklet
Graph Paper

READ THESE INSTRUCTIONS FIRST

Do not turn over this question paper until you are told to do so

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

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

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

Section A
Answer **all** questions.

Section B
Answer **one** question.

A Data Booklet is provided.

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

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

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.

Question	Section A			Section B		Total
	1	**2**	**3**	**4**	**5**	
Marks	**19**	**19**	**22**	**20**	**20**	**80**

This question paper consists of **11** printed pages and **1** blank page.

Section A

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

1 **(a)** 3–chloropropanoic acid, $CH_2C\mathit{l}CH_2CO_2H$, is a weak Brønsted acid. A 0.100 mol dm^{-3} solution of $CH_2C\mathit{l}CH_2CO_2H$ has a pH of 2.49.

(i) Calculate the pK_a of 3–chloropropanoic acid. [3]

Since pH = 2.49, $[H^+] = 10^{-2.49}$

$$K_a = \frac{[CH_2C\mathit{l}CH_2CO_2^-][H^+]}{[CH_2C\mathit{l}CH_2CO_2H]}$$

$$= \frac{[10^{-2.49}][10^{-2.49}]}{[0.100]}$$

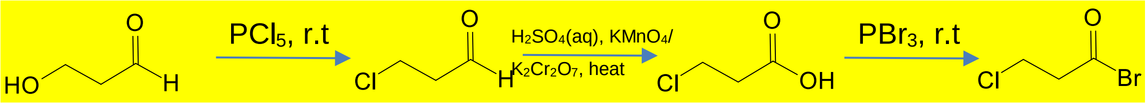
$$= 1.05 \times 10^{-4}$$

$pK_a = -\lg(1.05 \times 10^{-4}) = 3.98$

(ii) State and explain the differences in the relative acid strength between 3–chloropropanoic acid and propanoic acid. [2]

3–chloropropanoic acid is a stronger acid than propanoic acid. Due to the presence of the electron withdrawing group, C*l*, the negative charge of O on the carboxylate anion is dispersed. ; This causes the conjugate base of 3–chloropropanoic acid to be more stable. Hence, acidity increases. ;

(iii) 3-chloropropanoyl bromide is the acid derivative of 3–chloropropanoic acid. Propose a 3-step synthetic route for the formation of 3-chloropropanoyl bromide, using 3-hydroxypropanal as the starting reagent. State clearly the reagents and conditions used for each step. [5]



1m x 3 reagents and conditions

1m x 2 correct intermediates

(b) A student investigated the rate of reaction between 3–chloropropanoic acid and aqueous sodium carbonate.

The rate of the reaction may be determined by measuring how long it takes for the gas to be completely released.

A series of experiments were carried out to study the order of reaction with respect to 3–chloropropanoic acid and sodium carbonate. The following results were obtained.

Experiment Number	Volume / cm^3			Time / s
	3–chloropropanoic acid	Na_2CO_3	H_2O	
1	20.0	40.0	40.0	78
2	20.0	30.0	50.0	100
3	5.0	20.0	25.0	75

(i) Write an equation, including state symbols, for the reaction between sodium carbonate and 3–chloropropanoic acid. [1]

$2CH_2C\mathit{l}CH_2CO_2H(aq) + Na_2CO_3(aq) \rightarrow 2CH_2C\mathit{l}CH_2CO_2^-Na^+(aq) + CO_2(g) + H_2O(\mathit{l})$

(ii) State the relationship between time and rate. [1]

Inverse relationship

(iii) Determine the order of the reaction with respect to 3–chloropropanoic acid and sodium carbonate. [2]

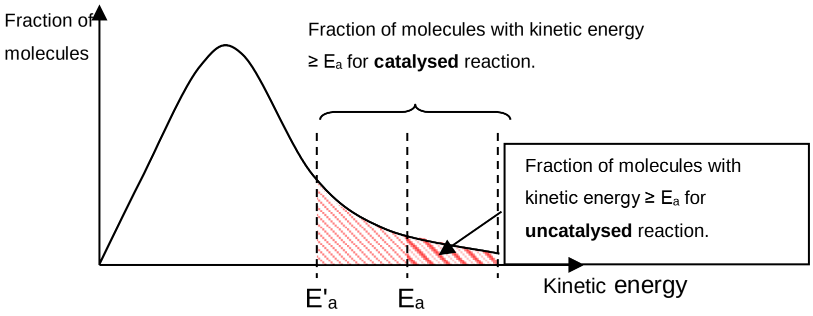
Comparing Expt 1 and 2, while volume of 3–chloropropanoic acid is kept constant and volume of Na_2CO_3 is 4/3 times, rate is 100/78 times. Order with respect to Na_2CO_3 is 1.

Comparing Expt 1 and 3, while volume of Na_2CO_3 is kept constant after multiplying the volume by two, volume of 3–chloropropanoic acid is halved, rate stays relatively constant. Order with respect to 3–chloropropanoic acid is 0.

(iv) Hence, write the rate equation, stating the units of k. [2]

Rate = $k[Na_2CO_3]$
$k = s^{-1}$

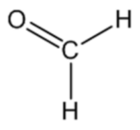
(v) With the aid of an appropriate diagram, explain how the addition of a catalyst can increase the rate of a reaction between 3–chloropropanoic acid and sodium carbonate. [3]



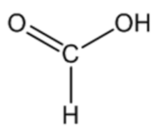
A catalyst provides an alternative pathway for the reaction, lowering the activation energy required. Hence, there is a greater fraction of molecules with energy greater than activation energy. Frequency of effective collisions increases, leading to increase rate of reaction. (2m for diagram, 1m for explanation)

[Total: 19]

2 **(a)** Using only the elements C, H and O, draw the structural formulae of **two** different **organic** compounds, each containing a **single** carbon atom with an oxidation state of 0 and +2 respectively. [2]



O.S. = 0



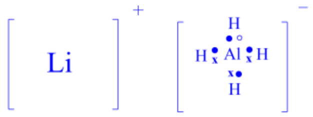
O.S. = +2

(b) A symmetrical organic compound **A**, $C_2H_4N_2O_2$, upon reacting with hot dilute NaOH(aq) produces a colourless, pungent gas that turns moist red litmus paper blue.

(i) Draw the structure of compound **A** and state the functional group present. [2]

$(CONH_2)_2$, amide

(ii) The functional group present in compound **A** can be reduced by lithium aluminium hydride, $LiAlH_4$. Draw the dot-and-cross diagram for $LiAlH_4$. [1]



(iii) Other than $LiAlH_4$, $NaBH_4$ can also be used for the reduction of certain functional groups. $LiAlH_4$ is able to produce hydride ion, H^- more readily than $NaBH_4$. Suggest why $LiAlH_4$ is a more powerful reducing agent than $NaBH_4$. [1]

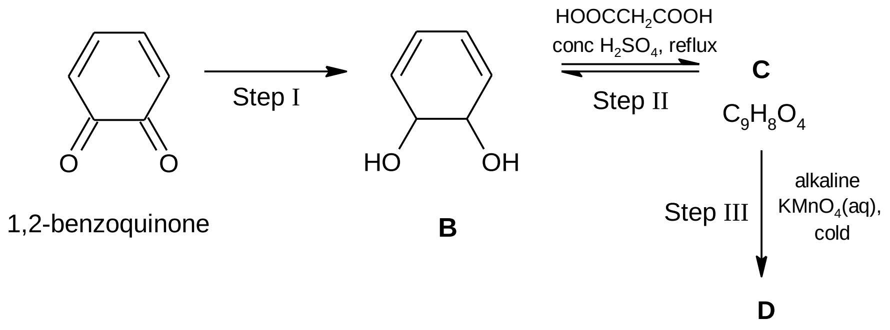
The electronegativity of Al is lesser than that of B. Hence, H bonded to Al can produce H^- more readily than H bonded to B. Thus, reduction occurs more readily for $LiAlH_4$, proving that it is a stronger reducing agent.

OR

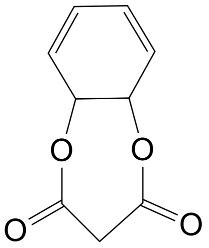
The size of A*l* atom is larger compared to B, thus the orbital overlap between A*l* and H is less effective. Therefore the bond length of A*l*–H bond is longer than that of B–H bond. ; Less energy is required to break the weaker A*l*–H bond, resulting in a greater ease of generating H^- for the reduction process.

(c) Quinones are used in photography as a reducing agent. Quinone compounds are multifunctional as they exhibit properties of both ketones and alkenes.

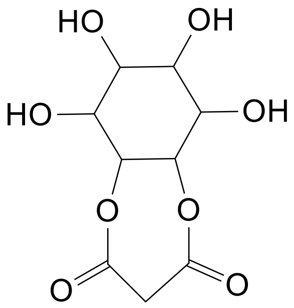
The following scheme involves 1, 2-benzoquinone, where step I involves the use of $LiAlH_4$.



(i) Draw the structures of **C** and **D**. [2]

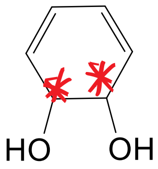


C



D

(ii) Identify the chiral centres on **B**. Hence, explain why it does not display optical activity.[2]



It does not display optical activity as there is a plane of symmetry in the compound.

(iii) Using a simple chemical test, suggest how 1,2-benzoquinone can be distinguished from compound **B**. In your answer, state all reagents and conditions used and the expected observations. [2]

2,4-DNPH, warm.

Orange ppt observed for 1,2-benzoquinone, no orange ppt observed for **B**.

OR

PCl_5, r.t.

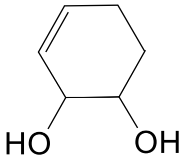
White fumes observed for **B**, no white fumes observed for 1,2-benzoquinone.

OR

$K_2Cr_2O_7/H_2SO_4$(aq), heat.

Orange $K_2Cr_2O_7$ turns green for **B**, orange $K_2Cr_2O_7$ remains orange for 1,2-benzoquinone.

