PIONEER JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION
HIGHER 2

CANDIDATE NAME

CT GROUP	1	6	S		

INDEX NUMBER

CHEMISTRY

9729/01

Paper 1 Multiple Choice

22 September 2017

1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, highlighters, glue or correction fluid.
Write your name, Centre number and index number on the Answer Sheet in the spaces provided unless this has been done for you.

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

Read the instructions on the Answer Sheet very carefully.

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

Section A

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

1 Equal volumes of 1 mol dm^{-3} hydrogen sulfide and sulfur dioxide (each containing a different isotope of sulfur) are mixed to precipitate sulfur according to the equations shown below:

$$H_2{}^{32}S(aq) \rightarrow {}^{32}S(s) + 2H^+(aq) + 2e^-$$
$${}^{34}SO_2(aq) + 4H^+(aq) + 4e^- \rightarrow {}^{34}S(s) + 2H_2O(l)$$

What is the relative atomic mass of the sulfur precipitated?

A 32.1

B 32.7

C 33.0

D 33.3

2 50 cm^3 of a 0.0400 mol dm^{-3} solution of acidified Fe^{2+} was oxidised to Fe^{3+} by 100 cm^3 of 0.0100 mol dm^{-3} of an oxidising agent, XO_3^-.

What is the final product of **X**?

A $\mathbf{X}O_2$

B $\mathbf{X}O^-$

C $\mathbf{X}O_2^-$

D $\mathbf{X}^-$

3 Paramagnetism refers to the magnetic state of an atom with one or more unpaired electrons. The greater the number of unpaired electrons in an atom, the greater the paramagnetism.

Which atom has the greatest paramagnetism?

A Oxygen

B Chlorine

C Scandium

D Vanadium

4 Which of the following statements about the nitrate(V) ion, NO_3^-, are correct?

1 The hybridisation of the nitrogen atom is sp^2.

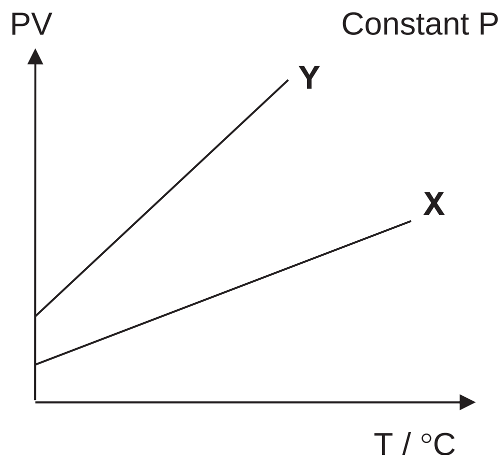
2 All the nitrogen–oxygen bond lengths in NO_3^- are equal in length.

3 NO_3^- has a total of twenty-four valence electrons.

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

5 Which graph correctly describes the behaviour of fixed masses of the ideal gases **X** and **Y**, where **X** has a higher M_r than **Y**?

A



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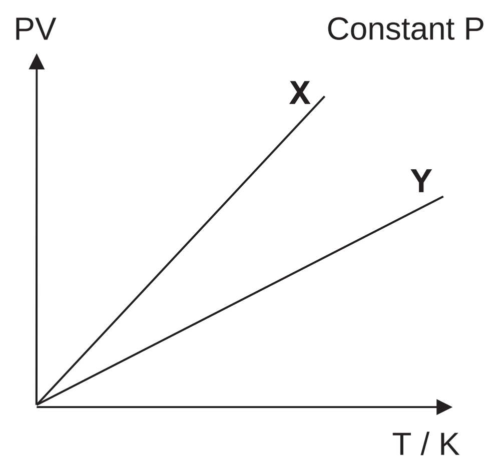
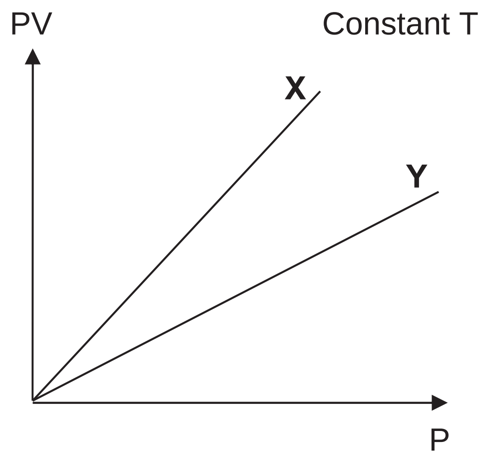
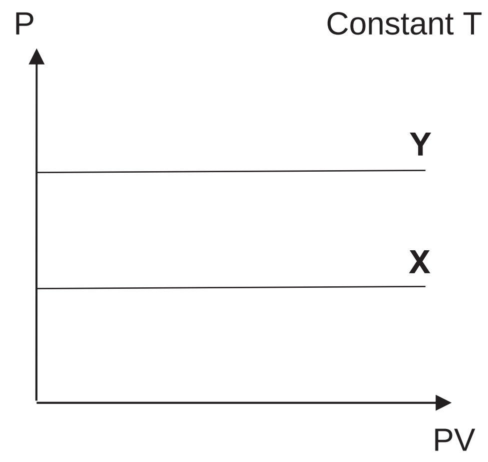


C



D



6 A student dissolved 10.5 g of sodium fluoride, NaF, in 250 g of water. The following data is obtained:

Lattice energy of NaF	−918 kJ mol^{-1}
Enthalpy change of hydration of F$^-$	−457 kJ mol^{-1}
Enthalpy change of hydration of Na$^+$	−390 kJ mol^{-1}

Given that the specific heat capacity of water is 4.2 J g^{-1} K^{-1}, what would be the final temperature of the solution, if the initial temperature of water is 30^{o}C?

A 6.5^{o}C **B** 13.1^{o}C **C** 16.9^{o}C **D** 46.9^{o}C

7 The kinetics of the reaction between iodide and peroxodisulfate can be investigated by varying the volume of the reactants used. The two reactants are mixed in the presence of a known amount of $Na_2S_2O_3$ and a little starch.

$$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

The time taken for an intense blue colour to be observed is then determined.

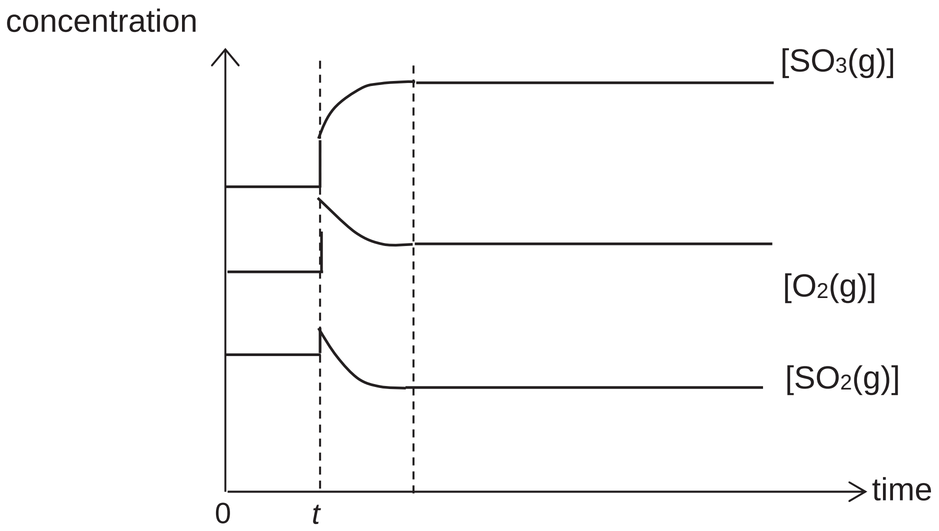
Experiment	Volume used / cm^3			Time / s
	1.0 mol dm^{-3} KI	0.040 mol dm^{-3} $Na_2S_2O_8$	H_2O	
1	10.0	5.0	25.0	170
2	15.0	5.0	20.0	113
3	15.0	10.0	15.0	56.5
4	20.0	***x***	***y***	21.3

What are the values of ***x*** and ***y*** in Experiment 4?

	x	***y***
A	5.0	15.0
B	10.0	10.0
C	15.0	5.0
D	20.0	0.0

8 An equilibrium mixture containing gaseous SO_2, O_2 and SO_3 is subjected to a change at time *t*. The mixture is allowed to reach equilibrium again. The variation of the concentrations of SO_2, O_2 and SO_3 with time is given below.

$$SO_3(g) \rightleftharpoons SO_2(g) + \tfrac{1}{2}O_2(g) \qquad \Delta H > 0$$



Which of the following changes made at time *t* would result in the above variation of the concentrations of the gases?

A Increasing the temperature.

B Decreasing the temperature.

C Adding a catalyst.

D Reducing the volume of the vessel.

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

$$2CHClF_2(g) \rightleftharpoons C_2F_4(g) + 2HCl(g) \qquad \Delta H = +128 \text{ kJ mol}^{-1}$$

Which of the following changes will increase the amount of tetrafluoroethene, C_2F_4, present at equilibrium?

1 decrease pressure

2 increase temperature

3 use a catalyst

A 1 only

B 1 and 2 only

C 2 and 3 only

D 1, 2 and 3

10 Three unknown solutions **P**, **Q** and **R** contain a strong monobasic acid, a weak monobasic acid and a strong monoacidic base, but not necessarily in this same order. The concentration and pH of each solution are shown below.

P	**Q**	**R**
1.000 mol dm^{-3} pH = 2.4	0.010 mol dm^{-3} pH = 12.0	0.001 mol dm^{-3} pH = 3.0

Which of the following statements **are** correct?

1 **Q** contains a strong base.

2 **P** contains a weak acid.

3 Mixing 100 cm^3 of **P** and 100 cm^3 of **R** produces a buffer solution.

A 1 only is correct.

B 1 and 2 only are correct.

C 2 and 3 only are correct.

D 1, 2 and 3 are correct.

11 The numerical values of the solubility product of AgBr, $AgIO_3$ and Ag_2CO_3 are given in the table below.

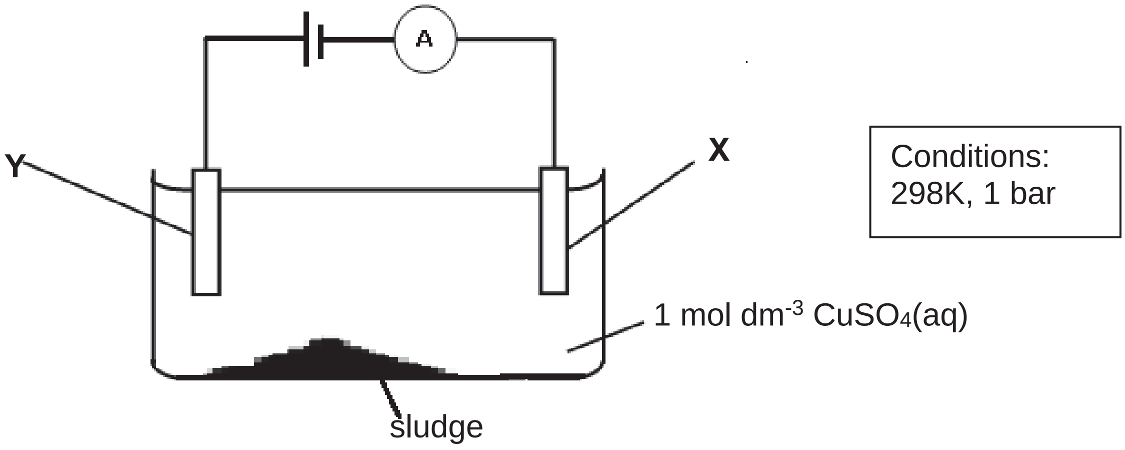
compound	solubility product
AgBr	5×10^{-13}
$AgIO_3$	2×10^{-8}
Ag_2CO_3	5×10^{-12}

An aqueous solution of $AgNO_3$ was added slowly, until in excess, to a solution containing 1.5 mol dm^{-3} of NaBr, 1.5 mol dm^{-3} of KIO_3 and 1.5 mol dm^{-3} of Na_2CO_3.

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

	first to precipitate	$\longrightarrow$	last to precipitate
A	AgBr	$AgIO_3$	Ag_2CO_3
B	AgBr	Ag_2CO_3	$AgIO_3$
C	Ag_2CO_3	AgBr	$AgIO_3$
D	$AgIO_3$	Ag_2CO_3	AgBr

12 *Use of the Data Booklet is relevant to this question.* The circuit shown in the diagram was set up to purify impure Cu, which contains Ag and Fe impurities.
(In the diagram below, A represents ammeter)



What of the following represents the substance used as electrode **X**, the products formed at the anode and cathode, and the substance present in the sludge after some time?

	Electrode X	**Products at anode**	**Products at cathode**	**sludge**
A	Impure Cu	Cu^{2+}	Cu	Ag
B	Impure Cu	Fe^{2+}	Cu^{2+}	Ag
C	Pure Cu	Ag^+, Fe^{2+}	Cu^{2+}	Zn
D	Pure Cu	Cu^{2+}, Fe^{2+}	Cu	Ag

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

An electrochemical cell is set up using a Fe^{2+}(aq)|Fe(s) half–cell and a VO_2^+(aq),VO^{2+}(aq)|Pt(s) half–cell.

Which of the following gives a correct effect on the E_{cell} and a correct explanation for the effect when each of the changes is made to the cell separately?

	Change	Effect on E_{cell}	Explanation
1	Add KCN(aq) to the Fe^{2+}(aq)|Fe(s) half–cell	Increases	Concentration of Fe^{2+}(aq) decreases
2	Add water to the VO_2^+(aq),VO^{2+}(aq)|Pt(s) half–cell	Decreases	Concentration of water increases
3	Add NaOH(aq) to Fe^{2+}(aq)|Fe(s) half–cell	No change	pH has no effect on E_{cell}

A 1 only

B 1 and 3 only

C 2 and 3 only

D 1, 2 and 3

14 These information relates to element **S**.

- **S** is in Period 3 of the Periodic Table.
- **S** forms an acidic oxide on exposure to air.
- **S** atom has a half-filled subshell in its ground state.

What is the identity of **S**?

A Na

B Si

C P

D S

15 Coloured glass, as used in church windows, requires three oxides; one of a transition metal, and two other oxides: one macromolecular and one ionic**.**

Which combination is likely to produce a coloured glass?

A	Al_2O_3	MgO	SnO
B	P_4O_{10}	CaO	CuO
C	SiO_2	CaO	CuO
D	SiO_2	PbO	ZnO

16 The carbonates of Group 2 decompose according to the following equation.

$MCO_3(s) \longrightarrow MO(s) + CO_2(g)$

For this reaction, ΔH value increases down the group.

Carbonate	Mg	Ca	Sr	Ba
ΔH / kJ mol^{-1}	+ 101	+ 178	+ 235	+ 269

Which property best explains this trend?

A The first and second ionisation energy of the metal

B The lattice energy of the metal carbonate

C The ionic radius of the metal ion

D The proton number of the metal

17 A yellow-green solution is formed when concentrated hydrochloric acid is added to blue aqueous copper(II) chloride solution. Addition of potassium iodide to the mixture results in the formation of a brown solution and a white precipitate.

Which process does **not** occur in this sequence?

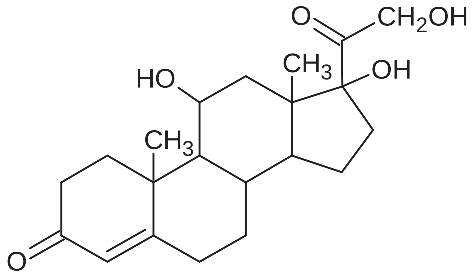
A dative bond formation

B complex ion formation

C precipitation of copper(II) iodide

D reduction of Cu^{2+} ions

18 Hydrocortisone is the active ingredient in some anti-inflammatory skin cream.



hydrocortisone

How many sp^3 hybridised carbon atoms and chiral centres are present in a hydrocortisone molecule?

	sp^3 carbon atoms	**chiral centres**
A	16	6
B	16	7
C	17	6
D	17	7

19 Ethane reacts with chlorine gas in the presence of ultraviolet light to form a mixture of products via free radical substitution.

Which statements about this reaction are correct?

1 Homolytic fission occurs only in the initiation step.

2 Chloroethane is formed in the propagation and termination steps.

3 Bond formation occurs only in the termination step.

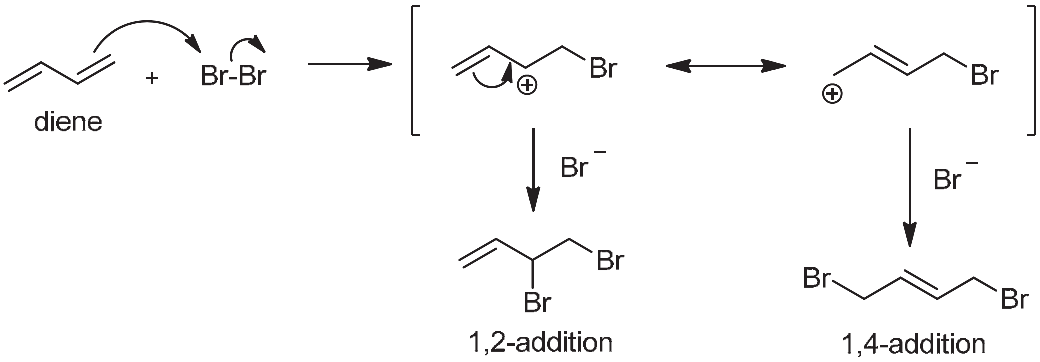
A 2 only

B 2 and 3 only

C 1 and 3 only

D 1, 2 and 3

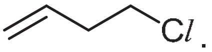
20 When a conjugated diene undergoes electrophilic addition with Br_2, it forms two products through the 1,2–addition and the 1,4–addition, which is shown in the mechanism below.