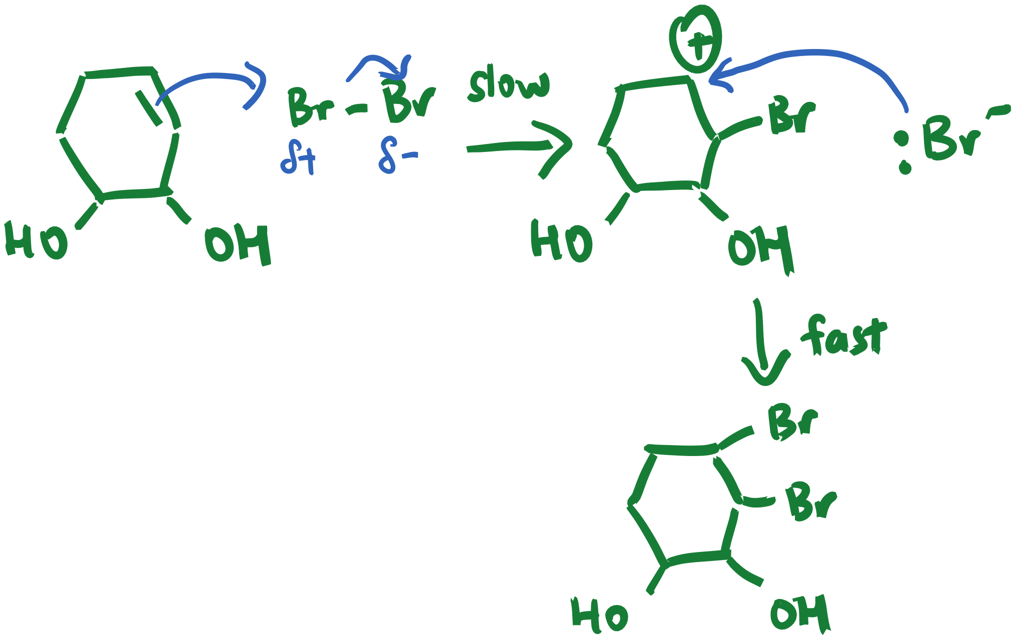
(iv) When compound **B** undergoes partial hydrogenation, it forms compound **E**.



E

Describe the mechanism of the reaction when compound **E** reacts with Br_2 in CCl_4 in the dark. In your answer, show all relevant charges and movement of electrons clearly. [3]

Electrophilic addition



1m for correct intermediate, 1m for name of mechanism, 1m for correct movement of electrons

(d) $K_2Cr_2O_7$ and $KMnO_4$ are common oxidising agents used in organic synthesis where $KMnO_4$ is the more powerful of the two. Compound **F**, C_4H_8O, reacted with $K_2Cr_2O_7$ and $KMnO_4$ separately to yield different products as shown in the reactions below.

$$\underset{\textbf{F}}{C_4H_8O} \xrightarrow[K_2Cr_2O_7/H_2SO_4]{} \underset{\textbf{G}}{C_4H_6O_2}$$

$$\underset{\textbf{F}}{C_4H_8O} \xrightarrow[KMnO_4/H_2SO_4]{} \underset{\textbf{H}}{C_2H_4O_2}$$

Given the following information,

- All three compounds, **F**, **G** and **H** react with sodium metal.
- **G** and **H** react with Na_2CO_3, but **F** does not.
- **F** and **G** decolourise aqueous bromine.

Suggest the structures of compounds **F**, **G** and **H**, explaining the chemistry involved. [4]

F: $CH_3CH{=}CHCH_2OH$;

G: $CH_3CH{=}CHCOOH$;

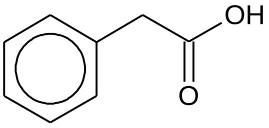
H: CH_3COOH ;

1m for explanation

All three compounds, **F**, **G** and **H** react with sodium metal	All 3 compounds contain the -OH functional group
G and **H** react with Na_2CO_3, but **F** does not	Presence of carboxylic acid in C and D
F and **G** decolourise aqueous bromine.	Presence of alkene

[Total: 19]

3 **(a)** Phenylethanoic acid is used as a treatment for hyperammonemia, a condition where there is an accumulation of ammonia in the human body.



phenylethanoic acid

(i) In a titration experiment, 60 cm^3 of 0.10 mol dm^{-3} of sodium hydroxide was added to 20 cm^3 of 0.20 mol dm^{-3} of phenylethanoic acid in a conical flask. Calculate the pH of the final solution when all 60 cm^3 of sodium hydroxide was added to the flask. [3]

Amount of acid present = 20/1000 x 0.2 = 0.004 mol

Volume of NaOH required at equivalence point = 0.004 / 0.1 = 40 cm^3 ;

When 60 cm^3 of NaOH is added:

$$[OH^-] = [NaOH] = \frac{\text{moles of excess NaOH}}{\text{new volume of solution}} = \frac{[(60 - 40)/1000] \times 0.10}{(20 + 60)/1000}$$

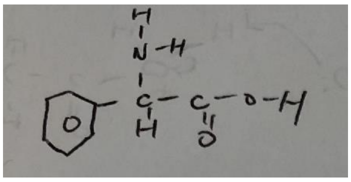
= 0.0250 mol dm^{-3} ;

pOH = - $\log_{10}$ 0.0250 = 1.60

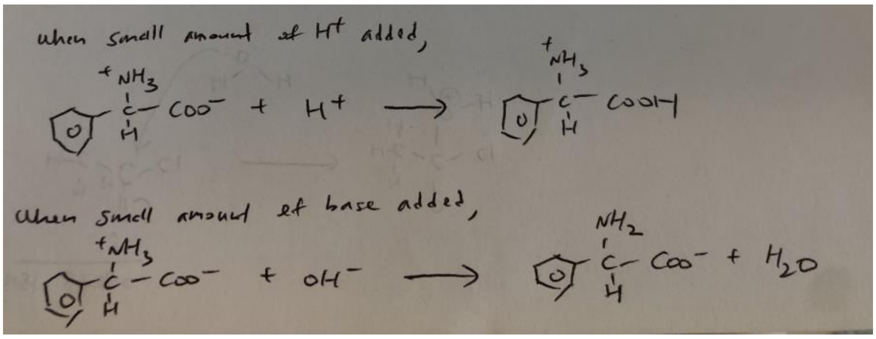
pH = 14 – pOH = 14 – 1.60 = 12.4 ;

(ii) 2-amino-2-phenylethanoic acid can be synthesised from phenylethanoic acid through a series of substitution reactions.

Draw the displayed formula of 2-amino-2-phenylethanoic acid. [1]



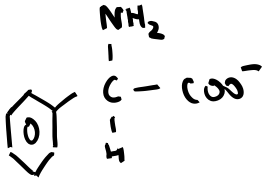
(iii) Write two equations to show how an aqueous solution of 2-amino-2-phenylethanoic acid is able to resist the change in pH upon addition of small amounts of acid and base. [2]



when small amount of H+ added,

when small amount of base added,

(iv) Draw the structure of the predominant form when 2-amino-2-phenylethanoic acid is in an aqueous solution of pH 10. [1]



(b) **(i)** Predict and explain whether phenylethanoyl chloride or phenylethanoic acid has a higher reactivity towards nucleophilic reagents. [2]

Phenylethanoyl chloride is more reactive as the reactive carbon is more electron deficient since it is attached to two highly electronegative atoms (Cl and O) which results in the nucleophiles to attack it more readily.

(ii) Given that phenylethanoyl chloride has a boiling point of 95 °C and phenylethanoic acid has a boiling point of 266 °C, explain this difference in terms of structure and bonding. [2]

Phenylethanoic acid will have a higher boiling point ; due to the presence of strong intermolecular hydrogen bonding between its molecules, compared to the weaker permanent dipole-permanent dipole forces of attraction between molecules of phenylethanoyl chloride. ; More energy is required to overcome the stronger H-bonding between phenylethanoic acid, resulting in a higher boiling point.

(iii) State the number of sp^2 and sp^3 hybridised carbon atoms found in one molecule of phenylethanoic acid. [1]

7 sp^2 and 1 sp^3 C

(iv) State the number of sigma and pi bonds in one molecule of phenylethanoic acid. [1]

18 sigma and 4 pi

(c) Acid chloride reacts instantly with cold water. The reaction is very exothermic in which steamy white fumes of hydrogen chloride gas are released and the carboxylic acid is formed. The mechanism of the reaction takes place in two stages as described below.

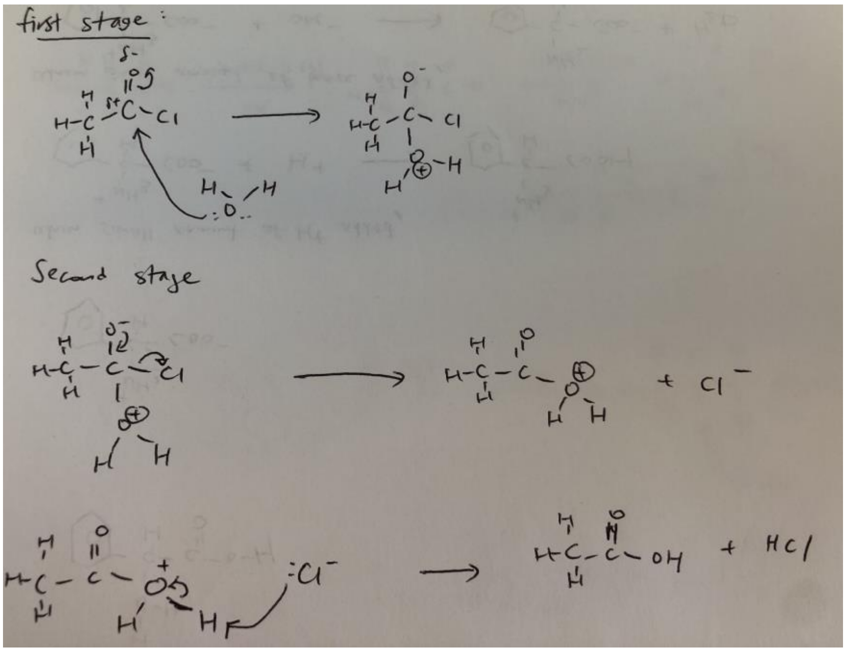
First stage

- The lone pair on the oxygen atom of water molecule attacks the electron deficient carbon atom of the acid chloride, causing the π bond of the C=O bond to break.

Second stage

- The carbon-oxygen double bond reforms and a chloride ion is released.
- As a result, a hydrogen ion is removed by the chloride ion to give the carboxylic acid and hydrogen chloride.

(i) Using ethanoyl chloride as an example, illustrate the mechanism of the reaction when ethanoyl chloride reacts with cold water. [3]



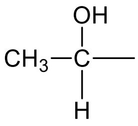
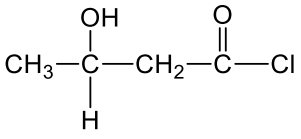
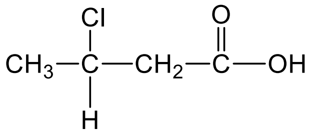
1m for each step

(ii) State the type of reaction occurring in the first stage of the mechanism. [1]

Nucleophilic addition

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

Suggest the structures of compounds **Y** and **Z**. Explain your answers. [5]

- Compound Y is an acyl chloride that undergoes hydrolysis in water, giving a solution of lower pH value since HC*l* is formed. ;
- White precipitate of AgC*l* is formed when Y is added to aqueous silver nitrate, Y is an acyl chloride. No white precipitate of AgC*l* is formed when Z is added to aqueous silver nitrate, Z contains a chloroalkane. ;
- Compound Z is a carboxylic acid as it gives an acidic solution upon partial dissociation of H^+ ions in water. ;
- Both Z and Y contains  $CH_3-\underset{H}{\overset{OH}{C}}-$.
- Y is  $CH_3-\underset{H}{\overset{OH}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-Cl$;
- Z is  $CH_3-\underset{H}{\overset{Cl}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OH$;

[Total: 22]

Section B

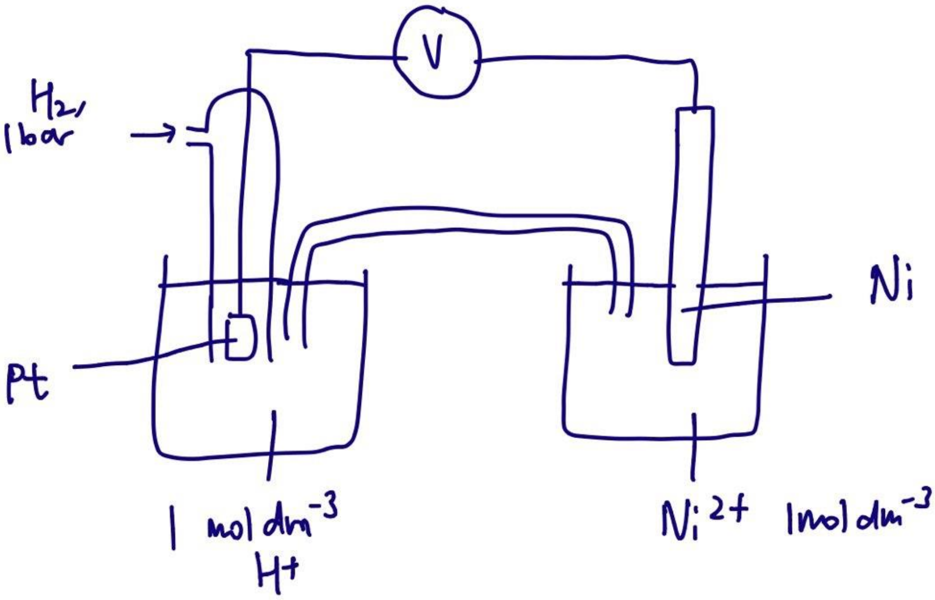
Answer **one** question from this section.

4 **(a)** Nickel is a transition metal and can exhibit variable oxidation states. The reducing power of Ni can be determined through its oxidation to Ni^{2+}.

(i) Define the term standard electrode potential. [1]

The **Standard electrode potential, $E^{\ominus}$,** of an electrode, is the relative potential of this electrode under standard conditions compared with the standard hydrogen electrode whose electrode potential is assigned as zero.

(ii) Draw a fully labelled diagram of the electrochemical cell that you would set up in order to measure the standard reduction potential of Ni^{2+}/Ni under standard conditions. [3]



(iii) Hence or otherwise, suggest what happens to the value of the voltmeter reading when a more concentrated nickel(II) solution is used in part **(ii)**. [1]

The reading will become less positive.

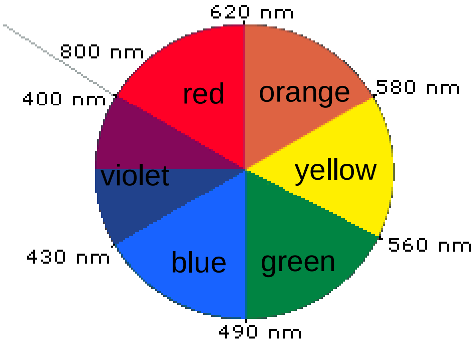
(iv) An electrolytic cell contains $Ni(NO_3)_2$ and $Mn(NO_3)_2$ in an aqueous electrolyte uses graphite as the electrodes. Determine the products discharged at the cathode and anode and write the overall balanced equation for the electrolytic cell. [3]

Cathode: Ni discharged, $Ni^{2+} + 2e \longrightarrow Ni$

Anode: O_2 discharged, $2H_2O \longrightarrow O_2 + 4H^+ + 4e$

Overall: $2Ni^{2+} + 2H_2O \longrightarrow 2Ni + O_2 + 4H^+$

(b) Aqueous nickel salts are coloured. $[Ni(NH_3)_6]^{2+}$ ions absorb at 600 nm, whereas $[NiCl_4]^{2-}$ ions absorbed at 420 nm. The colour and the respective wavelengths are given in the colour wheel below.



(i) State the oxidation number of nickel in $[NiCl_4]^{2-}$. [1]

+2

(ii) Suggest the colour of:

I: $[Ni(NH_3)_6]^{2+}$

II: $[NiCl_4]^{2-}$ [2]

$[Ni(NH_3)_6]^{2+}$ is blue, while $[NiCl_4]^{2-}$ is yellow

(iii) Explain why the two complexes are coloured. [3]

In the presence of an octahedral ligand field, the degenerate d-orbitals will split into two energy levels. In the partially-filled d orbitals (d4), electrons are able to promote from the lower to the higher level by absorbing energy in the visible spectrum (blue-green). The colour shown is the complementary colour (orange-red or yellow).

(c) The stability of complexes can be determined by the stability constant of the complexes. Consider the formation of $[Ni(NH_3)_6]^{2+}$ from $[Ni(H_2O)_6]^{2+}$. The stability constant, K_{stab}, is given by

$$K_{stab} = \frac{[[Ni(NH_3)_6]^{2+}]}{[[Ni(H_2O)_6]^{2+}][NH_3]^6}$$

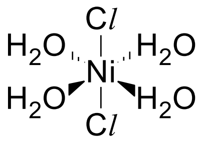
Complex	Stability constant
$Ni(H_2O)_6]^{2+} + 6NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+} + 6H_2O$	4.8×10^7
$Ni(H_2O)_6]^{2+} + 3\ en \rightleftharpoons [Ni(en)_3]^{2+} + 6H_2O$	2.0×10^{18}

State and explain if the en ligand will replace the NH_3 ligand for the nickel complexes. [2]

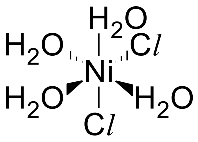
Yes, ligand exchange will take place as the stability constant for $[Ni(en)_3]^{2+}$ is higher than that of $[Ni(NH_3)_6]^{2+}$. Hence this implies that $[Ni(en)_3]^{2+}$ is more stable and will tend to be formed more.

(d) **(i)** The coordination compound $NiCl_2(H_2O)_4$ has an octahedral geometry. Draw and identify the type of isomerism present in the compound. [2]

Cis-trans isomerism



Trans



cis

(ii) Explain why [Ni(en)$_3$]Cl_2 can dissolve in water. [2]

[Ni(en)$_3$]Cl_2 is ionic in nature. The energy evolved in the formation of ion-dipole interaction is sufficient to overcome the ionic bonds between the oppositely charged ion and hence it is soluble in water.

[Total: 20]

5 **(a)** **(i)** State the structure and describe the bonding present in the chlorides of sodium and aluminium respectively. [2]

Sodium chloride – giant ionic structure with strong electrostatic forces of attraction between the opposite charged ions ;

Aluminium chloride – simple covalent structure with id-id between the molecules and covalent bonds between Al and Cl atoms;

(ii) Construct a fully labelled energy level diagram for the formation of sodium chloride using the following values and relevant values from the *Data Booklet* and calculate the standard enthalpy change of formation of sodium chloride. [3]

Thermochemical term	**ΔH / kJ mol^{-1}**
Lattice energy of NaC*l*(s)	-788
Enthalpy change of atomisation of Na(s)	+108
First electron affinity of Cl(g)	-349

ΔH_f = (+108) + (+494) + (+122) + (-349) + (-788) = -413 kJ mol^{-1} ;

2m for correct energy level diagram

(iii) Describe what happens when the chlorides of aluminium and silicon are dissolved in water. Write the relevant equations and state the observation when Universal Indicator is added. [4]

$AlCl_3 + 6H_2O \longrightarrow [Al(H_2O)_6]^{3+} + 3Cl^-$

$[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}(aq) + H_3O^+(aq)$;

$AlCl_3$ undergoes partial hydrolysis to produce a pH 3 solution which appears red in the presence of universal indicator. ;

$SiCl_4\ (l) + 2H_2O\ (l) \rightarrow SiO_2\ (s) + 4HCl\ (aq)$;

$SiCl_4$ undergoes complete hydrolysis to produce a pH 2 solution which appears red in the presence of universal indicator.;

(b) The reactions of different halogens with hydrogen differ due to their reactivity. Explain the relative stability of the hydrogen halides with reference to the Data Booklet. [3]

As the **size of the Halogen increases down the Group;** , **the H–X bond becomes longer and weaker due to the less effective overlap of the orbitals** ; and so it is easily broken. Thus, the thermal stability of the hydrides decreases down the Group, due to the decrease in strength of the H–**X** bond.

Bond	**Bond energy / kJ mol^{-1}**
H–F	568
H–C*l*	431
H–Br	366
H–I	299

(c) The iodine clock reaction involves 2 reactions.

First reaction involves peroxydisulfate ($S_2O_8^{2-}$) and excess iodide ions. The second reaction involves thiosulfate ($S_2O_3^{2-}$) ion reacting with the iodine produced.