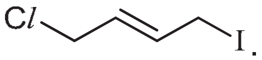


Which of the following statements is **not** correct?

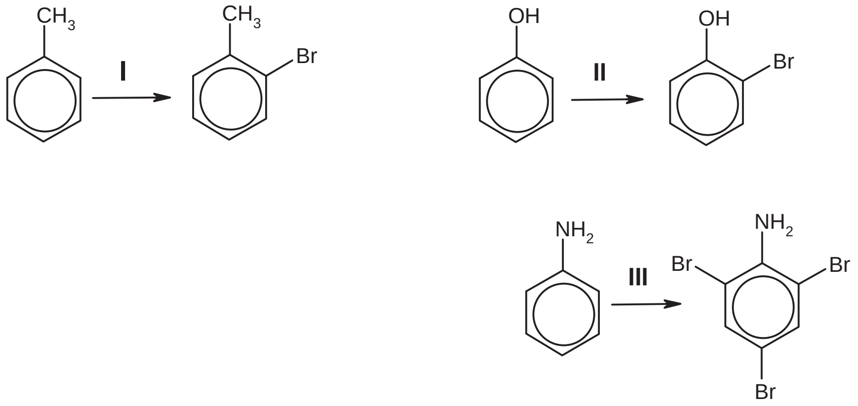
A The overall rate law is second order.

B The carbocation intermediates are resonance stabilised.

C The 1,2–addition product formed when HCl is used is .

D The 1,4–addition product formed when ICl is used is .

21 Methylbenzene, phenol and phenylamine all undergo electrophilic substitution with suitable reagents.



Which of the following could the reagents be for steps **I** to **III**?

	I	**II**	**III**
A	Br_2, Fe	Br_2 in CCl_4	Br_2(aq)
B	Br_2, $FeBr_3$	Br_2(aq)	Br_2 in CCl_4
C	Br_2(aq)	Br_2 in CCl_4	Br_2, Fe
D	Br_2 in CCl_4	Br_2, $FeBr_3$	Br_2(aq)

22 2–methylpropanoic acid can be synthesised from 1–chloropropane through a series of reactions. Which set of reagents, used in sequential order, would be the most suitable for this synthesis?

A step I: aqueous HCN with trace KCN
step II: dilute NaOH

B step I: ethanolic KCN
step II: dilute HCl

C step I: aqueous KOH
step II: gaseous HCl
step III: ethanolic KCN
step IV: dilute HCl

D step I: ethanolic KOH
step II: gaseous HBr
step III: ethanolic KCN
step IV: dilute H_2SO_4

23 Which of the following statements on the nucleophilic substitution of 3-bromo-3-methylhexane with aqueous sodium hydroxide is **not** true?

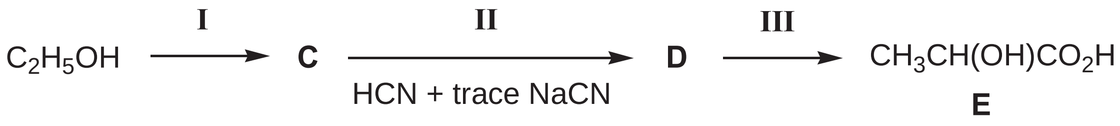
A The product has a chiral centre.

B The intermediate is a carbocation.

C The reaction produces an optically inactive mixture.

D The OH^- nucleophile attacks 3-bromo-3-methylhexane just as the Br^- leaves.

24 Lactic acid (2-hydroxypropanoic acid), **E**, occurs in soured milk. It can be synthesised from ethanol by the following series of reactions.



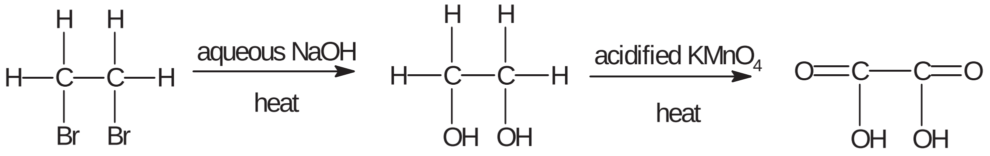
$$C_2H_5OH \xrightarrow{\text{I}} \textbf{C} \xrightarrow[\text{HCN + trace NaCN}]{\text{II}} \textbf{D} \xrightarrow{\text{III}} \underset{\textbf{E}}{CH_3CH(OH)CO_2H}$$

Which of the following correctly represent the reagents and conditions for step **I**, and the structures of compounds **C** and **D**?

	step **I**	**C**	**D**
A	$KMnO_4$(aq), H_2SO_4(aq), heat	CH_3COOH	CH_3COCN
B	$KMnO_4$(aq), H_2SO_4(aq), distil	CH_3CHO	$CH_3CH(CN)OH$
C	$K_2Cr_2O_7$(aq), H_2SO_4(aq), heat	CH_3COOH	CH_3COCN
D	$K_2Cr_2O_7$(aq), H_2SO_4(aq), distil	CH_3CHO	$CH_3CH(CN)OH$

25 Which is the most feasible synthesis route?

A



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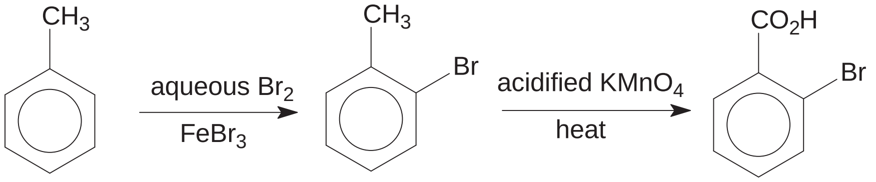

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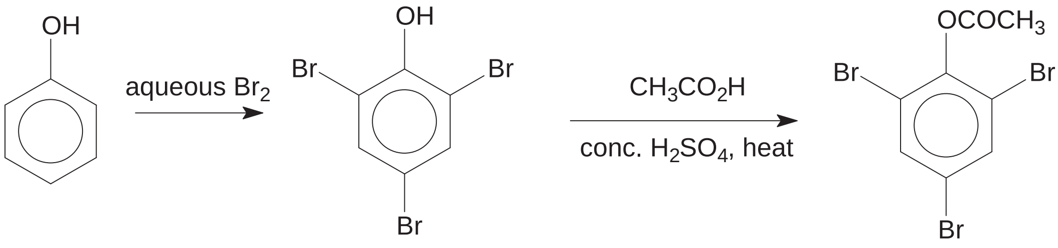

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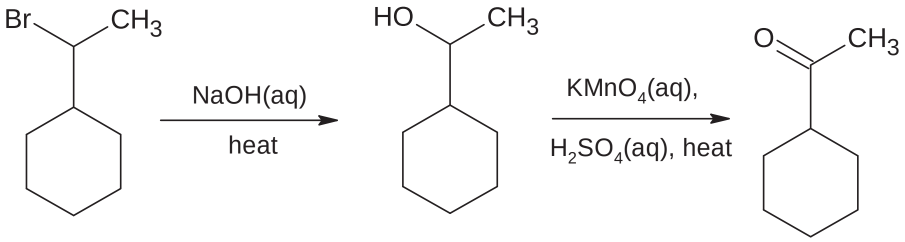
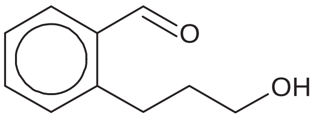


26 Compound **X** gives a positive result when treated with $[Ag(NH_3)_2]^+$ and PCl_5 but a negative result when treated with alkaline Cu(II) complex.
What could **X** be?

A



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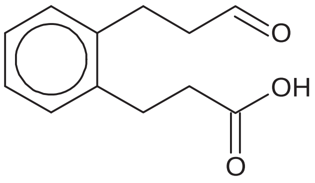

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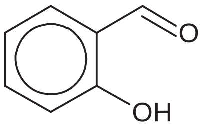

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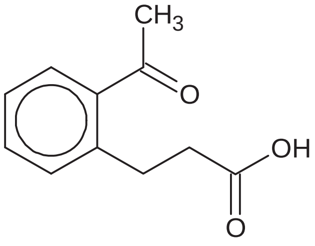
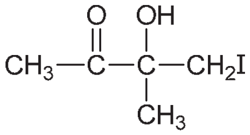


27 Compound **Y** has the following properties.

- It changes the colour of acidified sodium dichromate(VI) from orange to green.
- It gives yellow precipitate with warm, alkaline aqueous iodine.

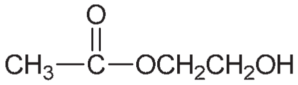
Which compound could be **Y**?

A



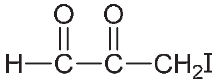
$CH_3COC(OH)(CH_3)CH_2I$

B



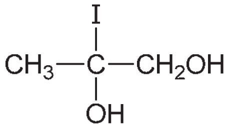
$CH_3COOCH_2CH_2OH$

C



$HCOCOCH_2I$

D



$CH_3C(I)(OH)CH_2OH$

28 An ester **Z** was heated with aqueous NaOH and the resulting mixture was then distilled. The distillate obtained decolourised hot, acidified potassium manganate(VII), giving effervescence that forms white precipitate with aqueous $Ca(OH)_2$. The residue in the distillation flask, after acidification, gave a white precipitate insoluble in water.

Which of these could be **Z**?

A $C_6H_5CO_2CH_3$

B $CH_3CO_2C_6H_5$

C $CH_3CO_2CH_2C_6H_5$

D $CH_3CH_2CO_2CH_2C_6H_5$

29 Which reaction produces a carbon compound incorporating deuterium, D? (D= $^{2}_{1}H$, an isotope of hydrogen)

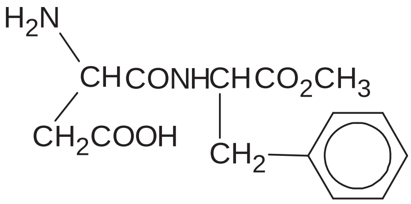
A $CH_3CH_2CN \xrightarrow[D_2O]{NaOD}$

B $CH_3CD_2OH \xrightarrow[\text{heat}]{\text{acidified } KMnO_4}$

C $CH_3COCI_3 \xrightarrow[D_2O]{NaOD}$

D $(CH_3)_3COH \xrightarrow[\text{heat}]{\text{conc. } D_2SO_4}$

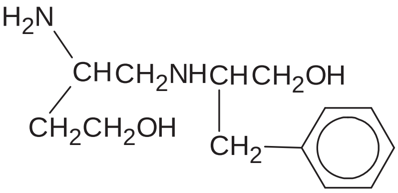
30 *Aspartame* is widely used as a sweetener in canned drinks.



Aspartame

When *Aspartame* is treated with $LiAlH_4$ in dry ether, what is the final product obtained?

A



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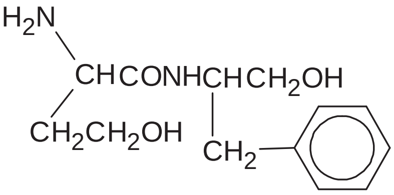

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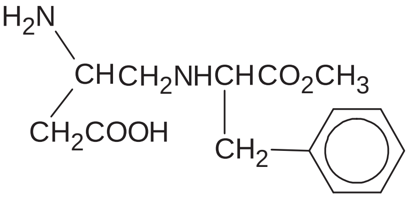
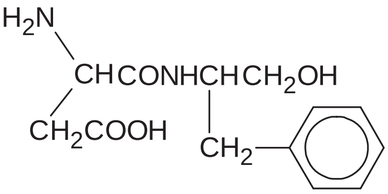


D



End of Paper

PIONEER JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION
HIGHER 2

CANDIDATE NAME

CT GROUP	1	6			

INDEX NUMBER

CHEMISTRY **9729/02**

Paper 2 Structured

12 September 2017

2 hours

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your class, index number and name on all work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough workings.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

FOR EXAMINER'S USE			
Paper 1			**/ 30**
Paper 2			
1	/ 14	4	/ 12
2	/ 8	5	/ 13
3	/ 11	6	/ 17
Penalty		sf	unit
Paper 2			**/ 75**
Paper 3			**/ 80**
Paper 4			**/ 55**
Total			

This document consists of 19 printed pages.

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

1 **(a)** Carbon dioxide, produced mainly from the burning of fossil fuels, is a greenhouse gas which trapped heat within the Earth's atmosphere, causing global warming and potentially catastrophic global climate change. One major source of carbon dioxide produced worldwide is from the rapidly expanding aviation industry.

(i) Commercial passenger jet-liners combust kerosene as fuel. The formula of kerosene may be taken as $C_{14}H_{30}$. Write a balanced equation, with state symbols, for the complete combustion of kerosene.

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

In 2017, Singapore Airlines announced that it will be launching the world's longest commercial non-stop passenger flight from Singapore to New York, with a flight distance of 15,000 km. The ultra-long range Airbus A350 aircraft used on this route burns 7.5 kg of kerosene per km.

(ii) Calculate the mass of carbon dioxide produced, in tonnes, during this flight.
[1 tonne = 1000kg]

[3]

(iii) Apart from carbon dioxide, nitrogen dioxide is another air pollutant found in the flue gases from the jet engine of aircrafts. Explain how nitrogen dioxide is produced in the jet engine.

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

(iv) Why is it important to remove nitrogen dioxide from the flue gases?

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

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

(b) Scientists have been studying the idea of carbon capture and storage technologies to try to remove atmospheric carbon dioxide on an industrial scale. One promising technology is called *calcium looping*. This process involved using calcium oxide to react with the atmospheric carbon dioxide to form calcium carbonate (i.e. limestone) which can then be stored away in abandoned mines.

$$CaO(s) + CO_2(g) \rightarrow CaCO_3(s) \quad \Delta H_1$$

(i) Using the space below, construct a fully labelled energy cycle diagram to calculate ΔH_1 using the following data.

standard enthalpy change of formation of CaO(s)	-635 kJ mol^{-1}
standard enthalpy change of formation of $CaCO_3$(s)	-1207 kJ mol^{-1}
standard enthalpy change of combustion of C(s)	-394 kJ mol^{-1}

[3]

(ii) Like calcium carbonate, aluminum oxide is a major components of naturally occurring rocks. Explain clearly, in terms of bonding and structure, why aluminum oxide is insoluble in water.

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………………………………………………………………………………………… [3]

(c) Carbonate buffers are widely used for biochemical purposes.

A student wishes to form a CO_3^{2-}/ HCO_3^- buffer in the laboratory.

Given that the carbonate ion has a K_b of 1.8×10^{-4} mol dm^{-3}, calculate the volume of 0.10 mol dm^{-3} of hydrochloric acid that he has to add to 25.0 cm^3 of 0.12 mol dm^{-3} of Na_2CO_3, to form a resulting buffer solution of pH 9.50.