(i) Write the equations for the two reactions of the clock reaction. [2]

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

$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$

(ii) If 30 cm^3 of 0.002 mol dm^{-3} of $S_2O_3^{2-}$ is used in the reaction, determine the mass of potassium peroxydisulfate needed for the first step. [2]

Amount of $S_2O_3^{2-}$ = 0.00006 mol

Amount of $K_2S_2O_8$ = 0.00003 mol

Mass of $K_2S_2O_8$ = 0.00003 mol x 270.4 = 0.00811g

(iii) Iron(II) ions are sometimes added to the reaction between peroxydisulfate and iodide. Write the equations to show how iron(II) ions aid in the speeding up the rate of reaction.

[2]

$2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$

$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$

(d) Iron is also used in other reactions, such as the Haber Process. State the role of iron in the Haber Process and explain why iron is suitable for this role. [2]

It acts as a heterogenous catalyst. It has partially-filled d-orbitals that can accept electron pairs from reactant particles.

[Total: 20]

Class	Adm No

Candidate Name: ____________________

Shift
Laboratory

H

millennia institute

2019 Preliminary Exams
Pre-University 3

H2 CHEMISTRY **9729/04**

Paper 4 Practical

4th Sept 2019

2 hour 30 mins

Candidates answer on the Question paper.

READ THESE INSTRUCTIONS FIRST

Do not turn over this question paper until you are told to do so

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

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

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

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

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

You may lose marks if you do not show your working or if you do not use appropriate units.

Qualitative Analysis Notes are printed at the back of the Question Paper.

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.

Question	**1**	**2**	**3**	**4**	Total
Marks	/**18**	/**22**	/**9**	/**6**	/**55**

1 Determination of titration value at equivalence point

The reaction between acid and carbonates is well known. In the presence of excess acid, the following reaction occurs:

$$CO_3^{2-}(aq) + H^+(aq) \rightleftharpoons HCO_3^-(aq) \qquad pK_a(HCO_3^-) = 10.32 \qquad \textbf{equation 1}$$

$$HCO_3^-(aq) + H^+(aq) \rightleftharpoons H_2CO_3(aq) \qquad pK_a(H_2CO_3) = 6.37 \qquad \textbf{equation 2}$$

$$H_2CO_3(aq) \rightleftharpoons CO_2(aq) + H_2O(l) \qquad \textbf{equation 3}$$

$CO_2(aq)$ is then released from the solution as $CO_2(g)$, which is observed as effervescence. The entire reaction is known to release heat.

FA 1 is 1.8 mol dm^{-3} of aqueous potassium carbonate, K_2CO_3.
FA 2 is nitric acid, HNO_3, of concentration between 1.9–2.1 mol dm^{-3}.

Assuming that the first equivalent of H^+ fully reacts with CO_3^{2-} before reacting with the HCO_3^- produced, the reaction between **FA 1** and the first equivalent of **FA 2** can be simplified as:

$$CO_3^{2-}(aq) + H^+(aq) \rightarrow HCO_3^-(aq) \qquad \Delta H_{rxn}$$

And the reaction between **FA 1** and the second equivalent of **FA 2** can be simplified as:

$$HCO_3^-(aq) + H^+(aq) \rightarrow H_2CO_3(aq)$$

As the precise concentration of **FA 2** is unknown, determination of ΔH_{rxn} can be done using a thermometric titration to simultaneously determine both the concentration of **FA 2** as well as ΔH_{rxn}. Thermometric titration is a technique whereby equivalence points of a reaction can be located by observing temperature changes, hence eliminating the need for an indicator.

In **1(a)**, you will perform an acid-carbonate thermometric titration. The data from this titration will be used to determine:

- the titration value at the first equivalence point, V_{eq1},
- the precise concentration of **FA 2**, [HNO_3],
- the maximum temperature change, ΔT_{max},
- the enthalpy change of reaction, ΔH_{rxn}.

(a) **(i)** 25.0 cm^3 of **FA 1** is reacted with **FA 2**.

Calculate the **theoretical volume of** FA 2 needed for the first equivalence point, V_{eq1}', and the second equivalence point, V_{eq2}', of the reaction between **FA 1** and **FA 2**. Assume [HNO_3] to be 2.0 mol dm^{-3}.

V_{eq1}' = …………… cm^3 **M1**

V_{eq2}' = …………… cm^3 **M2**

[2]

Determination of V_{eq1} and ΔH_{rxn} using thermometric titration

For this experiment, you will need to measure the **maximum temperature** of the reaction mixture when specified volumes of **FA 2** have been added to **FA 1**.

In an appropriate format in the space provided below, prepare a table to record your results. Record all values of temperature, T, to 0.1°C, and each total volume of **FA 2** added.

Note: You should aim to perform each subsequent addition of **FA 2** quickly.

1. Fill a burette with **FA 2**.
2. Using a pipette, transfer 25.0 cm^3 of **FA 1** into a Styrofoam cup. Place this cup inside a second Styrofoam cup, which is placed in a 250 cm^3 glass beaker.
3. Stir and measure the temperature of this **FA 1**. Record this temperature.
4. Add 4.00 cm^3 of **FA 2** from the burette to the **FA 1** in the Styrofoam cup.
5. Using the thermometer, stir the mixture thoroughly and record the maximum temperature reached and the volume of **FA 2** added.
6. Repeat steps **4** and **5** until a total volume of 48.00 cm^3 of **FA 2** has been added.

Results

[2]

(ii) Plot a graph of temperature, T, on the y-axis, against volume of **FA 2** added, on the x-axis on the grid in **Fig. 1.1**.

The temperature axis should allow you to include a point at least 1.0 °C greater than the maximum temperature recorded.

Fig. 1.1

Draw **two** most appropriate best-fit lines in **Fig. 1.1**, taking into account all of your plotted points. Extrapolate (extend) these two best-fit lines until they cross each other. [3]

(iii) From your graph in **Fig. 1.1**, determine:

- the titre at equivalence point, V_{eq},
- the maximum temperature reached, T_{max},
- the maximum temperature change, ΔT_{max}.

On your graph, show clearly how you obtained these values.

V_{eq1} = ... cm^3

T_{max} = ... °C

ΔT_{max} = ... °C

[3]

(iv) Determine the concentration of HNO_3, $[HNO_3]$, in **FA 2**.

$[HNO_3]$ in **FA 2** = ... [1]

(v) Determine the enthalpy change of reaction, ΔH_{rxn}.

$$CO_3^{2-}(aq) + H^+(aq) \rightarrow HCO_3^-(aq) \qquad \Delta H_{rxn}$$

Assume that the reaction mixture has a density of 1.00 g cm^{-3} and a specific heat capacity, c, of 4.18 J g^{-1} K^{-1}.

ΔH_{rxn} = ... [3]

(b) **(i)** With reference to your graph in **Fig. 1.1**, explain why the titre at second equivalence point, V_{eq2}, cannot be determined from this experiment.

…………………………………………………………………………………………………....

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[1]

(ii) Suggest, using chemistry concepts, a possible explanation for the observation in **(b)(i)**.

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…………………………………………………………………………………………………....

[1]

(iii) The value of V_{eq1} could also have been determined via a regular acid-base titration with a suitable indicator.

Suggest which titration method is likely to give a more accurate value of V_{eq1} and give two reasons for why this is so.

Method:

I. ………………………………………………………………………………………

………………………………………………………………………………………

II. ………………………………………………………………………………………

………………………………………………………………………………………

[2]

[Total: 18]

2 Investigation of the kinetics of an acid-carbonate reaction via gravimetric analysis

FA 1 is 1.8 mol dm^{-3} of K_2CO_3.
FA 3 is dilute nitric acid, HNO_3, of concentration 1.0 mol dm^{-3}.

$$K_2CO_3 + 2HNO_3 \rightarrow 2KNO_3 + CO_2 + H_2O$$

The rate equation of the reaction between **FA 1** and **FA 3** is expressed as such:

$$\text{Rate} = k[K_2CO_3]^a[H^+]$$

where *a* represents the order of reaction with respect to K_2CO_3, and is an integer value of either 0, 1, or 2.

The acid-carbonate reaction results in the release of CO_2(g), which escapes the reaction vessel as effervescence. To determine the kinetics of a reaction involving the loss of a gas, gravimetric analysis can be used, where the change in mass of the reaction vessel is monitored over time.

In this experiment, you will use gravimetric analysis to determine the value of *a*.

(a) Determination of orders of reaction via the 'continuous method'

The orders of reaction can be determined via either the 'continuous method' or the 'initial rates method'. In the 'continuous method', a single reaction is carried out and a measurement (e.g. concentration; mass) is monitored over time.

You will be using the 'continuous method' in this part of the experiment, monitoring the change in mass over time.

1. Weigh and record the mass of an empty 100 cm^3 measuring cylinder.
2. Measure out 80 cm^3 of **FA 3** into this measuring cylinder and record the mass of the measuring cylinder with **FA 3**.
3. Measure out 20 cm^3 of **FA 1** using a 25 cm^3 measuring cylinder into an empty 250 cm^3 conical flask. Weigh and record the mass of the conical flask with **FA 1**.
4. Place the conical flask with **FA 1** on the mass balance provided individually.
5. Start the stopwatch and **simultaneously** pour the **FA 3** in the measuring cylinder into the conical flask. **Do not swirl the flask**.
6. Record the mass readings at 10s intervals until 90s has elapsed, then at 30s intervals. Continue taking readings **until it is appropriate to stop**.

   Given that:
   initial mass of conical flask with **FA 1** and **FA 3**
   = initial mass of **FA 3** + initial mass of conical flask with **FA 1**

In an appropriate form in the space on the next page, record all your time values, balance readings, and mass of CO_2(g) evolved.

Results

[6]

(i) Plot a graph of mass of $CO_2(g)$ evolved, *m*, on the *y*-axis, against time of reaction, *t*, on the *x*-axis on the grid in **Fig. 2.1**.