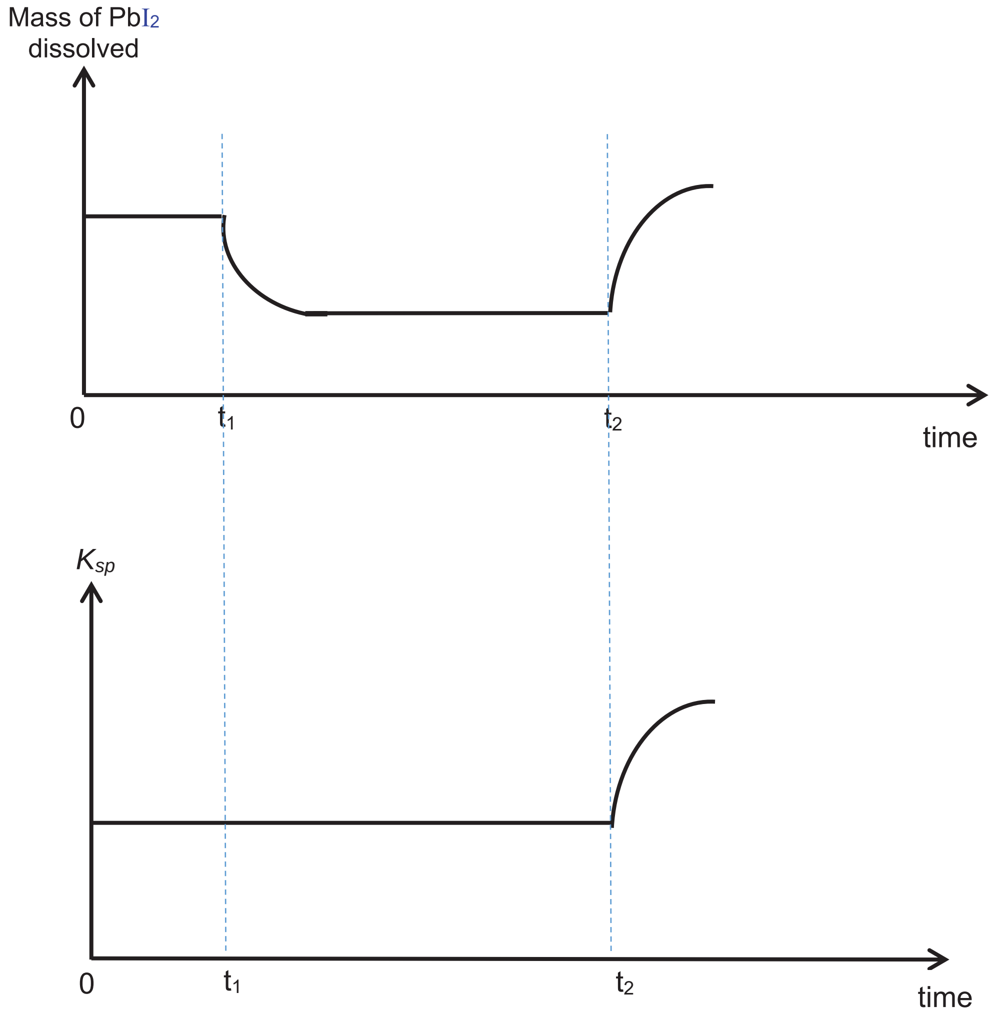
[2]

[Total:14]

2 **(a)** This question is about lead(II) halides. PbI_2 is a sparingly soluble salt:

$$PbI_2(s) + aq \rightleftharpoons Pb^{2+}(aq) + 2\,I^-(aq) \qquad \Delta H>0$$

A student aimed to investigate the solubility product and solubility of PbI_2 under different conditions. He first added some solid PbI_2 into 100 cm^3 of water at 15°C, and subsequently made two changes at t_1 and t_2. The graphs below show the mass of PbI_2 dissolved and solubility product of PbI_2 against time.



Some possible changes listed below were made by the student at t_1 and t_2.

1. Cool reaction mixture to 10°C in water bath
2. Heat reaction mixture to 50°C in water bath
3. Add $AgNO_3$(s)
4. Pump in $Pb(NO_3)_2$(aq)

With reference to **both** graphs, suggest and explain which of the above changes (1)-(4), was made at t_1 and t_2 respectively.

change made at t_1: ....

explanation:..

....[2]

change made at t_2: ....

explanation:...

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

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

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

(b) The values of the solubility products of two salts, lead(II) iodide, PbI_2, and silver (I) iodide, AgI are given below.

$$K_{sp}\ (PbI_2) = 3.97 \times 10^{-9}\ mol^3\ dm^{-9}$$
$$K_{sp}\ (AgI) = 8.3 \times 10^{-17}\ mol^2\ dm^{-6}$$

A lab technician added solid PbI_2 into water, shaking it thoroughly. He filtered off the remaining solid, leaving a saturated solution **H**.

He added drops of aqueous silver nitrate to **H**, until AgI just precipitates. Determine the concentration of Ag^+ when AgI just precipitates.

[2]

(c) When a precipitate is formed, $\Delta G^\ominus_{ppt}$, in J mol^{-1}, is given by the following expression.

$$\Delta G^\ominus_{ppt} = 2.303\ RT \log K_{sp}$$

Given that for lead(II) chloride, $PbCl_2$, K_{sp} = 1.70 x 10^{-5} mol^3 dm^{-9} at 298 K, calculate $\Delta^\ominus G_{ppt}$ for $PbCl_2$ at 298K. Thus explain if $PbCl_2$ is soluble at 298K.

[2]
[Total:8]

3 **(a)** Chlorine has been extensively used in the manufacture of many compounds.

One such compound is household bleach, which contains sodium chlorate(I), $NaClO$.

The chlorate(I) ion acts as a powerful oxidising agent in acidic solution:

$$2ClO^-(aq) + 4H^+(aq) + 2e^- \rightleftharpoons Cl_2(g) + 2H_2O(l) \qquad E^\ominus = +1.64\text{ V}$$

(i) Define the term *standard electrode potential*.

……………………………………………………………………………………………

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

(ii) Draw a fully labelled diagram, to show how the standard electrode potential, $E^\ominus(ClO^-/Cl_2)$, could be measured.

[3]

(b) Use the *Data booklet* to predict the reaction, if any, that would occur when the following pairs of reagents are mixed in acidified aqueous solution. If a reaction occurs, write a balanced equation and calculate $E^\ominus_{cell}$.

(i) $NaClO(aq)$ and $H_2O_2(aq)$

[2]

(ii) $NaClO(aq)$ and $Cr(NO_3)_3(aq)$

[2]

(c) When a few drops of aqueous sodium carbonate was added to chromium(III) nitrate, carbon dioxide gas and a grey-green precipitate, **R**, were obtained.

With the aid of equation(s), explain why CO_2 is given off in the above reaction**,** and identify precipitate **R**.

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……………………………………………………………………………………………… [3]

[Total:11]

4 Manganese is a first row d-block element in the Periodic table with a melting point of 1246°C. Like many other d-block elements, manganese shows properties that are atypical from other s-block metals, such as potassium and calcium.

Its minerals are widely distributed, with manganese dioxide and manganese carbonate being the most common. Manganese is also an essential element in living organisms, where many types of enzymes make use of the variable oxidation states of manganese to take part in the various redox reactions.

(a) **(i)** Explain why manganese has a much higher melting point than calcium, which is found in the same period.

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…………………………………………………………………………………… [3]

(ii) Explain briefly why the density of manganese is significantly greater than that of calcium.

…………………………………………………………………………………………

…………………………………………………………………………………… [1]

(b) Heating a mixture of KOH and MnO_2 in air gives potassium manganite, K_2MnO_4, which is an important precursor to potassium permanganate, $KMnO_4$, a common oxidising agent.

(i) State the oxidation state of manganese and hence, write the electronic configuration of the manganese ion in each of the following compounds:

MnO_2 :
Oxidation state: ………………………………

Electronic configuration: ………………………………

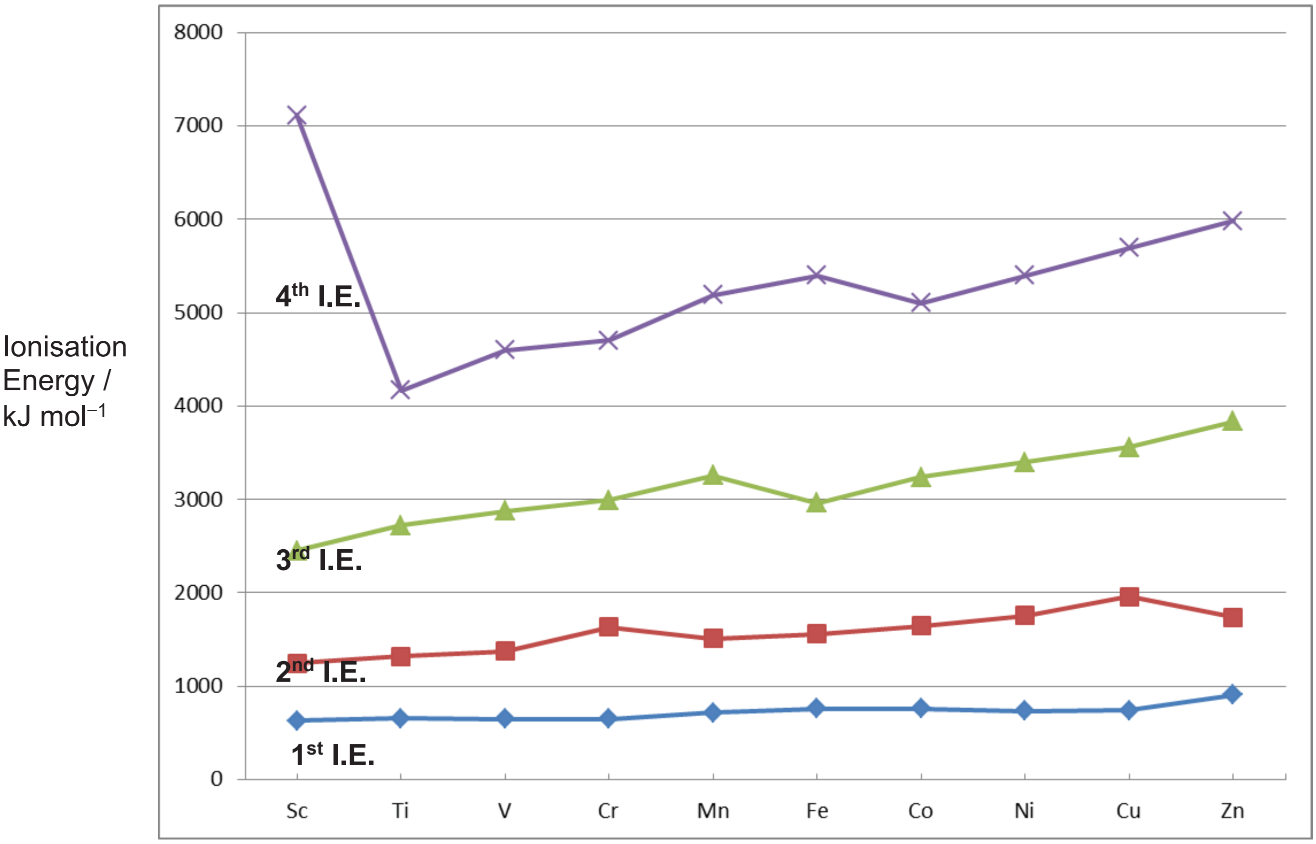
K_2MnO_4:
Oxidation state: ………………………………

Electronic configuration: ……………………………… [2]

(ii) Write a balanced equation for the redox reaction between MnO_2, KOH and air.

……………………………………………………………………………………[1]

(c) The graph below shows the variation of the first to fourth ionisation energies for the first row d–block elements scandium to zinc.



(i) Give an equation that represents the second ionisation energy of manganese.

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

(ii) Explain why the first ionisation energies of the elements Ti to Cu, are relatively invariant across the Period.

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

(iii) Explain why the fourth ionisation energy of cobalt is lower than that of iron.

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

[Total:12]

5 **(a)** Structure elucidation is an important skill that chemists must acquire to help them determine the chemical structures of organic compounds.

A novice chemist requires your assistance in determining the structure of an aromatic organic compound **P**, that she found in the laboratory. The molecular formula of compound **P** is $C_9H_{11}ON$, and **P** contains two functional groups.

(i) An orange precipitate is observed when **P** is reacted with 2,4-dinitrophenylhydrazine. Name the type of reaction that occured. From this observation only, name two different functional groups that could be present in **P**.

Type of reaction: ……………………………………………………….…………………

Functional groups: ………………………… and ………………….………………

[2]

(ii) No silver mirror is formed when **P** is warmed with hot ammoniacal silver nitrate (mixture of aqueous ammonia and aqueous silver nitrate). Which of the functional groups you named in **(a)(i)**, is confirmed by this observation?

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

(iii) When compound **P** is reacted with bromine water in excess, a white solid which has M_r = 385.7, is formed. Deduce the molecular formula of the white solid that is formed.

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

(iv) Compound **P** reacts with hot potassium manganate(VII) in aqueous sodium hydroxide. A product with the molecular fomula, $C_8H_5NO_4Na_2$, is formed.
Draw the structure of the product.

[1]

(v) You now have enough information to determine the structural formula of compound **P**. Draw the structure for **P**, explaining clearly why you have placed each of the two functional groups in their respective positions.

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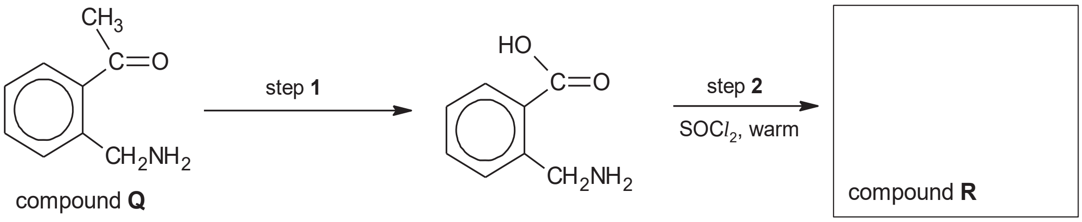
…………………………………………………………………………………………..

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

(b) Compound **Q**, $C_9H_{11}ON$, is a structural isomer of compound **P**.

The diagram below shows a possible reaction scheme for converting compound **Q** to **R,** C_8H_7NO.

(i) Complete the diagram by suggesting the reagents and conditions for step **1**, and give the structural formula of compound **R**.



[2]

(ii) It was found that the yield of **R** was low. Suggest a reason for this.

…………………………………………………………………………………………..

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

(c) The table below shows the pK_b values of two organic nitrogen compounds in aqueous solutions.

Compound	***p*K$_b$**
methylamine, CH_3NH_2	3.36
trimethylamine, $(CH_3)_3N$	4.19

Using the data provided in the table above, suggest an explanation on the relative basicities of these two compounds.

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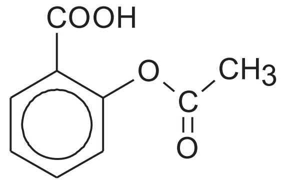
…………………………………………………………………………………………………… [3]

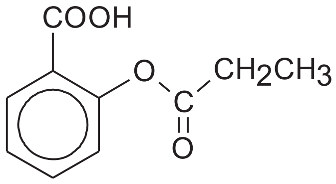
[Total:13]

6 **(a)** Acetylsalicylic acid (ASA), which is extracted from the leaves of the willow tree, has been used for its health effects for at least 2,400 years. It is an important medication that is used to treat pain, fever, and inflammation.



Acetylsalicylic acid

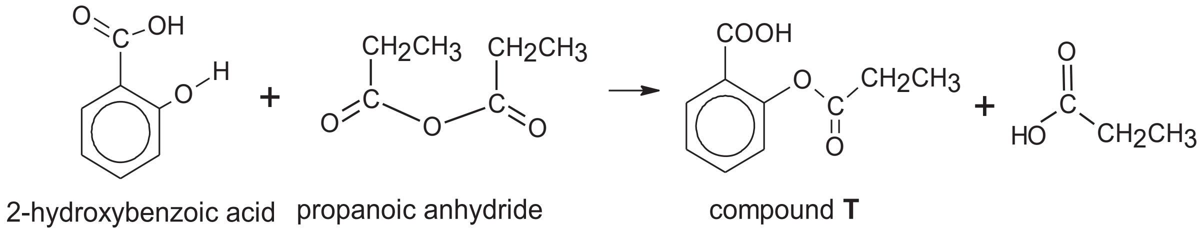
A chemist wanted to form a derivative of ASA, compound **T** below:



Compound **T**

One method to form compound **T** was to react 2-hydroxybenzoic acid and propanoic anhydride in reaction **1** below.

Reaction **1**



(i) State the type of reaction that has occurred in reaction **1**.

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

<u>The mechanism of reaction **1** consists of four steps and is described below:</u>

Step **1**:
The phenol group on 2-hydroxybenzoic acid acts as a nucleophile and attacks one of the reactive carbons in propanoic anhydride to form only one intermediate **W**. The intermediate **W** contains both a cationic oxygen and an anionic oxygen.

Step **2**:
A proton is released from intermediate **W** to form intermediate **X**.

Step **3**:
From intermediate **X**, a carboxylate anion is expelled as a leaving group, and an ester **Y** is formed as the other product.

Step **4**:
Protonation of the carboxylate anion formed in step **3** produces a carboxylic acid.

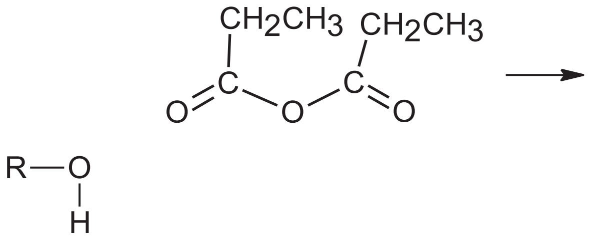
(ii) Draw all four steps in the full mechanism for the reaction between 2-hydroxybenzoic acid and propanoic anhydride.

(you may use ROH to represent 2-hydroxybenzoic acid in your answer.)

For the first step of the mechanism, *complete* the diagram shown below and draw the remaining three steps of the mechanism in the space given below. Show all intermediates, relevant charges, lone pairs of electrons and indicate the movement of electron pairs with curly arrows in **all** the steps.

Step **1**

Let R–O–H represents 2-hydroxybenzoic acid.



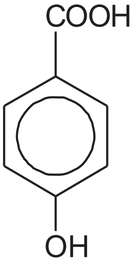
Step **2**

Step **3**

Step **4**

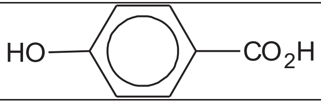
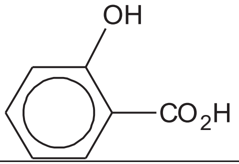
[4]

(iii) An isomer of 2-hydroxybenzoic acid is shown below:



4-hydroxybenzoic acid

Both 2-hydroxybenzoic acid and 4-hydroxybenzoic acid are dibasic acids that ionises in two stages. The acid dissociation constant, pK_1, for the first stage of dissociation is given below.

	pK_1
	4.54
	2.97

With the aid of a diagram, explain why 2-hydroxybenzoic acid has a lower pK_1.

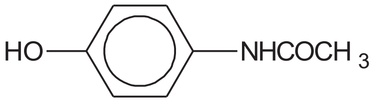
…………………………………………………………………………………………..

…………………………………………………………………………………………..

…………………………………………………………………………………………..

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

(b) Another medicine that is used widely to treat fever and pain is paracetamol, or commonly known as panadol.



Paracetamol

Some information on paracetamol is provided in Table 1 below.

Data on paracetamol	
Molecular Formula	$C_8H_9NO_2$
Density	1.263 g/cm^3
Melting Point	169^{o}C
Boiling Point	420^{o}C
Solubility in water	14 mg/ml
Bioavailability*	75% (oral) 100% (intravenous)
Biological half-life**	2 hours

Table 1

**Bioavailability refers to the percentage of a drug which enters the blood circulation when introduced into the body and hence able to have an active and effective effect.*

***Biological half-life of a drug is the time taken for the drug to reduce to half its original amount in the body.*

(i) Paracetamol can be produced from the reaction between 4-aminophenol and ethanoic anhydride as shown below.

$$\underset{(M_r : 109)}{\underset{\text{4-aminophenol}}{C_6H_7NO}} + \underset{(M_r : 102)}{\underset{\text{ethanoic anhydride}}{C_4H_6O_3}} \rightarrow \underset{(M_r : 151)}{\underset{\text{paracetamol}}{C_8H_9NO_2}} + C_2H_4O_2$$

It is known that the yield of this reaction is only 60%.

Calculate the minimum masses of the reactants that are required to produce 10 g of paracetamol.

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

(ii) A doctor wishes to prescribe oral medication for one of his patients suffering from headache. In order for the medicine to be effective, the patient requires a recommended dosage of 560 mg of paracetamol in her body.

How many 250 mg paracetamol tablets should the patient take each time?

[2]

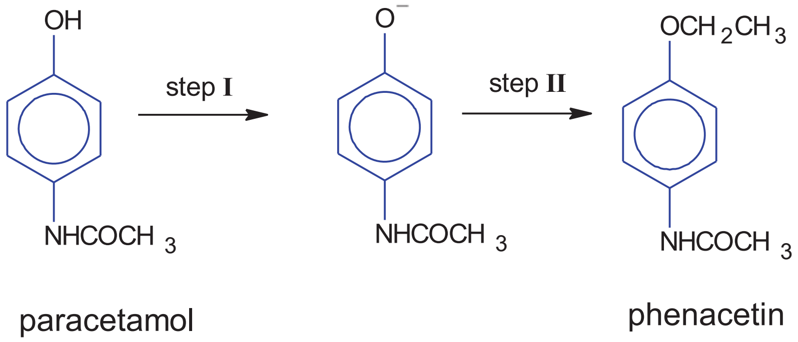
(iii) A patient suffering from acute dental pain is advised to consume orally, four 250 mg paracetamol tablets.

To effectively alleviate his pain, at any point of time, the amount of paracetamol in his body **must not** drop below 93 mg.

With reference to relevant data from Table 1, and the use of suitable calculations, determine the maximum number of hours that the oral medication prescribed above remains effective, and show clearly whether the doctor should advise the patient to take four tablets of paracetamol once in every 4 hours, 6 hours, or 8 hours.

[2]

(c) **(i)** Phenacetin was once used as an analgesic (pain killing drug). It can be synthesised from paracetamol below.



Suggest reagents and conditions for step **I** and **II**.

step **I:** ....

step **II**: ....

[2]

(ii) A student added aqueous sulfuric acid to paracetamol and heated it. Give the structures of the products obtained.

[2]

[Total:17]

End of paper

H

PIONEER JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION
HIGHER 2

CANDIDATE NAME

CT GROUP 1 6

INDEX NUMBER

CHEMISTRY **9729/03**

Paper 3 Free Response **15 September 2017**

2 hours

Candidates answer on separate paper.

Additional Materials:	Answer Paper Data Booklet Cover Page

READ THESE INSTRUCTIONS FIRST

Write your name, index number and CT group on all work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough workings.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question.

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

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

This document consists of **17** printed pages.

Section A

Answer **all** questions in this section.

1 Compounds containing halogens form a large class of chemicals, which are of industrial importance and are synthesised in huge quantities worldwide.

(a) Phosgene, $COCl_2$, is a gas which was produced during World War I, and was used as a chemical weapon. One method to produce phosgene from trichloromethane is as shown below.

$$2CHCl_3(g) + O_2(g) \rightarrow 2COCl_2(g) + 2HCl(g) \qquad \Delta H = -346 \text{ kJ mol}^{-1}$$

Using the data below, calculate the standard enthalpy change of formation of HCl(g).

standard enthalpy change of formation of $CHCl_3$(g)	-103 kJ mol^{-1}
standard enthalpy change of formation of $COCl_2$(g)	-184 kJ mol^{-1}

[1]

(b) Aqueous hydrochloric acid is another chemical with many industrial uses. It can be obtained by reacting hydrogen gas and chlorine gas in the presence of UV light, followed by dissolving the hydrogen chloride gas in water.

The equation for this reaction is shown below.

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g) \rightarrow H^+(aq) + Cl^-(aq) \qquad \Delta H_r$$

Using the Data Booklet, the data in the table below, and your answer in **(a)**, construct an appropriate energy-level diagram to calculate ΔH_r.

	$\Delta H^\ominus$/ kJ mol^{-1}
First ionisation energy of H(g)	+1310
First electron affinity of Cl(g)	– 364
Standard enthalpy change of hydration of Cl^-(g)	– 381
Standard enthalpy change of hydration of H^+(g)	– 1130

[4]

(c) When heated, Group 17 hydrides, HX, undergo thermal decomposition.

$$HX \longrightarrow \tfrac{1}{2}H_2 + \tfrac{1}{2}X_2$$

Using the data on bond energies of the various H-X bonds given below, predict and explain how the thermal stability of the hydrides varies down Group 17.

Bonds	**Bond energies/ kJ mol^{-1}**
H-C*l*	+431
H-Br	+366
H-I	+299

[2]

(d) Seawater is an important source of ionic halides like sodium chloride, sodium bromide and sodium iodide.

When silver nitrate is added to separate test-tubes containing aqueous sodium chloride, sodium bromide and sodium iodide, the various AgX (X = C*l*, Br and I) precipitates were observed. The solubilities of these precipitates upon addition of dilute NH_3 and concentrated aqueous NH_3, are recorded below.

	NaC*l*	**NaBr**	**NaI**
To NaX(aq), add $AgNO_3$(aq)	white ppt observed	cream ppt observed	yellow ppt observed
To the resulting mixture, add dilute NH_3(aq)	soluble	insoluble	Insoluble
To the resulting mixture, add excess concentrated aqueous NH_3(aq)	soluble	soluble	Insoluble

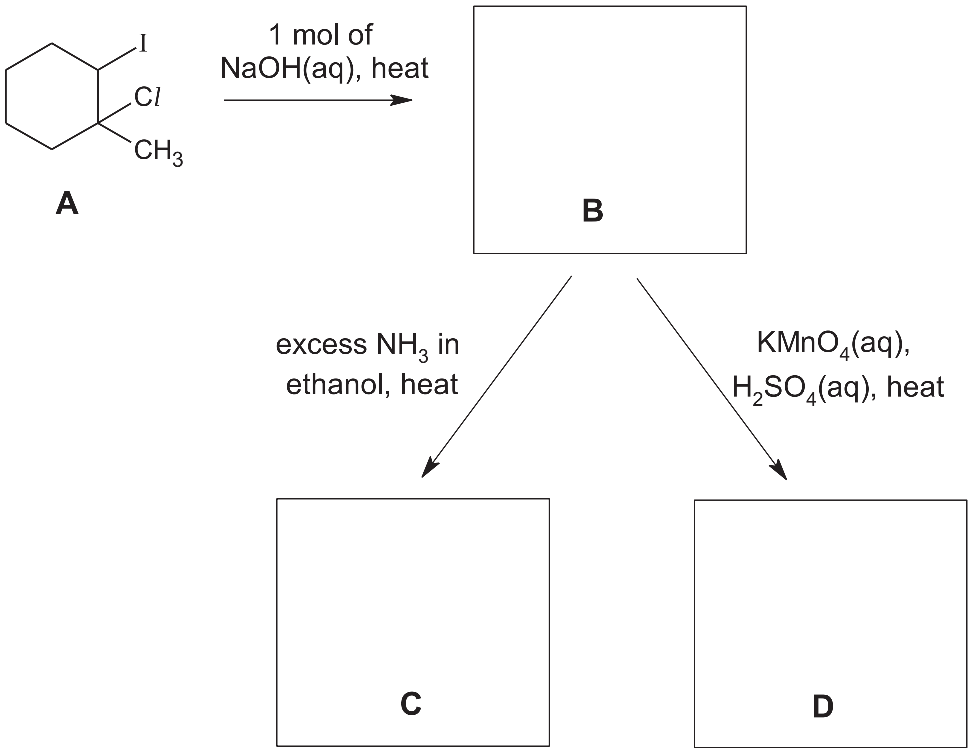
(i) Write the balanced ionic equation for the formation of the cream precipitate from adding silver nitrate to sodium bromide. [1]

(ii) Explain the effect of adding aqueous ammonia to each of the resulting mixture and clearly account for any difference in the observation. [3]

(e) Halogenoalkanes are widely synthesised by reacting halogens with alkenes. In turn, halogenoalkanes can undergo nucleophilic substitution using aqueous sodium hydroxide to form alcohols commercially.

(i) Give one reason why iodoalkanes are more reactive towards nucleophilic substitution with aqueous NaOH than the corresponding chloroalkanes. [1]

(ii) A sequence of reactions, starting from compound **A**, a dihalogeno compound, is shown on the next page.

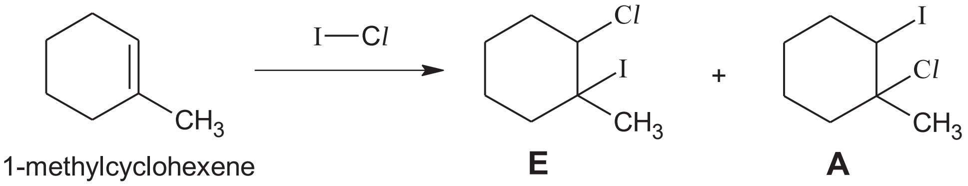


Draw the structures of compounds **B**, **C** and **D**.

[3]

(iii) The halogens form many interhalogen compounds, one such example is I*Cl*, commonly known as Wijs' reagent.

Wijs' reagent can react with 1-methylcyclohexene to form a mixture of compound **E** and **A**. Explain why **A** is the major product for this reaction.



[2]

(f) **(i)** Below outlines a reaction scheme of phosgene with NaOH(aq).

$$COCl_2 \xrightarrow[\text{stage 1}]{OH^-} COCl(OH) \xrightarrow[\text{stage 2}]{} CO_2 + HCl$$

State the types of reaction occurring in stage 1, and stage 2. [2]

(ii) To remove any phosgene present in chloroform, a small amount of methanol is added. Use the information in **(f)(i),** suggest the structure of the organic compound formed when phosgene reacts with methanol. [1]

[Total:20]

2 **(a)** Carbon monoxide reacts with steam over a copper / zinc catalyst, to form a mixture of carbon dioxide and hydrogen gas.

Reaction 1: $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$

When an equimolar mixture of hydrogen and carbon dioxide at an initial total pressure of 4 atm is allowed to reach equilibrium at 1000 K, the percentage of steam in the mixture of gases is found to be 15%.

(i) Calculate K_p of the system in **reaction 1** at 1000 K. [2]

(ii) Suggest, with a reason, whether a higher pressure will favour the formation of steam. [1]

(b) Sodium ethanoate can be used to prepare ethane by an electrochemical reaction, which is known as the Kolbe electrolysis reaction.

Ethane is formed at the anode by the following reaction:

$$2CH_3CO_2^- \rightarrow C_2H_6 + 2CO_2 + 2e^-$$

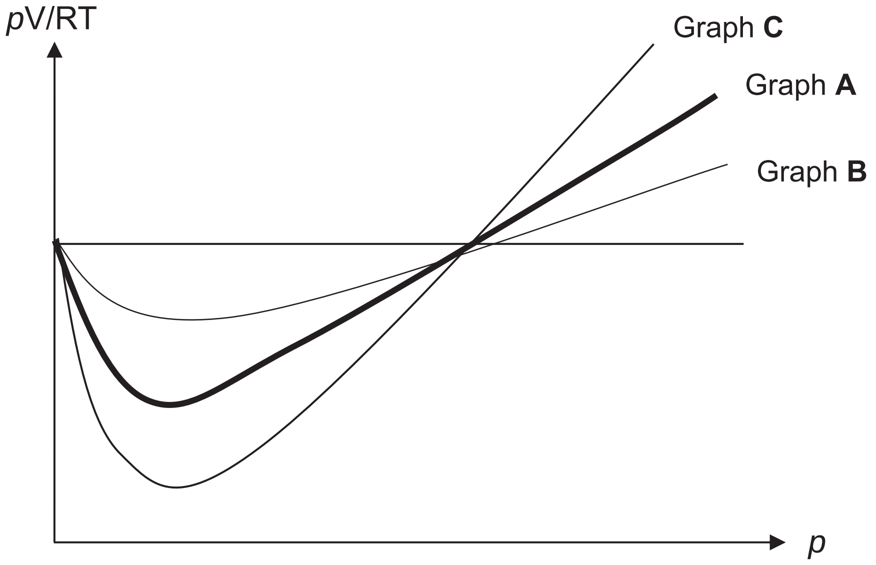
A student investigated the electrolysis of an aqueous solution of sodium ethanoate, using graphite electrodes in a litmus solution.

(i) Give the equation for the reaction occurring at the cathode, and state the final colour expected at the cathode.

Construct an equation for the **overall** reaction. [2]

(ii) Calculate the time, in minutes, needed by the student to pass a current of 5.0 A through a solution of sodium ethanoate, to produce 1.50 g of ethane. [2]

(c) **(i)** The value of pV/RT is plotted against p for the following three gases, where p is the pressure and V is the volume of the gas.
Given that graph **A** represents 1 mol of CO_2 at 298 K, identify which of the following graphs, **B** or **C,** represent 1 mol of CO_2 at 500 K. Explain your answer.



[2]

(ii) Sulfur dioxide is used by the Romans in winemaking, when they discovered that burning sulfur candles inside empty wine vessels keeps them fresh and free from vinegar smell.

One such cylinder of sulfur dioxide has an internal volume of 2.5 dm^3, and a mass of 2.3 kg.

Calculate the pressure (in pascals) that the sulfur dioxide would exert inside the cylinder at room temperature. [1]

(d) Sulfuric acid is used in many industrial processes of major importance.

The process used to produce sulfuric acid involves a three–stage process. The first stage is to pass air over burning sulfur. The emerging gas is then passed over a catalyst, V_2O_5, which is maintained at 450-550ºC in the reaction chamber.

Stage **I**: $S(s) + O_2(g) \rightarrow SO_2(g)$
Stage **II**: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
Stage **III**: $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(l)$

(i) Draw dot-and-cross diagrams to show the bonding in SO_2 and H_2SO_4.
State the bond angle, with respect to sulfur atom, in each of them. [4]

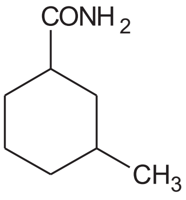
(ii) The boiling points of sulfur trioxide and sulfur dioxide are 45^{o}C and -10^{o}C respectively. Account for the difference in boiling points for both compounds, in terms of structure and bonding. [2]

(e) For each of the following pairs of compounds, suggest **one** simple chemical test to distinguish them from each other. State the reagents and conditions needed and give the expected observations for each compound.

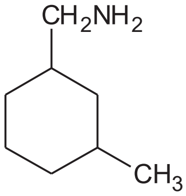
(i) $CH_2{=}CHCH_2CH(CH_3)OH$ **J** $CH_2{=}CHC(CH_3)_2OH$ **K**

[2]

(ii)



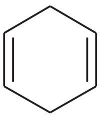
L



M

[2]

(iii)



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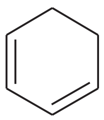


Q

[2]

[Total:22]

3 Nitrous oxide, N_2O, is commonly known as laughing gas due to the euphoric effects of inhaling it. At a temperature of 1000 K, in the presence of chlorine catalyst, N_2O decomposes to its elements according to the following equation:

$$2N_2O(g) \rightarrow 2N_2(g) + O_2(g)$$

The experimental rate equation for this reaction is:

$$\text{Rate} = kP_{N_2O}^{a}\,P_{Cl_2}^{b}\,,$$

where P_{N_2O} and P_{Cl_2} are the partial pressures of N_2O and Cl_2 respectively, and a and b are non-zero constants.