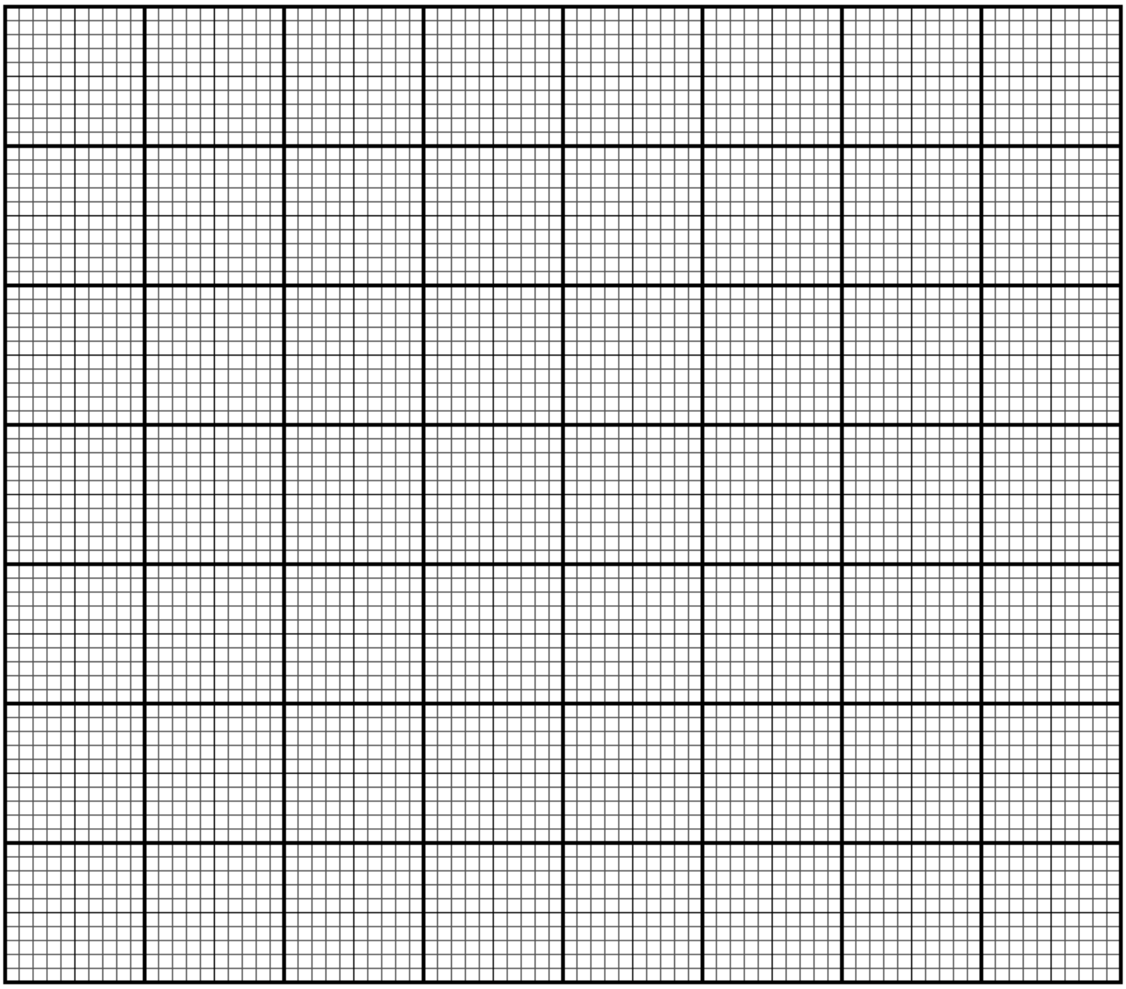

Fig. 2.1

[3]

(ii) By means of a suitable extrapolation drawn on your graph in **Fig. 2.1**, determine a value for the mass of $CO_2(g)$ evolved when the reaction is complete.

mass of $CO_2(g)$ evolved = ... g [1]

(iii) The observed half-life ($t_{1/2}$) of a reaction would be constant if the reaction proceeds with an overall order of 1. The table below shows the percentage of reactants and products in the reaction vessel at different instances of time elapsed:

time elapsed	**% of reactants**	**% of products**
0	100	0
$t_{1/2}$ x 1	50	50
$t_{1/2}$ x 2	25	75
$t_{1/2}$ x 3	12.5	87.5
⋮		
$t_{1/2}$ x ∞	0	100

Assume that the reaction proceeds with an overall order of 1.

Using your answer from **(a)(ii)**, calculate the theoretical total mass of CO_2(g) evolved after the first half-life has elapsed, and then after the second half-life has elapsed.

total mass of CO_2(g) evolved after first half-life = ... g

total mass of CO_2(g) evolved after second half-life = ... g [1]

(iv) Hence, determine from your experiment whether the acid-carbonate reaction has a consistent half-life, and state if the reaction has an overall order of 1.

Show your working clearly on your graph in **Fig. 2.1** and in the space below.

[2]

(v) Rate = $k[K_2CO_3]^a[H^+]$, where *a* is an integer value of either 0, 1, or 2.

Identify a possible value of *a*.

[1]

(b) **Planning**

The ‘initial rates method’ can also be used to determine the orders of reaction. Unlike the ‘continuous method’, multiple reactions have to be carried out, each time varying the concentrations of certain solutions.

Although the initial rate of a single reaction can be determined from the gradient of the tangent to a graph plotted at $t = 0$ (such as in **Fig 2.1**), the process is tedious as the graphs for multiple experiments have to be plotted.

A simplified ‘initial rates method’ experiment would involve determining the time elapsed for a certain *condition* to be met, then simply taking the reciprocal of time elapsed as the initial rate. A common example of such an experiment is iodine-clock reaction, whereby the time taken for the colouration formed to obscure text is measured.

It is important to keep the measured durations of time elapsed for the reactions short (maximum 120s), or the reciprocal becomes a poor approximation of rate.

(i) Plan an experiment using the simplified “initial rates method” by carrying out multiple reactions to determine the order of reaction with respect to K_2CO_3, *a*, for the reaction between K_2CO_3 and HNO_3.

You may assume that you are provided with

- **FA 1**,
- the same apparatus used in **Experiment 2(a)**,
- 4.0 mol dm^{-3} of nitric acid, HNO_3(aq),
- the glassware and equipment normally found in a school or college laboratory.

In your plan you should include brief details of

- the quantities you would choose for the experiment and why,
- the procedure for the multiple reactions carried out,
- the measurements you would take,
- an outline of how you would use your results to determine the value of *a* non-graphically.

You may wish to consider the best mode of presentation for your answers.

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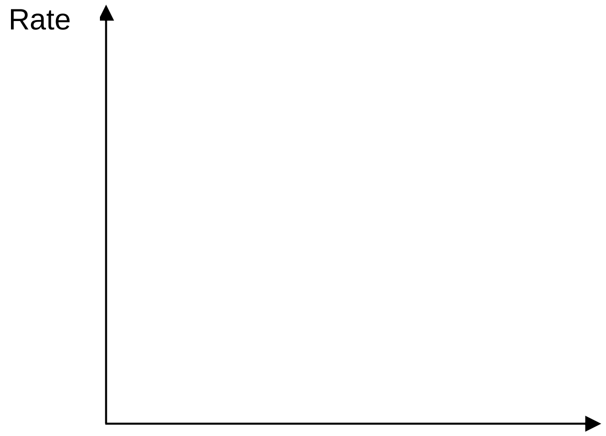
[6]

(ii) The orders of reaction can also be determined graphically.

Assuming that HNO_3 is in large excess, and *a* = 2, label the x-axis and sketch the expected rate-concentration graph that you would expect to obtain from **(b)(i)**.

Explain your answer briefly.



explanation ………………………………………………………………………………………..

…………………………………………………………………………………………………

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

[Total: 22]

3 Qualitative Analysis of an unknown salt mixture

FA 4 is a salt mixture comprising of an insoluble salt and a soluble salt. It contains **two cations** and **two anions**.

(a) Transfer 1 spatula of **FA 4** into a test tube and observe its appearance.

State, with explanation, a possible deduction that can be made about the identity of (at least) one of the ions present in **FA 4**.

…………………………………………………………………………………………………

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

(b) Perform the tests described in **Table 3.1**, and record your observations in the table. Test and identify any gases evolved.

Table 3.1

tests		observations
1.	To the test tube from **(a)**, add 2 cm depth of HNO_3, then dropwise until all the **FA 4** dissolves. The resulting solution will be known as '**FA 5 solution**'.	
2.	Add about 1 cm depth of **FA 5 solution** to a fresh boiling-tube, followed by NaOH(aq) dropwise, until excess (a further 2 cm depth). Warm the solution gently.	
3.	Add about 1 cm depth of **FA 5 solution** into a test-tube. To this test-tube, add silver nitrate dropwise.	

[4]

(c) Based on your observations, deduce the identities of the ions present in **FA 5**.

cation 1: …….... cation 2: …….... anion 1: …….... anion 2: ……....

[2]

(d) Explain in detail, the observations in **(b)(2.)**.

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

[Total: 9]

4 Planning

Consider the following organic compounds.

butanal but-3-enol 1-hydroxypropan-2-one propanone

Plan an investigation, using test-tube reactions, which would allow you to identify each of these four organic compounds.

Each compound should be identified by at least one positive test result. It is not sufficient to identify a compound simply by eliminating all the others.

Your plan should include:

- details of the reagents and conditions to be used,
- an outline of the sequence of steps you would follow,
- an explanation of how you would analyse your results in order to identify each compound.

Once a compound has been clearly identified, your plan should concentrate on distinguishing the remaining compounds. [6]

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[Total: 6]

End of Paper 4

Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	***reaction with***	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq),	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt. insoluble in excess	green ppt. insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt. insoluble in excess	off-white ppt. insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

ions	*reaction*
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, $Cl^-(aq)$	gives white ppt. with $Ag^+(aq)$ (soluble in $NH_3(aq)$)
bromide, $Br^-(aq)$	gives pale cream ppt. with $Ag^+(aq)$ (partially soluble in $NH_3(aq)$)
iodide, $I^-(aq)$	gives yellow ppt. with $Ag^+(aq)$ (insoluble in $NH_3(aq)$)
nitrate, $NO_3^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and A*l* foil
nitrite, $NO_2^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and A*l* foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, $SO_4^{2-}(aq)$	gives white ppt. with $Ba^{2+}(aq)$ (insoluble in excess dilute strong acids)
sulfite, $SO_3^{2-}(aq)$	SO_2 liberated with dilute acids; gives white ppt. with $Ba^{2+}(aq)$ (soluble in dilute strong acids)

(c) Test for gases

ions	*reaction*
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	“pops” with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	*colour of element*	*colour in aqueous solution*	*colour in hexane*
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

Class	Adm No

Candidate Name: ____________________

H

Shift
Laboratory

millennia institute

2019 Preliminary Exams
Pre-University 3

H2 CHEMISTRY **9729/04**

Paper 4 Practical

4th Sept 2019

2 hour 30 mins

Candidates answer on the Question paper.