The rate of decomposition of pure N_2O may be followed at constant temperature, by measuring the total pressure of the system with time.

The data below refers to a reaction in which pure N_2O decomposes in the presence of chlorine catalyst, Cl_2, (at partial pressure of 47 kPa).

Experiment 1:

time / s	0	40	80	140	240
P_{total} / kPa	87.0	91.3	93.0	98.0	102.2
P_{N_2O}	40	31. 4	25	18	9.6

(a) **(i)** Show that the partial pressure of N_2O at any instant is given by $P_{N_2O} = 214 - 2P_{total}$ [2]

(ii) Use the given data provided in the table above to plot a graph of P_{N_2O} against time on suitable axes.

Showing all your working and drawing clearly any construction lines on your graph, use your graph to determine the value of a, the order of reaction with respect to N_2O. [4]

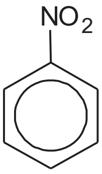
(iii) Two additional experiments, experiments 2 and 3 were carried out and the following results were obtained.

	P_{N_2O} / kPa	P_{Cl_2} / kPa	Initial rate/ kPa s^{-1}
experiment 2	70	35	0.306
experiment 3	70	70	0.613

Determine b, the order of reaction with respect to chlorine. Explain your reasoning. [1]

(iv) Hence write the rate equation for the reaction. [1]

(b) Nitrobenzene is an organic compound used to mask unpleasant odors in shoe and leather dressings.



(i) Suggest the type of hybridisation of N in nitrobenzene. [1]

(ii) Nitrobenzene can be formed from reacting benzene with concentrated nitric acid and sulfuric acid. Name and outline the mechanism of the nitration of benzene. Indicate the rate-determining step and draw the formula of the organic intermediate. [3]

(iii) Given that the nitration of benzene is exothermic, sketch the reaction pathway diagram of the reaction, labelling clearly the reactant, intermediate and product on your diagram. [2]

(c) To investigate the mechanism of nitration of benzene, every hydrogen atom on benzene is replaced by its isotope, deuterium, to form C_6D_6.

Carbon–deuterium (C-D) bond has higher bond energy than a carbon–hydrogen (C-H) bond.

If the rate-determining step involves the breaking of a C–H bond, replacing the C–H bond with a C–D bond will change the rate constant, k, of the reaction. This is known as the deuterium isotope effect.

Deuterium isotope effect = $\frac{k_H}{k_D}$

k_H = rate constant for nitration of C_6H_6

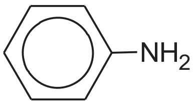
k_D = rate constant for nitration of C_6D_6

If $\frac{k_H}{k_D} = 1$, it is said that the deuterium isotope effect is absent.

If $\frac{k_H}{k_D} >> 1$, it is said that the deuterium isotope effect is present.

Predict with reasoning, if the deuterium isotope effect would be present in the nitration of benzene. [1]

(d) **(i)** Nitrobenzene can be converted to phenylamine, which is used in the synthesis of polyurethane, a polymer used in making tyres.



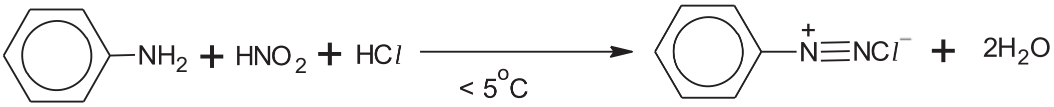
phenylamine

Suggest the reagents and conditions to convert nitrobenzene to phenylamine. [1]

(ii) The following equations illustrate the formation of phenol from phenylamine, in two steps:

In step **1**, phenylamine reacts with cold nitrous acid, HNO_2, and hydrochloric acid, HC*l*, to form phenyldiazonium chloride.

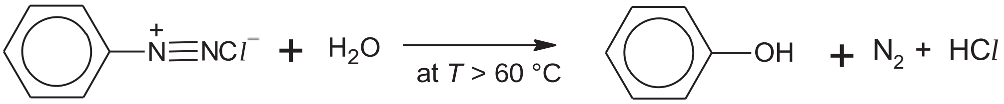
<u>step **1**</u>



phenyldiazonium chloride

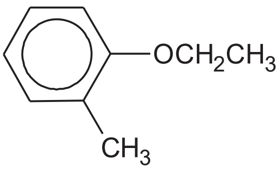
In step **2**, phenyldiazonium chloride can react with water upon heating to give phenol.

<u>step **2**</u>



phenyldiazonium chloride

Propose a two-step synthetic pathway for the conversion of 2-methylphenylamine to compound **S** below.



Compound **S**

[2]

[Total:18]

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Section **B**

Answer **one** question from this section.

4 (a) A blood test can detect abnormally high levels of an amino acid which is one of the signs of the disease phenylketonuria, a rare condition in which a person is unable to properly break down amino acids such as phenylalanine.

In acidic solution, phenylalanine is completely protonated and exists as $H_3N^+CHRCO_2H$, where R is $–CH_2C_6H_5$.

Protonated phenylalanine, $H_3N^+CHRCO_2H$, acts as a dibasic acid that ionises in stages.

$$H_3N^+CHRCO_2H \rightleftharpoons H_3N^+CHRCO_2^- + H^+ \qquad pK_1 = 1.83$$

$$H_3N^+CHRCO_2^- \rightleftharpoons H_2NCHRCO_2^- + H^+ \qquad pK_2 = 9.13$$

(i) Calculate the pH of a 0.80 mol dm^{-3} solution of protonated phenylalanine (ignore the effect of pK_2 on the pH). [1]

(ii) An amphiprotic species is one that can act as a Bronsted-Lowry acid or base. The pH of a solution containing an amphiprotic species is given by the following expression.

$$pH = ½(pK_1 + pK_2)$$

In the titration of protonated phenylalanine with NaOH, an amphiprotic species is formed.

Identify the amphiprotic species formed and calculate the pH of the solution.

[2]

(iii) Sketch the titration curve when 25.0 cm^3 of the protonated form of phenylalanine is being titrated with 70 cm^3 of NaOH(aq) of the same concentration. On your sketch, clearly mark the two pK_a values and the points you have calculated in **(i)** and **(ii)**. [3]

(iv) Suggest a suitable indicator from the following table to be used to detect the first equivalence point and state the colour change of the solution at this equivalence point.

indicator	pH range	acid solution	basic solution
Thymol Blue	1 – 3	red	yellow
Methyl Red	5 – 6	red	yellow
Phenol red	7 – 8	yellow	red
Phenolphthalein	8 - 10	colourless	red

[2]

(b) "Acidity regulators" are food additives that have a buffering action on the pH of food. A mixture of citric acid, $C_5H_7O_4CO_2H$, and its sodium salt is often used for this purpose.
You may assume that citric acid behaves as a monobasic weak acid.

$C_5H_7O_4CO_2H \rightleftharpoons C_5H_7O_4CO_2^- + H^+$; $K_a = 7.4 \times 10^{-4}$ mol dm^{-3}

(i) A citric acid / sodium citrate buffer mixture is prepared by mixing 40.0 cm^3 of 0.100 mol dm^{-3} citric acid and 60.0 cm^3 of 0.200 mol dm^{-3} sodium citrate.

Calculate the pH of the buffer solution. [1]

(ii) Write equations to show how this mixture of citric acid and sodium citrate regulates the acidity on addition of H^+ ions and OH^- ions. [2]

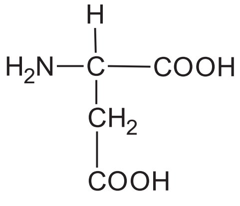
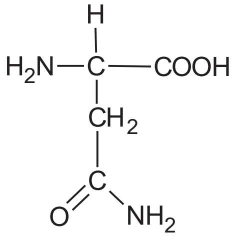
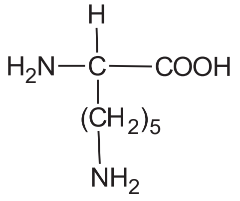
(c) **(i)** Describe the conditions needed to hydrolyse a protein non-enzymatically. [1]

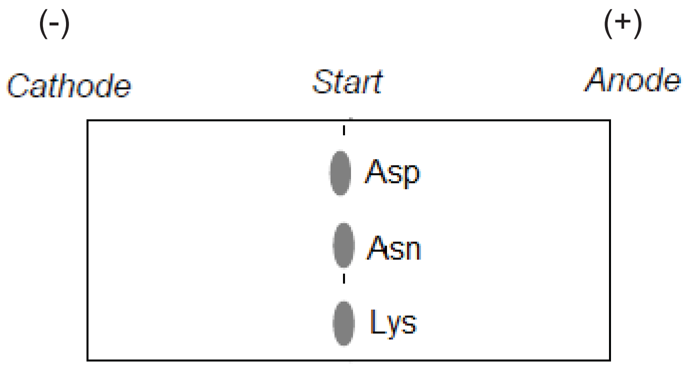
(ii) Histidine decarboxylase undergoes enzymatic hydrolysis. Upon hydrolysis, the polypeptide fragments of the enzyme's active site are isolated as shown below.

- Ala-Cys-Phe
- Gly-Gly
- Lys-Asp-Asp-Gly-Gly
- Phe-Arg-Lys

Deduce the sequence of the 9 amino acid residues of the enzyme's active site. [2]

(iii) A different segment of tripeptide, Asp-Asn-Lys, was subjected briefly to acidic hydrolysis which produced individual amino acids as well as various peptides. The resulting mixture buffered at pH 13 was separated in an electric field using electrophoresis.

Amino acid			
Abbreviation	Asp	Asn	Lys



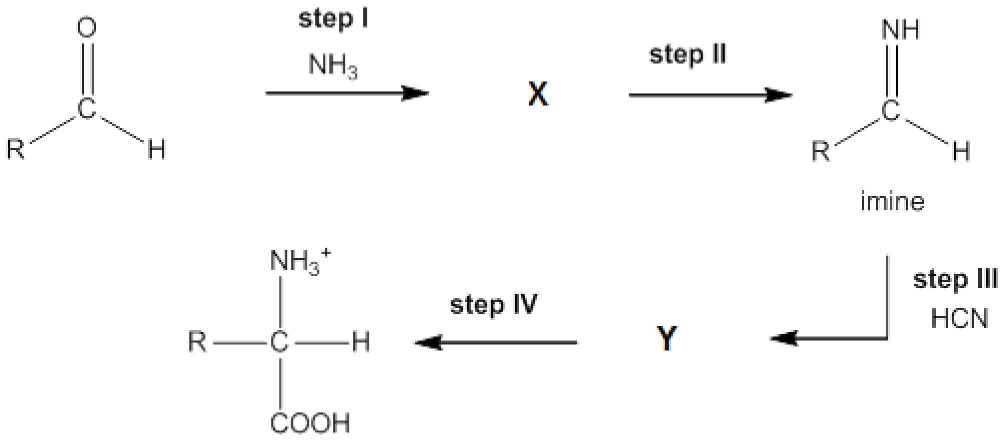
Using the above template, sketch and label the position of the three amino acids after the separation. State one factor that affects the rate at which the charged particles move during electrophoresis.

[3]

(d) The Strecker synthesis assembles an α-amino acid from the amine precursor and an aldehyde.

- Step **I** is a nucleophilic addition reaction.
- Step **II** involves the elimination of water from **X** to form an imine**.**
- Step **III** is similar to the formation of cyanohydrin when the imine undergoes nucleophilic addition with HCN and forms an α-amino nitrile, **Y**.
- Step **IV** is the hydrolysis of **Y** to form the carboxylic acid functional group.

In the following reaction flow scheme, draw the intermediate compounds **X** and **Y** and suggest the reagent and condition for step **IV** in the scheme.



[3]
[Total:20]

5 Copper is an important transition element that can readily form complex ions with *ligands*. Copper forms a large variety of compounds, usually with variable oxidation states. Copper compounds also act as useful *homogeneous catalysts*, commonly used in many industrial operations.

(a) Define the terms *ligand* and *homogeneous catalyst*. [2]

(b) In recent years, horseshoe crabs have generated great interest amongst scientists due to its blood with remarkable antibacterial properties. An unusual aspect of the blood is that it is bright blue, a consequence of using copper-based complexes, haemocyanin, to transport oxygen.

Two Haemocyanin (Hc) reversibly bind a single oxygen molecule, O_2, to form oxyhaemocyanin, HcO_2, according to the following equilibrium:

$$2Hc(aq) + O_2(aq) \rightleftharpoons 2HcO_2(aq) \quad \textit{equilibrium 1}$$

Oxygenation causes a color change between Cu(I) deoxygenated form and the Cu(II) oxygenated form.

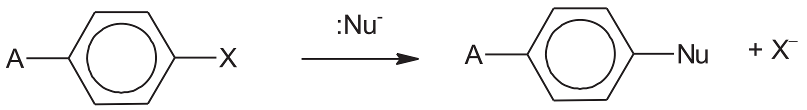
(i) By considering *equilibrium 1* and the level of oxygen in both the lungs and body cells, comment on how the crab cells receive oxygen from the air in the lungs.

[2]

(ii) Indicate the color change from Cu(II) oxygenated form to Cu(I) deoxygenated form. Hence explain why both copper complex ions exhibit different colours.

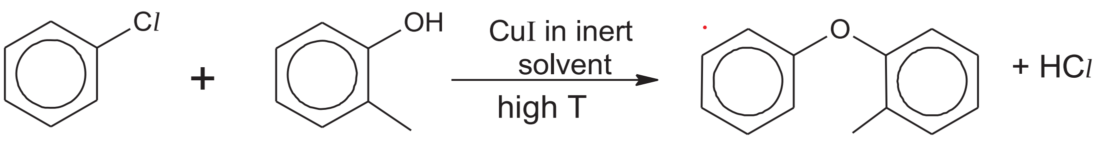
[5]

(c) Most aromatic compounds undergo electrophilic substitution. However it is possible for aryl halides to undergo a limited number of nucleophilic substitution reactions with strong nucleophiles. An example of a reaction is as follows:



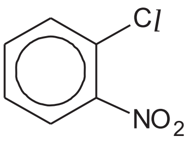
An example of an aryl nucleophilic substitution is the *Ullmann coupling* reaction where hydrocarbons fragments are coupled, using copper compounds as a catalyst.

An example is indicated in reaction **1** below.

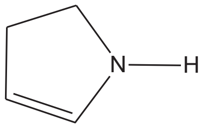


reaction **1**

(i) The conditions for the *Ullmann coupling* reactions are usually harsh conditions, and yet give low yield. In a similar reaction under the same temperature and pressure, the two compounds below were reacted together:



and



.

Deduce and draw the structure of the product for the above reaction. [1]

(ii) Predict, with reasoning, if the above reaction in **(c)(i)** will result in a higher or lower yield compared to reaction **1**. [2]

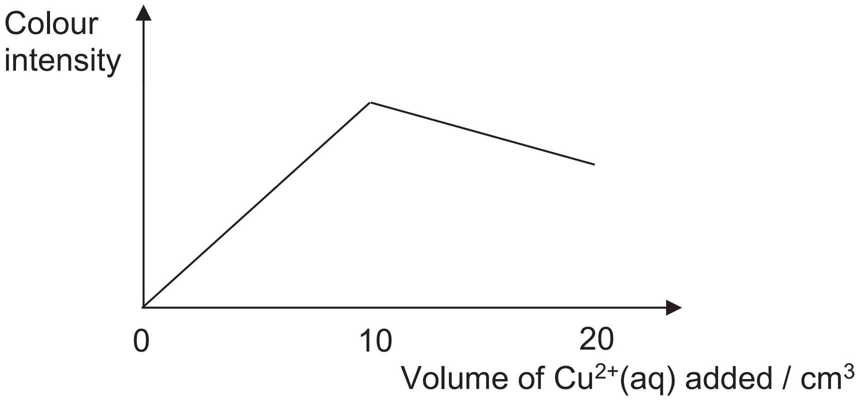
(iii) Like copper(I) iodide, aqueous Fe^{2+} is a good homogeneous catalyst used in the decomposition of aqueous hydrogen peroxide as indicated below.

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

With reference to relevant data in the *Data Booklet*, suggest a mechanism for the catalysis of the above reaction by aqueous Fe^{2+}. [3]

(d) Copper(II) species can have various coordination numbers.

The formula of a methylamine-copper complex ion, $[Cu(CH_3NH_2)_x(H_2O)_2]^{2+}$, can be determined using a colorimeter. In an experiment, a solution of 0.050 mol dm^{-3} of $Cu^{2+}(aq)$ was added 1 cm^3 at a time to 20 cm^3 of 0.100 mol dm^{-3} of aqueous CH_3NH_2. The colour intensity of the resultant solution after each addition was measured using a colorimeter. The following graph was obtained.



(i) Using the graph, determine the value of ***x.*** [2]

(ii) Draw the structure of the methylamine-copper complex ion. [1]

(e) Mercury is poisonous as it can cause many health problems ranging from neurological, respiratory to cardiovascular problems. One possible treatment for mercury poisoning involves administering a solution of $EDTA^{4-}$, a common hexadentate ligand which forms complexes with many metal ions.

Copper and calcium ions are essential minerals required by the body. Using relevant data from below, comment on the use of $EDTA^{4-}$ as a treatment for mercury poisoning and comment on its effect on the concentrations of copper and calcium ions in the body.

Equilibrium	K_c / mol^{-1} dm^3
$Ca^{2+} + EDTA^{4-} \rightleftharpoons [Ca(EDTA)]^{2-}$	6×10^{10}
$Cu^{2+} + EDTA^{4-} \rightleftharpoons [Cu(EDTA)]^{2-}$	5×10^{18}
$Hg^{2+} + EDTA^{4-} \rightleftharpoons [Hg(EDTA)]^{2-}$	6.3×10^{21}

[2]

[Total:20]

End of Paper

H

PIONEER JUNIOR COLLEGE

JC2 Preliminary Practical Examination
HIGHER 2

CANDIDATE NAME	

CT GROUP | 1 | 6 | | | |

INDEX NUMBER | | | | |

CHEMISTRY **9729/04**

Paper 4 Practical **28 August 2017**
2 hours 30 min

Candidates answer on the Question Paper

Additional Materials: As listed in your apparatus list

READ THESE INSTRUCTIONS FIRST

Write your CT group, index number and name on all work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough workings.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions.

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.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

Shift: ______________

Lab: ______________

For Examiner's Use	
Q1	/22
Q2	/15
Q3	/18
Total	/55

This document consists of **22** printed pages.

1 **Experiment to investigate the behaviour of acids and bases in aqueous solution**

FA 1 is 1.00 mol dm^{-3} sodium hydrogen carbonate, $NaHCO_3$
FA 2 is sodium hydroxide, NaOH, of concentration between 1.5 mol dm^{-3} to 2.0 mol dm^{-3}
FA 3 is 2.00 mol dm^{-3} sulfuric acid, H_2SO_4

An acid-base neutralisation reaction involves reacting the two solutions, to produce water molecules. The equation for this neutralisation reaction is given below.

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

The reaction between $H^+(aq)$ and $OH^-(aq)$ is an exothermic reaction and is used to perform a thermometric titration.

This task involves **two** different acid-base reactions.

The first reaction is between **FA 1**, $NaHCO_3$, and **FA 2**, NaOH.

Reaction 1 $NaHCO_3(aq) + NaOH(aq) \rightarrow Na_2CO_3(aq) + H_2O(l)$ $\Delta H_{reaction1}$

The molar enthalpy change for **reaction 1**, $\Delta H_{reaction1}$ is the enthalpy change when 1.00 mol of $NaHCO_3$ reacts completely with NaOH.

You will perform a thermometric titration to determine the equivalence point of the reaction. The equivalence point is the point where the $OH^-(aq)$ from the base completely neutralises the $H^+(aq)$ from the acid.

The second reaction is between **FA 1**, $NaHCO_3$, and **FA 3,** H_2SO_4,.

Reaction 2 $NaHCO_3(aq) + \frac{1}{2}H_2SO_4(aq) \rightarrow \frac{1}{2}Na_2SO_4(aq) + H_2O(l) + CO_2(g)$ $\Delta H_{reaction2}$

The molar enthalpy change for **reaction 2**, $\Delta H_{reaction\ 2}$, is the enthalpy change when 1.00 mol of $NaHCO_3$ reacts completely with H_2SO_4.

In the first experiment, you will perform a thermometric titration by adding portions of **FA 2** progressively to a known volume of **FA 1**. You will continue adding **FA 2** until the equivalence point is reached and passed. Throughout the experiment you will record the temperature of the mixture after each addition of **FA 2**.

You will then analyse your results graphically in order to determine the

- volume of **FA 2** at the equivalence point, $V_{equivalence}$,
- maximum temperature change, ΔT_{max1},
- molar enthalpy change for the reaction, $\Delta H_{reaction1}$, for **reaction 1.**

In your second experiment, you will mix together given volumes of **FA 1** and **FA 3**.

You will then determine the

- maximum temperature change, $\Delta T_{\text{max 2}}$,
- molar enthalpy change, $\Delta H_{\text{reaction 2}}$, for **reaction 2**.

Part 1: The reaction between FA 1 and FA 2

(a) **(i)** In this task you will need to record the maximum temperature of the reaction mixture when specified volumes of **FA 2** have been added. It is important that the volume of **FA 2** recorded is the **total** volume you have added up to that point when the temperature reading was made.

Note: If you overshoot on an addition, record the ***actual*** *total volume of* ***FA 2*** *added up to that point.*

Procedure for the reaction between FA 1 and FA 2

1 Fill a burette with **FA 2**.

2 Place a Styrofoam cup inside a second Styrofoam cup which is held in a beaker to prevent it from tipping over.

3 Using a pipette, transfer 25.0 cm^3 of **FA 1** to the first Styrofoam cup.

4 Stir the **FA 1** solution in the cup with the thermometer. Read and record its temperature.

5 From the burette, add 2.00 cm^3 of **FA 2** to the cup and stir the mixture thoroughly.

6 Read and record the maximum temperature of the mixture, T, and the volume of **FA 2** added.

Note: If you overshoot on an addition, record the **actual** total volume of **FA 2** added up to that point.

7 Repeat points **5** and **6** until a total of 30.00 cm^3 of **FA 2** has been added. After each addition of **FA 2**, record the maximum temperature of the mixture and the total volume of **FA 2** added up to that point in the table provided.

In an appropriate format in the space provided, record all values of temperature, *T*, to 0.1^{o}C, and each **total** volume of **FA 2** added to 0.05 cm^3.

Results

Initial temperature of **FA 1** : ____________

[2]

(ii) On the grid on below, plot a graph of maximum temperature, T (*y-axis*) against volume of **FA 2** added (*x-axis*).

(iii) Draw **two** smooth lines of best fit.

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

Note: Each line should have a shape best suited to its plotted points. [3]

(iv) Determine from your graph

- the maximum temperature reached, T_{max},
- the maximum temperature change ΔT_{max1},
- the volume, $V_{equivalence}$, of **FA 2** needed to completely react with 25.0 cm^3 of **FA 1**.

Record these values in the spaces provided below.

maximum temperature reached, T_{max} = _______ °C

maximum temperature change, ΔT_{max} = _______ °C

volume of **FA 2** used, $V_{equivalence}$ = _______ cm^3

[3]

Part 2: The reaction between FA 1 and FA 3

(b) The molar enthalpy change for reaction 2, $\Delta H_{reaction2}$, is the enthalpy change when 1.00 mol of $NaHCO_3$ reacts ***completely*** with H_2SO_4.

In this task you will calculate a value for the molar enthalpy change, $\Delta H_{reaction2}$. To do this you will need to calculate the maximum temperature change produced when 40 cm^3 of **FA 1**, $NaHCO_3$ and 15 cm^3 of **FA 3**, H_2SO_4 are mixed.

You should be aware that the reaction mixture will produce considerable frothing.

In this experiment, you will select a suitable apparatus to measure **FA1** and **FA 3**.

(i) Calculate the maximum percentage errors in 40 cm^3 of **FA 1** when using

- measuring cylinder

- burette

[1]

(ii) Explain your choice of apparatus for measuring **FA 1**.

…………………………………………………………………………………..

…………………………………………………………………………………..

[1]

(iii) **Procedure for the reaction between FA 1 and FA 3**

1. Label one Styrofoam cup, **A**. Label a second Styrofoam cup, **B.**
2. Place the cup **A** inside a Styrofoam cup which is held in a beaker to prevent it from tipping over.
3. Transfer 40 cm^3 of **FA 1** into cup **A** using your chosen apparatus.
4. Stir the **FA 1** solution in cup **A** with the thermometer. Read and record its temperature, T_{FA1}**.** This is the initial temperature of **FA 1**.
5. Wash and dry the thermometer.

6. Transfer 15.0 cm^3 of **FA 3** into cup **B**. Stir the **FA 3** solution with the thermometer. Read and record its temperature of the mixture, T_{FA3}. This is the initial temperature of **FA 3**.

7. Carefully add the contents of cup **B** to cup **A** in small portions to avoid too much frothing.

8. Place the lid on the cup and insert the thermometer through the lid. Stir the mixture.

9. Continue to stir the mixture. Measure and record the temperature, $T_{mixture}$ that shows the **maximum** change from the initial temperature.

In an appropriate format in the space provided below, record all values of measured temperatures for this experiment.

Results

[1]

Calculations

(c) For the purposes of these calculations, you should assume that the reaction mixture has a density of 1.00 g cm^{-3} and specific heat capacity, c, of 4.18 J g^{-1} K^{-1}. Use your results from **(a)(iv)** to calculate the following.

(i) The concentration of sodium hydroxide, [NaOH], in **FA 2**.

[NaOH] in **FA 2** = ______________________________

[1]

(ii) The heat change, q, for the reaction occurring in **(a)(i)**, and hence determine a value for the molar enthalpy change for **reaction 1**, $\Delta H_{reaction1}$.

q = ______________________________

$\Delta H_{reaction1}$ = ______________________________

[2]

(d) Use your results from **(b)** to calculate a value for the molar enthalpy change for **reaction 2**, $\Delta H_{reaction2}$.

For the experiment in **(b)**, the weighted average initial temperature, $\Delta T_{average,}$ of **FA 1** and **FA 3** may be calculated using the formula given below:

$$T_{average} = \frac{(V_{FA1} x T_{FA1}) + (V_{FA3} x T_{FA3})}{(V_{FA1} + V_{FA3})}$$

q = ______________________________

$\Delta H_{reaction2}$ = ______________________________

[5]

(e) Ionic equations for neutralisation, reaction **1**, and reaction **2** are shown below.

$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$	ΔH_{neu}= -57.1 kJ mol^{-1}
$HCO_3^-(aq) + OH^-(aq) \rightarrow CO_3^{2-}(aq) + H_2O(l)$	$\Delta H_{reaction1}$
$HCO_3^-(aq) + H^+(aq) \rightarrow H_2O(l) + CO_2(g)$	$\Delta H_{reaction2}$

Carbon dioxide reacts with solutions of carbonate ions according to the following equation.

reaction 3 $CO_2(g) + H_2O(l) + CO_3^{2-}(aq) \longrightarrow 2HCO_3^-(aq)$ $\Delta H_{reaction3}$

Using your calculated answers in **(c)(ii)** and **(d)**, together with the given value of enthalpy change of neutralisation, ΔH_{neu}, determine a value for the enthalpy change for this reaction, $\Delta H_{reaction3}$.

[3]

[Total: 22]

2 To investigate the kinetics of reaction in an iodine clock reaction

FA 4 is 0.100 mol dm^{-3} aqueous potassium iodide, KI.
FA 5 is 1.00 mol dm^{-3} dilute sulfuric acid, H_2SO_4 .
FA 6 is 0.100 mol dm^{-3} aqueous potassium bromate(V), $KBrO_3$
FA 7 is 5.00 x 10^{-3} mol dm^{-3} aqueous sodium thiosulfate, $Na_2S_2O_3$

You are also provided with starch indicator and deionised water.

This reaction starts from a solution containing potassium bromate(V), sulfuric acid, sodium thiosulfate and starch. To this, a solution of potassium iodide is added.

There are two reactions occurring in the solution. In the first slow reaction, iodine is formed.

Reaction **I** $6I^-(aq) + BrO_3^-(aq) + 6H^+(aq) \rightarrow 3I_2(aq) + Br^-(aq) + 3H_2O(l)$

Reaction **II** $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$

Since there is a small but constant amount of sodium thiosulfate added to the reaction mixture, the iodine being slowly produced by Reaction **I** will immediately react in Reaction **II** until all the sodium thiosulfate has been used up. At that point, free iodine will be present in the solution, which will cause a sudden appearance of a deep blue colour as starch is present.

You will perform a series of **three** experiments, by varying the volume of **FA 6** added, with each solution being made up to the same total volume with water. For each experiment, you will note the volume of **FA 6** added, V_{FA6}, and the time taken, **t**, for the solution to turn blue. Using your results, determine the order of reaction with respect to BrO_3^-.

(a) Experiment 1

1 Use appropriate measuring cylinders, add 10.0 cm^3 of **FA 5**, 20.0 cm^3 of **FA 7** and 1 cm^3 of starch indicator into the conical flask labelled reaction mixture. Note: 10 drops is approximately 1 cm^3.

2 Using a measuring cylinder, add 30.0 cm^3 of **FA 6** into the conical flask.

3 Swirl the contents of the flask.

4 Measure 10 cm^3 of **FA 4** using measuring cylinder. Add **FA 4** quickly into the conical flask. Start the stopwatch during this addition.

5 Mix the contents thoroughly by swirling the flask.

6 Stop the stopwatch when the blue colouration is observed.

7 Record the time, **t**, to the nearest 0.1 s.

8 Wash the conical flask thoroughly with water. Stand it upside down on a paper towel to drain.

Experiments 2 and 3

Carry out two more experiments by repeating steps 1 to 8, and varying the volumes of **FA 6**, so that you can determine the order of reaction with respect to BrO_3^-.

The volume of **FA 6** should **not** be more than that in experiment **1**. In each experiment, deionised water is added to keep the **total volume** of the final reaction mixture **constant**.

Prepare a table in the space provided to record, for each experiment:

- volumes of **FA 6**, V_{FA6}, and deionised water used,
- all values of t, to the nearest 0.1 s,

and

- calculated values of **(V_{FA6}) x t** and **(V_{FA6})^2× t** (to 3 significant figures)

*Note: As the volumes of **FA 4, FA5, FA 7** and starch indicator are constant for each experiment, you do not need to record these volumes in your table.*

Results

[3]

The rate of reaction is given by the equation:

$$\text{rate} \propto [\text{reactant}]^{n}$$

where ***n*** is the order of reaction with respect to the reactant investigated. The value of ***n*** can be 0, 1 or 2.

In this experiment, the rate of reaction $\propto \left(\frac{1}{\text{time}}\right)$,

and

[reactant] $\propto$ volume of reactant used.

Hence, $\left(\frac{1}{\text{time}}\right) \propto (\text{volume of reactant})^{n}$

Rewriting, $(\text{volume of reactant})^{n} \times \text{time} = \text{constant}$

(b) **(i)** Explain why $\left(\frac{1}{\text{time}}\right)$ is a measure of the rate of reaction, in this experiment.

………………………………………………………………………………..

……………………………………………………………………………….. [1]

(ii) From your results using Vt or V^2t values, deduce the order of the reaction with respect to bromate(V) ions.

………………………………………………………………………………..

……………………………………………………………………………….. [1]

(c) In an attempt to find the order of reaction with respect to H^+ ions, a student carried out experiments **4** and **5**, by varying volume of **FA 5, V_{FA5}**.

Only the numerical values of $V_{FA5} \times t$ and $(V_{FA5})^2 \times t$ are tabulated below.

Experiment	V_{FA5} / cm^3	$V_{FA5} \times t$	$(V_{FA5})^2 \times t$
4	**5.0**	**225**	**1130**
5	**15.0**	**75.0**	**1130**

From the above calculated values of $V_{FA5} \times t$ and $(V_{FA5})^2 \times t$, deduce the order of reaction with respect to H^+ ions.

………………………………………………………………………………………

……………………………………………………………………………………… [1]

(d) The order of reaction with respect to iodide ions, I^-, is given to be one.

The rate equation is written as;

$$\text{rate} = k\,[I^-]\,[BrO_3^-]^m\,[H^+]^n$$

where *m* and *n* are the order of reaction with respect to BrO_3^- and H^+ respectively.

In order to find half-life of the reaction, a student proposed that the rate equation can be rewritten as:

$$\text{rate} = k'[I^-],\ \textit{where } k' = k\,[BrO_3^-]^m\,[H^+]^n \quad \textit{equation 1}$$

From his *equation 1*, the student then proposed that the half-life of reaction can be calculated using $\frac{\ln 2}{k'}$.

Comment on the validity of his statement.

…………………………………………………………………………………………

…………………………………………………………………………………………

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

(e) Instead of washing and draining the conical flask as required in **step 8** of **(a)**, another student simply just poured away the reaction mixture. There was some leftover reaction mixture in the flask when he performed the subsequent experiment.

State and explain the effect on time, **t**, in his subsequent experiment.

…………………………………………………………………………………………

…………………………………………………………………………………………

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

(f) **Plan**

In **(a)** and **(c)**, the orders of reaction with respect to bromate(V) ions and H^+ were investigated using the initial rate method.

The order of reaction with respect to iodide ion was not investigated but was given as 1 in **(d)**.

Instead of doing a number of initial rate experiments, the order of reaction with respect to iodide ion, I^-, can be determined by following **one** reaction from the start to the end, in what is known as the *continuous method*.