READ THESE INSTRUCTIONS FIRST

Do not turn over this question paper until you are told to do so

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

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

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

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

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

You may lose marks if you do not show your working or if you do not use appropriate units.

Qualitative Analysis Notes are printed at the back of the Question Paper.

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.

Question	1	2	3	4	Total
Marks	18	22	9	6	55

1 Determination of titration value at equivalence point

The reaction between acid and carbonates is well known. In the presence of excess acid, the following reaction occurs:

$CO_3^{2-}(aq) + H^+(aq) \rightleftharpoons HCO_3^-(aq)$ $pK_a(HCO_3^-) = 10.32$ **equation 1**

$HCO_3^-(aq) + H^+(aq) \rightleftharpoons H_2CO_3(aq)$ $pK_a(H_2CO_3) = 6.37$ **equation 2**

$H_2CO_3(aq) \rightleftharpoons CO_2(aq) + H_2O(l)$ **equation 3**

CO_2(aq) is then released from the solution as CO_2(g), which is observed as effervescence. The entire reaction is known to release heat.

FA 1 is 1.8 mol dm^{-3} of aqueous potassium carbonate, K_2CO_3.
FA 2 is nitric acid, HNO_3, of concentration between 1.9–2.1 mol dm^{-3}.

Assuming that the first equivalent of H^+ fully reacts with CO_3^{2-} before reacting with the HCO_3^- produced, the reaction between **FA 1** and the first equivalent of **FA 2** can be simplified as:

$$CO_3^{2-}(aq) + H^+(aq) \rightarrow HCO_3^-(aq) \qquad \Delta H_{rxn}$$

And the reaction between **FA 1** and the second equivalent of **FA 2** can be simplified as:

$$HCO_3^-(aq) + H^+(aq) \rightarrow H_2CO_3(aq)$$

As the precise concentration of **FA 2** is unknown, determination of ΔH_{rxn} can be done using a thermometric titration to simultaneously determine both the concentration of **FA 2** as well as ΔH_{rxn}. Thermometric titration is a technique whereby equivalence points of a reaction can be located by observing temperature changes, hence eliminating the need for an indicator.

In **1(a)**, you will perform an acid-carbonate thermometric titration. The data from this titration will be used to determine:

- the titration value at the first equivalence point, V_{eq1},
- the precise concentration of **FA 2**, [HNO_3],
- the maximum temperature change, ΔT_{max},
- the enthalpy change of reaction, ΔH_{rxn}.

(a) **(i)** 25.0 cm^3 of **FA 1** is reacted with **FA 2**.

Calculate the **theoretical volume of** FA 2 needed for the first equivalence point, V_{eq1}', and the second equivalence point, V_{eq2}', of the reaction between **FA 1** and **FA 2**. Assume [HNO_3] to be 2.0 mol dm^{-3}.

Amount of K_2CO_3 reacted = 1.8 x 25.0 x 10^{-3} = 0.045 mol
Amount of H^+ for first equivalence point = 0.045 mol
$V_{eq1}' = \frac{0.045}{2.0} = 0.0225$ dm^3 = 22.5 cm^3 M1
V_{eq2}' = 22.5 x 2 = 45.0 cm^3 M2

V_{eq1}' = …………… cm^3

V_{eq2}' = …………… cm^3

[2]

Determination of V_{eq1} and ΔH_{rxn} using thermometric titration

For this experiment, you will need to measure the **maximum temperature** of the reaction mixture when specified volumes of **FA 2** have been added to **FA 1**.

In an appropriate format in the space provided below, prepare a table to record your results. Record all values of temperature, *T*, to 0.1°C, and each total volume of **FA 2** added.

Note: You should aim to perform each subsequent addition of **FA 2** quickly.

1. Fill a burette with **FA 2**.
2. Using a pipette, transfer 25.0 cm^3 of **FA 1** into a Styrofoam cup. Place this cup inside a second Styrofoam cup, which is placed in a 250 cm^3 glass beaker.
3. Stir and measure the temperature of this **FA 1**. Record this temperature.
4. Add 4.00 cm^3 of **FA 2** from the burette to the **FA 1** in the Styrofoam cup.
5. Using the thermometer, stir the mixture thoroughly and record the maximum temperature reached and the volume of **FA 2** added.
6. Repeat steps **4** and **5** until a total volume of 48.00 cm^3 of **FA 2** has been added.

Results

Vol of **FA 2** added / cm^3	Maximum T / °C
0.00	32.7
4.00	33.7
8.00	34.5
12.00	35.0
16.00	35.4
20.00	35.6
24.00	35.6
28.00	35.4
32.00	35.2
36.00	35.0
40.00	34.7
44.00	34.5
48.00	34.2

[2]

(ii) Plot a graph of temperature, *T*, on the *y*-axis, against volume of **FA 2** added, on the *x*-axis on the grid in **Fig. 1.1**.

The temperature axis should allow you to include a point at least 1.0 °C greater than the maximum temperature recorded.

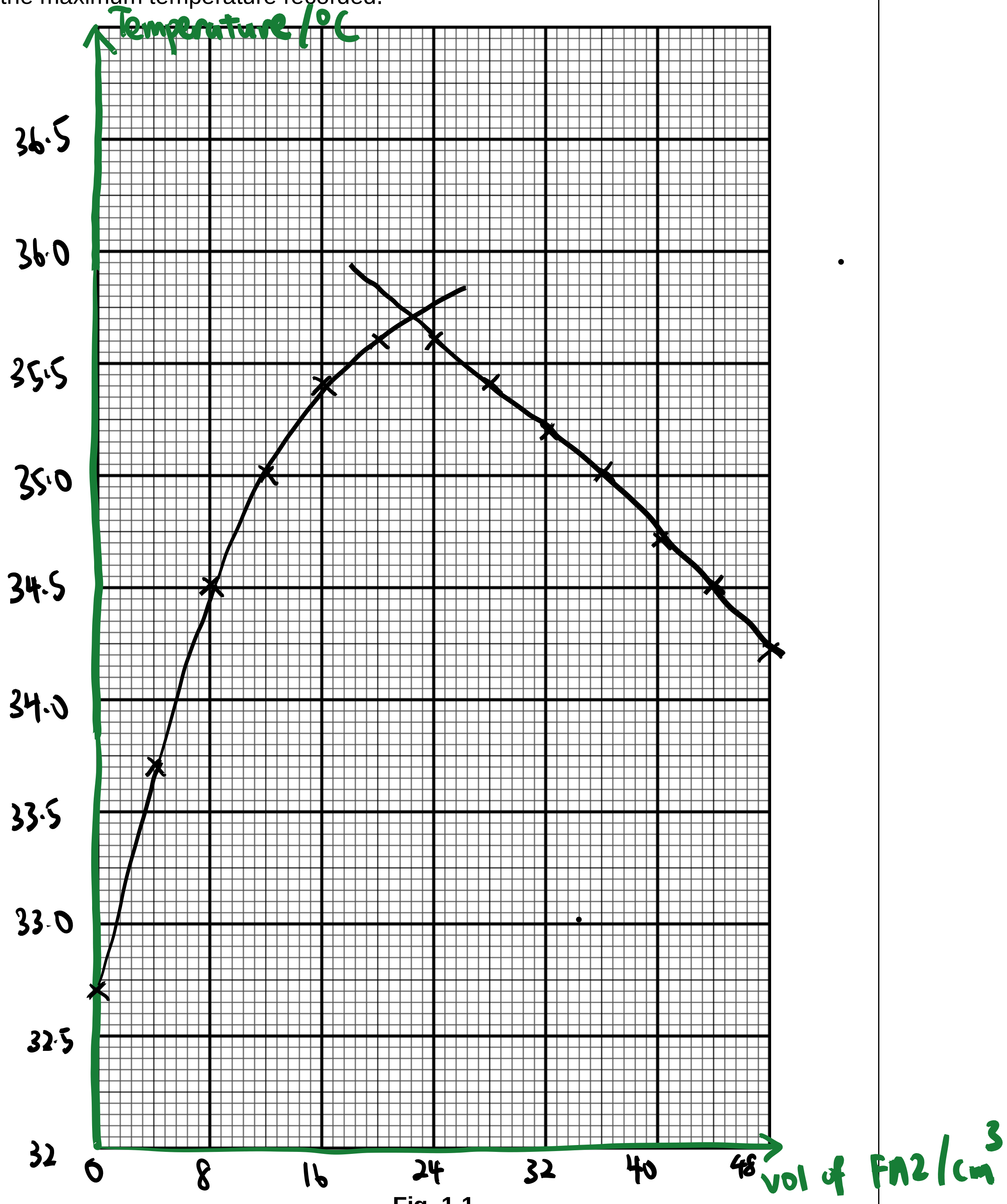


Fig. 1.1

Draw **two** most appropriate best-fit lines in **Fig. 1.1**, taking into account all of your plotted points. Extrapolate (extend) these two best-fit lines until they cross each other. [3]

(iii) From your graph in **Fig. 1.1**, determine:

- the titre at equivalence point, V_{eq},
- the maximum temperature reached, T_{max},
- the maximum temperature change, ΔT_{max}.

On your graph, show clearly how you obtained these values.

ΔT_{max} = 35.7 – 32.7 = 3.0 °C

V_{eq1} = 22.40 cm^3

T_{max} = 35.7 °C

ΔT_{max} = 3.0 °C

[3]

(iv) Determine the concentration of HNO_3, $[HNO_3]$, in **FA 2**.

Amount of K_2CO_3 reacted = 1.8 x 25.0 x 10^{-3} = 0.045 mol

Amount of HNO_3 reacted at V_{eq1} = 0.045 mol

[NaOH] = $\frac{0.045}{22.40\times10^{-3}}$ = 2.01 mol dm^{-3} (3sf)

$[HNO_3]$ in **FA 2** = …………… [1]

(v) Determine the enthalpy change of reaction, ΔH_{rxn}.

$$CO_3^{2-}(aq) + H^+(aq) \rightarrow HCO_3^-(aq) \qquad \Delta H_{rxn}$$

Assume that the reaction mixture has a density of 1.00 g cm^{-3} and a specific heat capacity, *c*, of 4.18 J g^{-1} K^{-1}.

m = 25.0 + 22.40 = 47.4 g

q = mcΔT = (47.4)(4.18)(3) = 594.4 J

$\Delta H_{rxn} = -\frac{q}{n_{LR}} \times \text{CLR} = -\frac{594.4}{0.045} \times 1$ = –13.2 kJ mol^{-1} (3 sf)

ΔH_{rxn} = …………… [3]

(b) **(i)** With reference to your graph in **Fig. 1.1**, explain why the titre at second equivalence point, V_{eq2}, cannot be determined from this experiment.