To do so, the reacting mixture is prepared with a known concentration of I^-, and known concentrations of H^+ and BrO_3^-, both of which must be in **excess**. Over time, the amount of, and concentration of I_2 increases. The appearance of I_2 is noted by the colour of the mixture turning yellow-orange. (Due to the low concentrations of I_2 used in this experiment, I_2 appears yellow-orange)

An investigation is planned to allow you to determine the order of reaction with respect to iodide ion, I^-.

You may assume you are provided with the following.

- 0.5 mol dm^{-3} H_2SO_4, 1.0 mol dm^{-3} KI and 1.0 mol dm^{-3} $KBrO_3$,
- standard iodine solutions of various concentrations,
- deionised water

(i) Suggest with reasoning, the volumes of H_2SO_4, KI, $KBrO_3$ and deionised water you would mix to obtain 250 cm^3 of the reaction mixture.

Reagent	Volume used/ cm^3
H_2SO_4	
KI	
$KBrO_3$	
Deionised water	

…………………………………………………………………………………

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………………………………………………………………………………… [2]

(ii) It is possible to determine the concentration of a solution of a coloured solute using a colorimeter.

A few cm^3 of the solution is placed inside a machine, known as a colorimeter. This machine measures the amount of light that is absorbed when a specific wavelength of visible light is shone through a coloured solution. It does this by comparing the amount of light passing through the sample with the amount of light passing through the pure solvent. The amount of light absorbed is expressed as an absorbance value.

According to Beer-Lambert's Law, the higher the concentration of the coloured substance, the higher the absorbance value. Using this relationship, it is possible to determine the progress of the reaction.

A colorimeter was first used to measure the absorbance of a standard solution of iodine, I_2, of concentration equal to that of the highest concentration of I_2 the reaction mixture can produce.

Then, the reaction mixture is prepared and placed in a 1 cm^3 cuvette. The cuvette is placed into the colorimeter and the absorbance of the solution is measured and recorded at regular time intervals.

The experiment is stopped when the absorbance reading reaches about 80% of that of the standard solution of iodine.

To determine the order of reaction with respect to iodide ion, a product time graph of absorbance against time is plotted and the order of reaction with respect to iodide ion can be determined.
The colorimeter is set to use the wavelength of light that is absorbed most strongly by iodine.

Suggest a colour in the visible spectrum from which a suitable wavelength of light might be chosen. Explain your answer.

Colour: ………………………………………………………………………

Explanation: ………………………………………………………………

[2]

(iii) Sketch the shape of the plot of absorbance of I_2 against time graph that you expect to obtain, in the space provided below.

Explain clearly, how it can be used to determine the order of reaction with respect to iodide ion.

[3]

[Total: 15]

3 Qualitative Analysis

(a) (i) **Before starting this analysis, ensure your Bunsen burner is turned off.**

In this question you will deduce the functional groups of two organic compounds, **FA 8** and **FA 9**.

FA 8 and **FA 9** each has only **one** functional group, and contains only carbon, hydrogen, and **one** oxygen atom.

You will perform a series of test-tube reactions and use the observations to help you deduce the functional groups present.

You are provided with liquid samples **FA 8** and **FA 9**. Perform the following tests described in Table **3.1**, on **FA 8** and **FA 9**, and record your observations in the table. If it appears that no reaction has taken place, this should be clearly recorded.

Use a fresh sample of each liquid in each test.

Samples FA 8 and FA 9 are provided in sample tubes. It is essential that you replace the lid as soon as you have removed the sample for each test.

You should also prepare a fresh solution of Tollens' reagent in **Test 1** of **Table 3.1**.

One test has already been carried out and the observation is recorded in **Table 3.1**.

Preparation of Tollens' reagent

To a 3 cm depth of aqueous silver nitrate in a test-tube, add 6 drops of aqueous sodium hydroxide.

To this mixture add aqueous ammonia dropwise. Stir with a glass rod until the brown solid just dissolves.

Keep this solution for use as Tollens' reagent in the question.

Table 3.1		
Test	**Observations with**	
	FA 8	**FA 9**
1. Label a test-tube **FA 8**. To this test-tube, add 2 cm^3 of Tollens' reagent, followed by 5 drops of **FA 8**. Prepare a hot water bath using hot water provided. Warm the mixture in the water bath for five minutes. **Repeat using FA 9, in place of FA 8.**		
2. Label a test-tube **FA 9**. To this test-tube, add 5 drops of **FA 9** and 6 drops of aqueous sodium hydroxide. Now add iodine solution, dropwise, until a permanent yellow / orange colour is present. Warm the mixture in the water bath for two minutes.	**Pale Yellow precipitate**	
3. Label a test-tube **FA 8**. To this test-tube, add 1 cm^3 of Fehling's solution A and 1 cm^3 Fehling's solution B. To this test-tube, add 1 cm^3 of **FA 8**. Warm the mixture in the water bath (at 80^{o}C) for 15 minutes. **Repeat using FA 9 in place of FA 8.**		
4. Label a test-tube **FA 8**. Place about 2 cm depth of aqueous sodium hydroxide in this test-tube. To this test tube, add 5 drops of **FA 8**, followed by 5 drops of aqueous potassium manganate (VII) solution. Warm the mixture in the water bath for five minutes. **Repeat using FA 9 in place of FA 8.**		[3]

		(ii)	Complete **Table 3.2** below, using observations in **Table 3.1**, to identify the functional groups present in **FA 8** and **FA 9**. In each case, give evidence to support your conclusion. [2]

Table 3.2

	Functional group present	**Evidence**
FA 8		
FA 9		

(b) **(i)** State the feature(s) present in the structure in the compounds which gave a positive result for **Test 2**.

[1]

(ii) Based on the results in **Table 3.1**, identify one of the compounds, **FA8** or **FA9**, and give its structural formula.

[1]

(c) Solid **FA 10** contains an unknown cation. The cation is **not** NH_4^+ or Pb^{2+}.

Dissolve 1 spatula full of **FA 10** into 10 cm^3 of deionised water in a test-tube. This stock solution will be required for the subsequent tests to identify the cation present.

Cation analysis

You are provided with the following bench reagents to identify the cation in **FA 10**.

- $HNO_3(aq)$
- $H_2SO_4(aq)$
- $Ca(OH)_2(aq)$
- $NaOH(aq)$
- $NH_3(aq)$

(i) Based on the colour of the solution, identify the possible cations in **FA 10**.

…………………………………………………………………………..

…………………………………………………………………………..

[1]

(ii) You are required to choose reagents that will allow you to carry out tests to identify the cation present in **FA 10**.

Indicate in the space below, the reagents selected and the observations of the tests. Hence, identify the cation in **FA10**.

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[4]

(d) **Plan**

Consider the following organic compounds.

pent-1-ene **1-chloropropane** **ethyl ethanoate** **ethanoyl chloride**

Plan an investigation, using test-tube reactions, **other** than those used in **(a)** 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.
DO NOT carry out the experiment.

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…………………………………………………………………………………………… [6]

[Total: 18]

[End of paper]

Answers

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

H

PIONEER JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION
HIGHER 2

CANDIDATE NAME

CT GROUP	1	6			

INDEX NUMBER				

CHEMISTRY

9729/02

Paper 2 Structured

12 September 2017

2 hours

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your class, index number and name on all work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough workings.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

FOR EXAMINER'S USE			
Paper 1			**/ 30**
Paper 2			
1	/ 14	4	/ 12
2	/ 8	5	/ 13
3	/ 11	6	/ 17
Penalty		sf	unit
Paper 2			**/ 75**
Paper 3			**/ 80**
Paper 4			**/ 55**
Total			

This document consists of **19** printed pages.

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

1 **(a)** Carbon dioxide, produced mainly from the burning of fossil fuels, is a greenhouse gas which trapped heat within the Earth's atmosphere, causing global warming and potentially catastrophic global climate change. One major source of carbon dioxide produced worldwide is from the rapidly expanding aviation industry.

(i) Commercial passenger jet-liners combust kerosene as fuel. The formula of kerosene may be taken as $C_{14}H_{30}$. Write a balanced equation, **with state symbols**, for the complete combustion of kerosene.

[1]

$C_{14}H_{30}(l) + 43/2\ O_2(g) \rightarrow 14CO_2(g) + 15H_2O(l)$

In 2017, Singapore Airlines announced that it will be launching the world's longest commercial non-stop passenger flight from Singapore to New York, with a flight distance of 15,000 km. The ultra-long range Airbus A350 aircraft used on this route burns 7.5 kg of kerosene per km.

(ii) Calculate the mass of carbon dioxide produced, in tonnes, during this flight.
[1 tonne = 1000kg]

[3]

Mass of $C_{14}H_{30}$ used in the flight = (7500 g) × 15,000 = 1.125×10^8 g

Amount of $C_{14}H_{30}$ = $(1.125 \times 10^8) \div [14(12.0) + 30(1.0)]$ = 5.682×10^5 mol

Since 1 mol of $C_{14}H_{30} \equiv 14$ mol of CO_2,

Therefore, 5.682×10^5 mol $\equiv 7.954 \times 10^6$ mol CO_2.

Mass of CO_2 produced = $(7.954 \times 10^6) \times (12.0 + 32.0) = 3.50 \times 10^8$g
= **350 tonnes**

(iii) Apart from carbon dioxide, nitrogen dioxide is another air pollutant found in the flue gases from the jet engine of aircrafts. Explain how nitrogen dioxide is produced in the jet engine. [1]
Atmospheric nitrogen gas and oxygen gas react under the high temperature and pressure of the jet engine to produce nitrogen dioxide.

(iv) Why is it important to remove nitrogen dioxide from the flue gases? [1]
Nitrogen dioxide is (covalent oxide) acidic oxide and dissolve in water to form acid rain which is corrosive.

(b) Scientists have been studying the idea of carbon capture and storage technologies to try to remove atmospheric carbon dioxide on an industrial scale. One possible technology is called *calcium looping*. This process involved using calcium oxide to react with the atmospheric carbon dioxide to form calcium carbonate (i.e. limestone) which can then be stored away in abandoned mines.

$$CaO(s) + CO_2(g) \rightarrow CaCO_3(s) \quad \Delta H_1$$

(i) Using the space below, construct a energy cycle diagram to calculate ΔH_1 using the following data.

standard enthalpy change of formation of CaO(s)	-635 kJ mol^{-1}
standard enthalpy change of formation of $CaCO_3$(s)	-1207 kJ mol^{-1}
standard enthalpy change of combustion of C(s)	-394 kJ mol^{-1}

[3]

$$\begin{tikzcd}
Ca(s) + C(s) + 3/2\ O_2(g) \arrow[r, "\Delta H_f(CaCO_3(s))"] \arrow[d, "\Delta H_f(CaO\ (s))"'] & CaCO_3(s) \\
CaO(s) + C(s) + O_2(g) \arrow[r, "\Delta H_c(C(s))"] & CaO(s) + CO_2(g) \arrow[u, "\Delta H_1"']
\end{tikzcd}$$

By Hess' Law,
$\Delta H_f(CaCO_3(s)) = \Delta H_f(CaO_3(s)) + \Delta H_c(C(s)) + \Delta H_1$
$(-1207) = (-635) + (-394) + \Delta H_1$
ΔH_1 = **-178 kJ mol^{-1}**

(ii) Like calcium carbonate, aluminum oxide is a major components of naturally occurring rocks. Explain clearly, in terms of chemical bonding and structure, why aluminum oxide is insoluble in water.

[3]

Aluminum oxide has a giant ionic lattice structure with its Al^{3+} cations and O^{2-} anions held by strong ionic bonds. Energy released during the formation of the ion-dipole interactions between water and the ions in aluminum oxide is insufficient to overcome the strong ionic bonds between the Al^{3+} cations and O^{2-} anions. Hence, aluminum oxide is insoluble in water.

(c) Carbonate buffers are widely used for biochemical purposes.

A student wishes to form a CO_3^{2-}/ HCO_3^- buffer in the laboratory.

Given that the carbonate ion has a K_b of 1.8×10^{-4} mol dm^{-3}, calculate the volume of 0.10 mol dm^{-3} of hydrochloric acid that he has to add to 25.0 cm^3 of 0.12 mol dm^{-3} of Na_2CO_3, to form a resulting buffer solution of pH 9.50. [2]

$pOH = pK_b + \log[HCO_3^-]/ [CO_3^{2-}]$

$14 - 9.5 = -(-3.745) + \log[HCO_3^-]/ [CO_3^{2-}]$
$[HCO_3^-]/ [CO_3^{2-}] = \underline{5.69}$

	CO_3^{2-} +	H^+ →	HCO_3^-
Initial amount	0.003	+x	0
Change in amount	-x	- x	+ x
Final amount	0.003 –x	0	x

$[HCO_3^-]/ [CO_3^{2-}] = 5.69 = x/V \div (0.003-x)/V$
Solving, $x = 2.55 \times 10^{-3}$, volume of HCl = $\underline{25.5 \text{ cm}^3}$

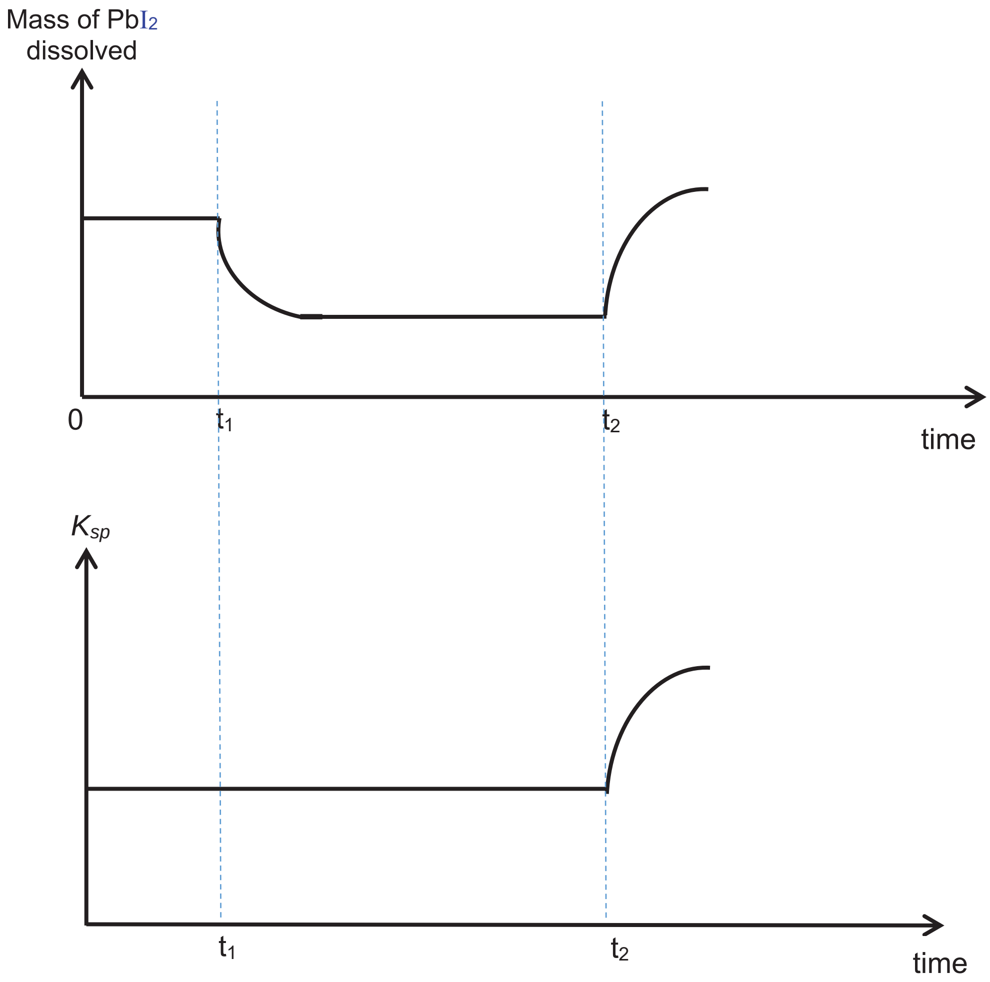
[Total:14]

2 This question is about lead (II) halides.

(a) $PbI_2\,(s) + aq \rightleftharpoons Pb^{2+}(aq) + 2\,I^{-}\,(aq)$ $\Delta H>0$

A student wanted to investigate the solubility product and solubility of PbI_2, a sparingly soluble salt, under different conditions. He first added some solid PbI_2 into 100 cm^3 water at 15°C, and subsequently made two changes at t_1 and t_2.

The graphs below show the mass of PbI_2 dissolved and solubility product of PbI_2 against time.



Some possible changes listed below were made by the student at t_1 and t_2.

1. Cool reaction mixture to 10°C in water bath
2. Heat reaction mixture to 50°C in water bath
3. Add $AgNO_3(s)$
4. Pump in $Pb(NO_3)_2(aq)$

With reference to **both** graphs, suggest and explain which of the above changes (1)-(4), was made at t_1 and t_2 respectively.

change made at t_1:

explanation:..
[2]

change made at t_2:

explanation:..
[2]

Change made at t_1: (4). Addition of $Pb(NO_3)_2(aq)$
$PbI_2\ (s) + aq \rightleftharpoons Pb^{2+}(aq) + 2I^-\ (aq)$ eqm

Explanation: Addition of $Pb(NO_3)_2(aq)$, hence $[Pb^{2+}]$ increases, according to Le Chatelier's Principle, position of equilibrium shifts left to decrease $[Pb^{2+}]$. Thus, less PbI_2 dissolve and K_{sp} remain constant as K_{sp} is temperature dependent.

change made at t_2 : Heat reaction mixture to 50 °C in water bath
explanation: According to Le Chatelier's Principle, as temperature increase, the position of equilibrium shifts right to favour the forward endothermic reaction, to absorb heat and decrease temperature.
Hence, $[Pb^{2+}]$ and $[I^-]$ increase. The mass of PbI_2 dissolved and K_{sp} increase.

(b) The values of the solubility products of two salts, lead (II) iodide, PbI_2, and silver (I) iodide, AgI are given below.

$$K_{sp}\,(PbI_2) = 3.97 \times 10^{-9}\ \text{mol}^3\ \text{dm}^{-9}$$
$$K_{sp}\,(AgI) = 8.3 \times 10^{-17}\ \text{mol}^2\ \text{dm}^{-6}$$

A lab technician added solid PbI_2 into water, shaking it thoroughly. He filtered off the remaining solid, leaving a saturated solution **H**.

He added drops of aqueous silver nitrate to **H**, until AgI just precipitates.

Determine the concentration of Ag^+ when AgI just precipitates. [2]

	$PbI_2(s)$	+ aq	$\rightleftharpoons$	$Pb^{2+}(aq)$	+ $2I^-(aq)$
Eqm conc / mol dm^{-3}				*s*	*2s*

$[Pb^{2+}][I^-]^2 = 3.97 \times 10^{-9} = (s)(2s)^2 = 4s^3$
$s = 9.975 \times 10^{-4}$ mol dm^{-3}

In X, $[I^-] = 2s = 2 \times 9.975 \times 10^{-4} = 1.996 \times 10^{-3}$ mol dm^{-3}
When AgI just precipitates; IP (AgI) = K_{sp} (AgI)
$[Ag^+][I^-] = 8.3 \times 10^{-17}$
$[Ag^+](1.996 \times 10^{-3}) = 8.3 \times 10^{-17}$
$[Ag^+] = 4.16 \times 10^{-14}$ mol dm^{-3} (3.s.f)

(c) When a precipitate is formed, $\Delta G^{\ominus}_{ppt}$, in J mol^{-1}, is given by the following expression.

$$\Delta G^{\ominus}_{ppt} = 2.303\ RT \log K_{sp}$$

Given that for lead(II) chloride, $PbCl_2$, K_{sp} = 1.70 x 10^{-5} mol^3 dm^{-9} at 298 K, calculate $\Delta^{\ominus}G_{ppt}$ for $PbCl_2$ at 298K.

Hence explain if lead(II) chloride is soluble at 298K. [2]

$\Delta G^{\theta}_{ppt}(PbCl_2) = 2.303\ RT \log K_{sp}(PbCl_2)$
$= 2.303 \times 8.31 \times (298) \log (1.70 \times 10^{-5})$
= **- 27200 J mol^{-1}** <0, hence energetically feasible to ppt out so it is **not soluble.**

[Total:8]

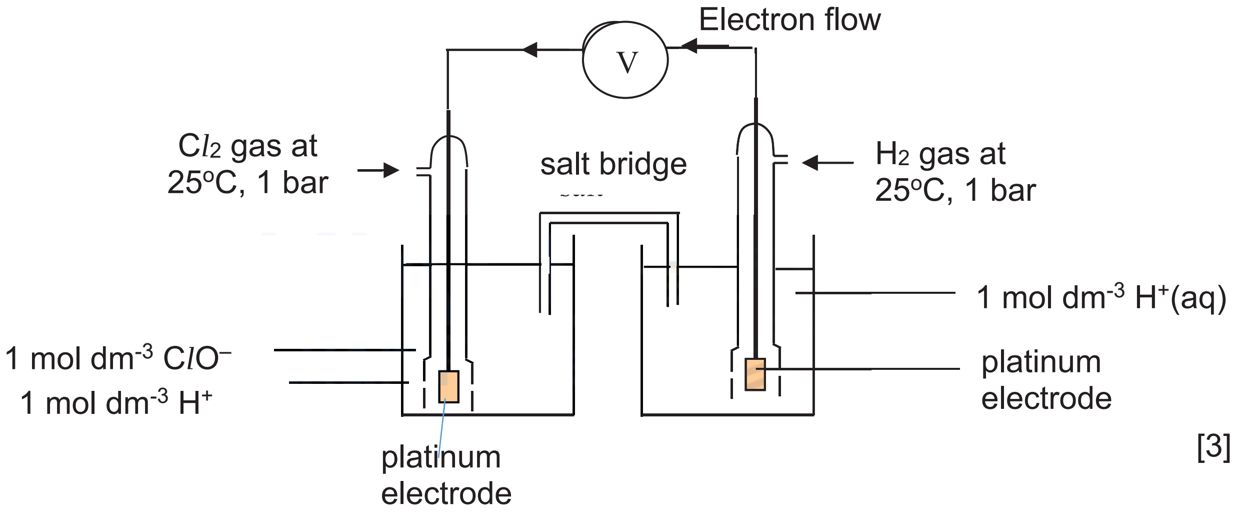
3 **(a)** Chlorine has been extensively used in the manufacture of many compounds. One such compound is household bleach, which contains sodium chlorate(I), $NaClO$.

The chlorate(I) ion acts as a powerful oxidising agent in acidic solution:

$$2ClO^-(aq) + 4H^+(aq) + 2e^- \rightleftharpoons Cl_2(g) + 2H_2O(l) \qquad E^{\ominus} = +1.64\ V$$

(i) Define the term *standard electrode potential*.
It is the **potential difference between a standard hydrogen electrode and a half cell** under standard conditions of **25°C**, **1 bar** and concentration of all ions involved is **1 mol dm^{-3}**.

(ii) Draw a fully labelled diagram, to show how the standard electrode potential, $E^{\ominus}(ClO^-/Cl_2)$, could be measured.



[3]

(iii) Draw a fully labelled diagram to show how the $E^{\ominus}$cell of the cell in **(a)(ii)** could be measured.
……………………………………………………………………………………………[3]

(b) Use the *Data booklet* to predict the reaction, if any, that would occur when the following pairs of reagents are mixed in acidified aqueous solution. If a reaction occurs, write a balanced equation and calculate $E^{\ominus}_{cell}$.

(i) NaC*l*O(aq) and H_2O_2(aq)

$2ClO^-(aq) + 4H^+(aq) + 2e^- \rightleftharpoons Cl_2(g) + 2H_2O(l)$ $E^{\ominus} = +1.64$ V

$H_2O_2 \rightleftharpoons O_2(g) + 2H^+(aq) + 2e^-$ $E^{\ominus}_{ox} = -0.68$ V

$E^{\ominus}_{cell}$ =+1.64 +-0.68 =**+0.96V>0 (3 s.f)**

$H_2O_2 + 2ClO^- + 2H^+ \rightarrow O_2 + Cl_2 + 2H_2O$ [2]

(ii) NaC*l*O(aq) and $Cr(NO_3)_3$(aq)

$2ClO^-(aq) + 4H^+(aq) + 2e^- \rightleftharpoons Cl_2(g) + 2H_2O(l)$ $E^{\ominus} = +1.64$ V

$2Cr^{3+} + 7H_2O \rightleftharpoons Cr_2O_7^{2-} + 14H^+ + 6e^-$ $E^{\ominus}_{ox} = -1.33$V

$E^{\ominus}_{cell}$ =+1.64-1.33 = +0.31V>0

$2Cr^{3+} + 1H_2O + 6ClO^-(aq) \rightarrow 3Cl_2 + Cr_2O_7^{2-} + 2H^+$ [2]

(c) When a few drops of aqueous sodium carbonate was added to chromium(III) nitrate, carbon dioxide gas and a grey-green precipitate, **R**, were obtained.

Explain why CO_2 is given off in the above reaction, and identify precipitate **R**.

Cr^{3+} has a high charge density. Hence $[Cr(H_2O)_6]^{3+}$ can undergo partial hydrolysis in water to produce H^+ ions, forming CO_2 with carbonate ions.

$Cr(OH)_3$

$[Cr(H_2O)_6]^{3+} \rightleftharpoons [Cr(H_2O)_5(OH)]^{2+} + H^+$

$2H^+ + CO_3^{2-} \rightarrow H_2O + CO_2$ [3]

[Total:11]

4 Manganese is a first row d-block element in the Periodic table with a melting point of 1246°C. Like many other d-block elements, manganese shows properties that are atypical from other s-block metals, such as potassium and calcium.

Its minerals are widely distributed, with manganese dioxide and manganese carbonate being the most common. Manganese is also an essential element in living organisms, where many types of enzymes make use of the variable oxidation states of manganese to take part in the various redox reactions.

(a) **(i)** Explain why manganese has a much higher melting point than calcium, which is found in the same period.

Both Mn and Ca are metals with strong metallic bonds/ electrostatic force of attraction between the positive metal ions and this sea of delocalized electrons.

- The small difference in energy between the 4d and 5s orbitals allows for the number of **delocalised** electrons in the metallic lattice to be increased.
- The ionic radius of manganese is smaller than that of calcium, hence increasing the charge density of manganese ions.
- With a bigger number of delocalised electrons and a higher charge density of manganese ions, more energy is required to break these stronger metallic bonds in manganese. Thus manganese has a much higher melting point than calcium.

....[3]

(ii) Explain why the density of manganese is significantly greater than that of calcium.

- Manganese has a greater atomic mass than calcium and has a smaller atomic radii than calcium.

- This results in manganese having higher density than calcium.

....[1]

(b) Heating a mixture of KOH and MnO_2 in air gives potassium manganite, K_2MnO_4, which is an important precursor to potassium permanganate, $KMnO_4$, a common oxidising agent.

(i) State the oxidation state of manganese and hence, write the electronic configuration of the manganese ion in each of the following compounds:

MnO_2 :

Oxidation state: +4
Electronic configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$

K_2MnO_4:

Oxidation state: +6
Electronic configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$

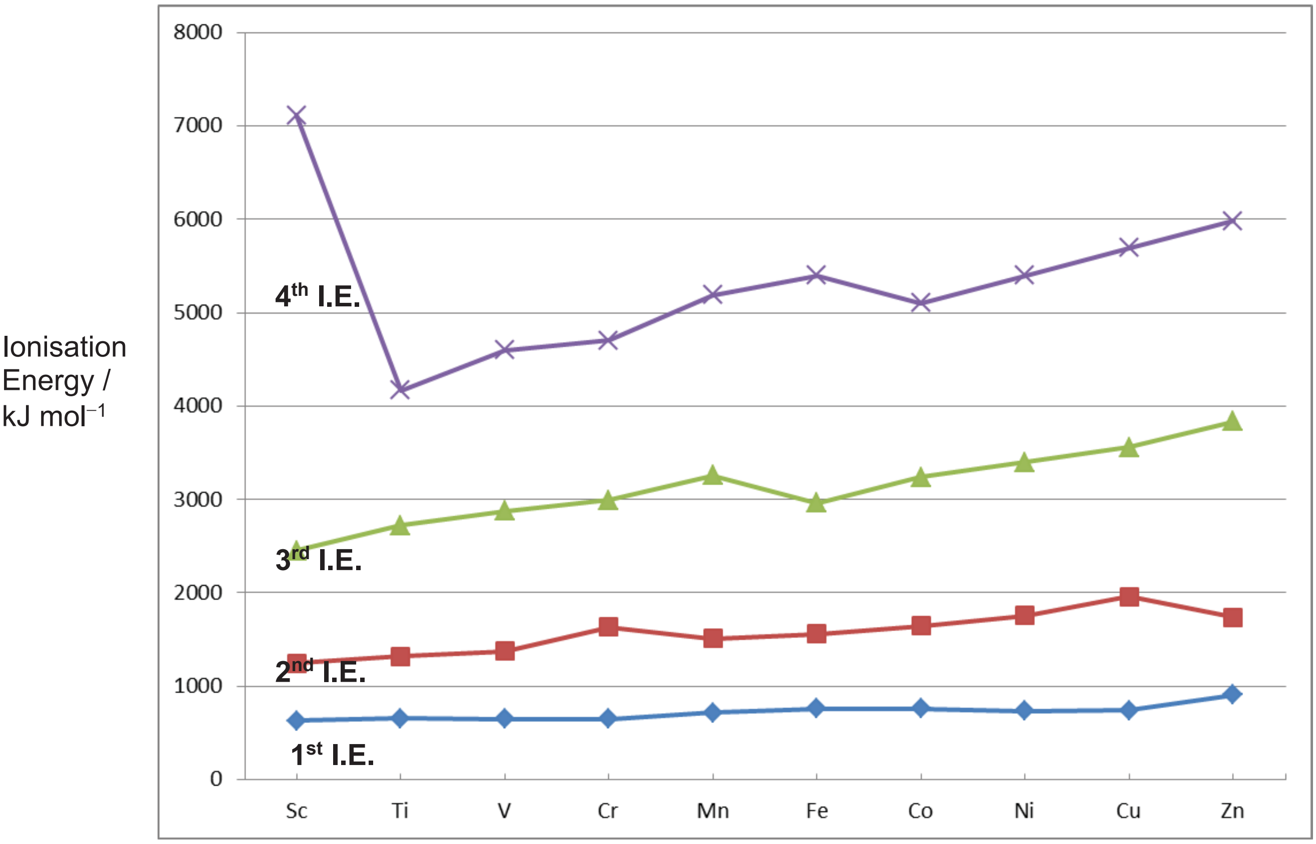
……………………………………………………………………………………………[2]

(ii) Write a balanced equation for the redox reaction between MnO_2, KOH and air.

$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$

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

(c) The graph below shows the variation of the first to fourth ionisation energies for the first row d–block elements scandium to zinc.



(i) Give an equation that represents the second ionisation energy of manganese.

$Mn^{+}(g) \longrightarrow Mn^{2+}(g) + e^{-}$

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

(ii) Explain why the first ionisation energies of the elements Ti to Cu, are relatively invariant across the Period. [2]

- Across the period from Ti to Cu, there is an increase in number of protons, hence nuclear charge increases.
- However, electrons are added to the penultimate shell (inner 3d sub-shell), resulting in an increase of shielding effect too.
- These 3d orbital electrons shielded the outer 4s orbital electrons from the increased nuclear charge. As a result, the effective nuclear charge is almost

constant (only increases very slightly) thus IE is almost constant.

(iii) Explain why the fourth ionisation energy of cobalt is lower than that of iron.

Fe: : [Ar]$3d^6 4s^2$
Co: [Ar]$3d^7 4s^2$

- Electronic configuration of
  Fe^{3+} : [Ar]$3d^5$
  Co^{3+} : [Ar]$3d^6$
  OR
- The 4th electron from Co is removed from 3d orbital containing a pair of electrons while the 4th electron from Fe is removed from a singly occupied 3d orbital.

Due to inter-electron repulsion between the paired 3d electrons in Co^{3+}, the energy required to remove the 4th electron in Co is lower than in Fe.

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

[Total:12]

5 **(a)** Structure elucidation is an important skill that chemists must acquire to help them determine the chemical structures of organic compounds.

A novice chemist requires your assistance in determining the structure of an aromatic organic compound **P**, that she found in the laboratory.

The molecular formula of compound **P** is $C_9H_{11}ON$, and **P** contains two functional groups.

(i) An orange precipitate is observed when compound **P** is reacted with 2,4-dinitrophenylhydrazine. Name the type of reaction that has taken place. From this observation, deduce the functional groups that could be present in compound **P**.

Condensation.

Aldehyde or Ketone (reject carbonyl)

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

(ii) No silver mirror is formed when compound **P** is heated with hot ammoniacal silver nitrate (mixture of aqueous ammonia and aqueous silver nitrate).
Which of the functional groups you named in **(a)(i)**, is confirmed by this observation?

Ketone.

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

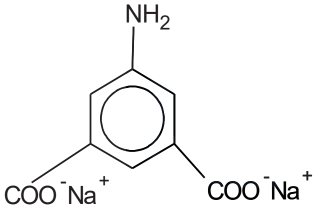
(iii) When compound **P** is reacted with bromine water in excess, a white solid which has M_r = 385.7, is formed.
Deduce the molecular formula of the white solid that is formed.

$C_9H_8NOBr_3$

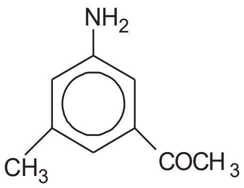
Phenylamine reacts with the aqueous bromine to form the white solid, which is a tribrominated substituted product in which 3 hydrogen atoms on the benzene ring are being substituted with bromine atoms.

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

(iv) Compound **P** reacts with hot potassium manganate(VII) in aqueous sodium hydroxide. A product with the molecular fomula, $C_8H_5NO_4Na_2$, is formed.
Draw the structure of the product.



(v) You now have enough information to determine the structural formula of compound **P**. Draw the structure for **P**, explaining clearly why you have placed each of the two functional groups in their respective positions.