The temperature does not increase / reaction is not exothermic for **equation 2**.

OR There is only one intersection point

OWTTE

[1]

(ii) Suggest, using chemistry concepts, a possible explanation for the observation in **(b)(i)**.

Equation 2 is not exothermic / the temperature does not increase as **equation 3** could be endothermic.

or

pK_a(H_2CO_3) is small compared to pK_a(HCO_3^-) and the energy released from the reaction is used to complete the reaction.

[1]

(iii) The value of V_{eq1} could also have been determined via a regular acid-base titration with a suitable indicator.

Suggest which titration method is likely to give a more accurate value of V_{eq1} and give two reasons for why this is so.

Method:

Accept any reasonable answer for both

Regular titration: heat loss to surroundings does not affect value of V_{eq1} unlike thermometric method; The first equivalent of H^+ fully reacts with CO_3^{2-} before reacting with HCO_3^- may not be true.

Thermometric titration: does not require use of indicator which may affect pH of solution and end point may not match exactly with equivalence point [2]

[Total: 18]

2 Investigation of the kinetics of an acid-carbonate reaction via gravimetric analysis

FA 1 is 1.8 mol dm^{-3} of K_2CO_3.
FA 3 is dilute nitric acid, HNO_3, of concentration 1.0 mol dm^{-3}.

$$K_2CO_3 + 2HNO_3 \rightarrow 2KNO_3 + CO_2 + H_2O$$

The rate equation of the reaction between **FA 1** and **FA 3** is expressed as such:

$$\text{Rate} = k[K_2CO_3]^a[H^+]$$

where *a* represents the order of reaction with respect to K_2CO_3, and is an integer value of either 0, 1, or 2.

The acid-carbonate reaction results in the release of $CO_2(g)$, which escapes the reaction vessel as effervescence. To determine the kinetics of a reaction involving the loss of a gas, gravimetric analysis can be used, where the change in mass of the reaction vessel is monitored over time.

In this experiment, you will use gravimetric analysis to determine the value of *a*.

(a) Determination of orders of reaction via the 'continuous method'

The orders of reaction can be determined via either the 'continuous method' or the 'initial rates method'. In the 'continuous method', a single reaction is carried out and a measurement (e.g. concentration; mass) is monitored over time.

You will be using the 'continuous method' in this part of the experiment, monitoring the change in mass over time.

1. Weigh and record the mass of an empty 100 cm^3 measuring cylinder.
2. Measure out 80 cm^3 of **FA 3** into this measuring cylinder and record the mass of the measuring cylinder with **FA 3**.
3. Measure out 20 cm^3 of **FA 1** using a 25 cm^3 measuring cylinder into an empty 250 cm^3 conical flask. Weigh and record the mass of the conical flask with **FA 1**.
4. Place the conical flask with **FA 1** on the mass balance provided individually.
5. Start the stopwatch and **simultaneously** pour the **FA 3** in the measuring cylinder into the conical flask. **Do not swirl the flask**.
6. Record the mass readings at 10s intervals until 90s has elapsed, then at 30s intervals. Continue taking readings **until it is appropriate to stop**.

   Given that:
   initial mass of conical flask with **FA 1** and **FA 3**
   = initial mass of **FA 3** + initial mass of conical flask with **FA 1**

In an appropriate form in the space on the next page, record all your time values, balance readings, and mass of $CO_2(g)$ evolved.

Results

Mass of empty measuring cylinder / g	
Mass of measuring cylinder + **FA 3** / g	
Mass of **FA 3** added / g	
Mass of conical flask + **FA 1** / g	
Total mass of conical flask + **FA 1** + **FA 3** before reaction / g	213.82

time / s	total mass / g	total mass of CO_2 evolved / g
0	213.82	0.00
10	213.02	0.80
20	212.91	0.91
30	212.84	0.98
40	212.77	1.05
50	212.72	1.10
60	212.68	1.14
70	212.64	1.18
80	212.61	1.21
90	212.59	1.23
120	212.53	1.29
150	212.49	1.33
180	212.47	1.35
210	212.47	1.35
240	212.47	1.35

[6]

(i) Plot a graph of mass of CO_2(g) evolved, *m*, on the *y*-axis, against time of reaction, *t*, on the *x*-axis on the grid in **Fig. 2.1**.

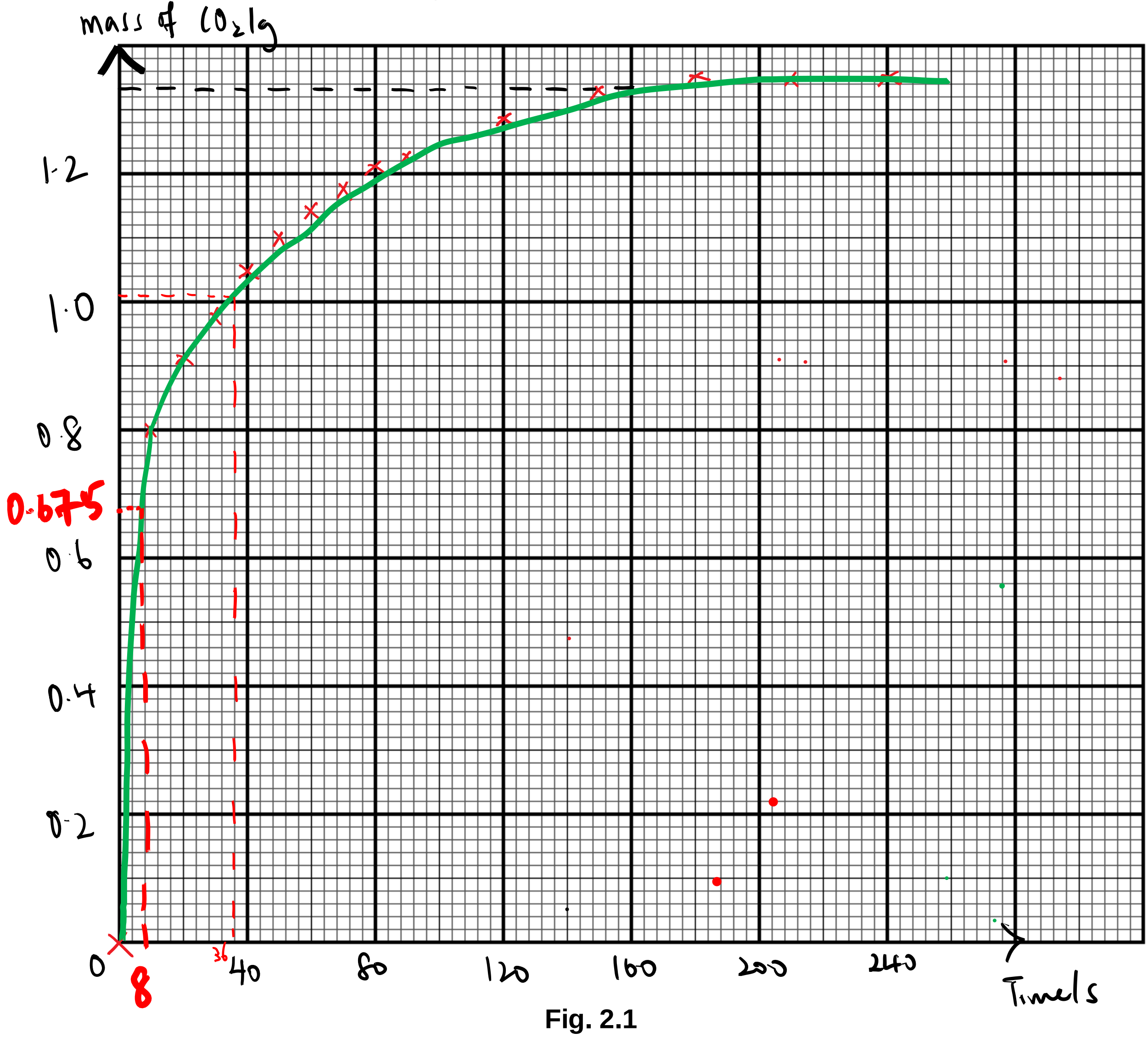


Fig. 2.1

[3]

(ii) By means of a suitable extrapolation drawn on your graph in **Fig. 2.1**, determine a value for the mass of CO_2(g) evolved when the reaction is complete.

mass of CO_2(g) evolved = 1.35 g [1]

(iii) The observed half-life ($t_{1/2}$) of a reaction would be constant if the reaction proceeds with an overall order of 1. The table below shows the percentage of reactants and products in the reaction vessel at different instances of time elapsed:

time elapsed	% of reactants	% of products
0	100	0
$t_{1/2}$ x 1	50	50
$t_{1/2}$ x 2	25	75
$t_{1/2}$ x 3	12.5	87.5
	⋮	
$t_{1/2}$ x ∞	0	100

Assume that the reaction proceeds with an overall order of 1.

Using your answer from **(a)(ii)**, calculate the theoretical total mass of CO_2(g) evolved after the first half-life has elapsed, and then after the second half-life has elapsed.

Mass of CO_2 produced at 1st $t_{1/2}$ = ½ x 1.35 = 0.675 g

Mass of CO_2 produced at 2nd $t_{1/2}$ = ¾ x 1.35 = 1.01 g

total mass of CO_2(g) evolved after first half-life = 0.675 g

total mass of CO_2(g) evolved after second half-life = 1.01 g [1]

(iv) Hence, determine from your experiment whether the acid-carbonate reaction has a consistent half-life, and state if the reaction has an overall order of 1.

Show your working clearly on your graph in **Fig. 2.1** and in the space below.

1st $t_{1/2}$ = 8s

2nd $t_{1/2}$ = 36 – 8 = 28s

Since $t_{1/2}$ is not constant, the reaction does not have an overall order of 1.

[2]

(v) Rate = $k[K_2CO_3]^a[H^+]$, where *a* is an integer value of either 0, 1, or 2.

Identify a possible value of *a*.

a could be 1 or 2

[1]

(b) Planning

The ‘initial rates method’ can also be used to determine the orders of reaction. Unlike the ‘continuous method’, multiple reactions have to be carried out, each time varying the concentrations of certain solutions.

Although the initial rate of a single reaction can be determined from the gradient of the tangent to a graph plotted at $t = 0$ (such as in **Fig 2.1**), the process is tedious as the graphs for multiple experiments have to be plotted.

A simplified ‘initial rates method’ experiment would involve determining the time elapsed for a certain *condition* to be met, then simply taking the reciprocal of time elapsed as the initial rate. A common example of such an experiment is iodine-clock reaction, whereby the time taken for the colouration formed to obscure text is measured.

It is important to keep the measured durations of time elapsed for the reactions short (maximum 120s), or the reciprocal becomes a poor approximation of rate.

(i) Plan an experiment using the simplified “initial rates method” by carrying out multiple reactions to determine the order of reaction with respect to K_2CO_3, *a*, for the reaction between K_2CO_3 and HNO_3.

You may assume that you are provided with

- **FA 1**,
- the same apparatus used in **Experiment 2(a)**,
- 4.0 mol dm^{-3} of nitric acid, HNO_3(aq),
- the glassware and equipment normally found in a school or college laboratory.

In your plan you should include brief details of

- the quantities you would choose for the experiment and why,
- the procedure for the multiple reactions carried out,
- the measurements you would take,
- an outline of how you would use your results to determine the value of *a* non-graphically.

You may wish to consider the best mode of presentation for your answers.

Concentrations chosen depends on [HNO_3] from previous part. Fix mass, **measure time taken to obtain fixed mass**. Pick a fixed mass of longest time allowed (120s) from graph in (a), then use higher concentrations (which will result in shorter times).

Run	Vol of HNO_3 / cm^3	Vol of FA 1 / cm^3	Vol of H_2O / cm^3	Total Vol / cm^3	Time / s	Rate / s^{-1}
1	20.0	20.0	60.0	100.0	120	
2	20.0	40.0	40.0	100.0		
3	20.0	60.0	20.0	100.0		

For a single run,

1. Measure out the volumes of FA 1, HNO_3 and H_2O as indicated in the tables above, using 25.0 / 50.0 cm^3 measuring cylinders.
2. Transfer HNO_3 and H_2O into a 250 cm^3 conical flask first, and place it on a weighing balance.

3. Record the initial mass, and take note of the final mass to stop the stopwatch.
4. Transfer FA 1 into the conical flask and start the stopwatch simultaneously.
5. Stop the stopwatch when 1.29 g of CO_2 is released and record the time elapsed.
6. Repeat steps 1-5 for the different runs.
7. Rate $\propto$ 1/t, thus calculate 1/t

If rate (or 1/t)

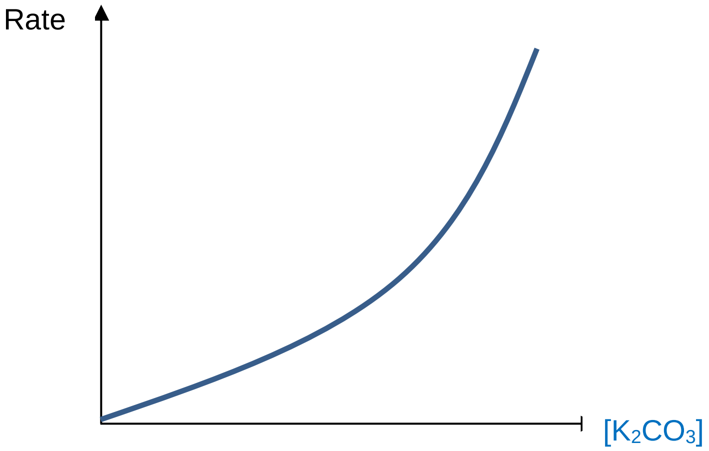
- remains the same from Run 1 to Run 2 to Run 3, reaction is 0^{th} order wrt to K_2CO_3
- doubles from Run 1 to Run 2 to Run 3, reaction is 1^{st} order wrt to K_2CO_3
- more than doubles from Run 1 to Run 2 to Run 3, reaction is 2^{nd} order wrt to K_2CO_3

[6]

(ii) The orders of reaction can also be determined graphically.

Assuming that HNO_3 is in large excess, and *a* = 2, label the x-axis and sketch the expected rate-concentration graph that you would expect to obtain from **(b)(i)**.

Explain your answer briefly.



explanation ……………………………………………………………………………………..

…………………………………………………………………………………………………

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

When HNO_3 is in large excess, order of reaction wrt to HNO_3 is 0.

∴ Rate = k[K_2CO_3]^2 and the graph has a " y=mx^2 " shape as rate ∝ [K_2CO_3].

[Total: 22]

3 Qualitative Analysis of an unknown salt mixture

FA 4 is a salt mixture comprising of an insoluble salt and a soluble salt. It contains **two cations** and **two anions**.

(a) Transfer 1 spatula of **FA 4** into a test tube and observe its appearance.

State, with explanation, a possible deduction that can be made about the identity of (at least) one of the ions present in **FA 4**.

It contains a transition metal since it is coloured. [1]

(b) Perform the tests described in **Table 3.1**, and record your observations in the table. Test and identify any gases evolved.

Table 3.1

tests		observations
1.	To the test tube from **(a)**, add 2 cm depth of HNO_3, then dropwise until all the **FA 4** dissolves. The resulting solution will be known as '**FA 5 solution**'.	A green solution is formed. Gas produced forms a white ppt in $Ca(OH)_2$.
2.	Add about 1 cm depth of **FA 5 solution** to a fresh boiling-tube, followed by NaOH(aq) dropwise, until excess (a further 2 cm depth).	Blue ppt forms, turns deep blue in excess NaOH(aq).
	Warm the solution gently.	Gas produced turns red litmus paper blue.
3.	Add about 1 cm depth of **FA 5 solution** into a test-tube. To this test-tube, add silver nitrate dropwise.	White ppt forms, soluble in excess NH_3(aq).

[4]

(c) Based on your observations, deduce the identities of the ions present in **FA 5**.

cation 1: Cu^{2+} cation 2: NH_4^+ anion 1: CO_3^{2-} anion 2: Cl^-

[2]

(d) Explain in detail, the observations in **(b)(2.)**.

Blue ppt of $Cu(OH)_2$ forms upon addition of NaOH. At the same time, NH_4^+ present in the solution reacts with NaOH to produce some NH_3, which is evolved when the solution is warmed and turns red litmus blue. ;

When more NaOH is added, sufficient NH_3 is produced to form the deep blue complex of $[Cu(H_2O)_2(NH_3)_4]^{2+}$. ; [2]

[Total: 9]

4 Planning

Consider the following organic compounds.

butanal but-3-enol 1-hydroxypropan-2-one propanone

Plan an investigation, using test-tube reactions, which would allow you to identify each of these four organic compounds.

Each compound should be identified by at least one positive test result. It is not sufficient to identify a compound simply by eliminating all the others.

Your plan should include:

- details of the reagents and conditions to be used,
- an outline of the sequence of steps you would follow,
- an explanation of how you would analyse your results in order to identify each compound.

Once a compound has been clearly identified, your plan should concentrate on distinguishing the remaining compounds. [6]

Unknowns: butanal, but-3-enol, 1-hydroxypropan-2-one, propanone
Step 1: Place 1 cm^3 of each unknown into clean test tubes. To each test tube, add of 2 cm^3 of Tollen's reagent, then warm in a water bath for 5 min.
Observation: A silver mirror forms only for butanal. Butanal is identified.

Unknowns: but-3-enol, 1-hydroxypropan-2-one, propanone
Step 2: Place 1 cm^3 of each remaining unknown into clean test tubes. To each test tube, add 1-2 drops of acidified $KMnO_4$, then warm in a water bath for 5 min.
Observation: Purple $KMnO_4$ turns purple for only but-3-enol and 1-hydroxypropan-2-one. Effervescence of a gas that forms a white ppt in $Ca(OH)_2$ observed for only but-3-enol. But-3-enol is identified.

Unknowns: 1-hydroxypropan-2-one, propanone
Step 3: Place 1 cm^3 of each remaining unknown into clean test tubes. To each test tube, add 1-2 drops of acidified $K_2Cr_2O_7$, then warm in a water bath for 5 min.
Observation: Orange $K_2Cr_2O_7$ forms only for 1-hydroxypropan-2-one. 1-hydroxypropan-2-one is identified.

Unknowns: propanone
Step 4: Place 1 cm^3 of the remaining unknown into a clean test tube. To this test tube, add excess 2,4-dinitrophenylhyrazine, then warm in a water bath for 5 min.
Observation: An orange precipitate forms for propanone. Propanone is identified.

other possible solutions include:

Unknowns: 1-hydroxypropan-2-one, propanone
Step ??: Place 1 cm^3 of the remaining unknown into a clean test tube. To this test tube, add 1 spatula of Na(s), test gas evolved with lighted splint.
Observation: Effervescence observed for 1-hydroxypropan-2-one. Gas extinguishes lighted splint with a 'pop' sound. 1-hydroxypropan-2-one is identified.

[Total: 6]

End of Paper 4

Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	***reaction with***	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq),	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt. insoluble in excess	green ppt. insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt. insoluble in excess	off-white ppt. insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

ions	*reaction*
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, $Cl^-(aq)$	gives white ppt. with $Ag^+(aq)$ (soluble in $NH_3(aq)$)
bromide, $Br^-(aq)$	gives pale cream ppt. with $Ag^+(aq)$ (partially soluble in $NH_3(aq)$)
iodide, $I^-(aq)$	gives yellow ppt. with $Ag^+(aq)$ (insoluble in $NH_3(aq)$)
nitrate, $NO_3^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and Al foil
nitrite, $NO_2^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and Al foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, $SO_4^{2-}(aq)$	gives white ppt. with $Ba^{2+}(aq)$ (insoluble in excess dilute strong acids)
sulfite, $SO_3^{2-}(aq)$	SO_2 liberated with dilute acids; gives white ppt. with $Ba^{2+}(aq)$ (soluble in dilute strong acids)

(c) Test for gases

ions	*reaction*
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	“pops” with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	*colour of element*	*colour in aqueous solution*	*colour in hexane*
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple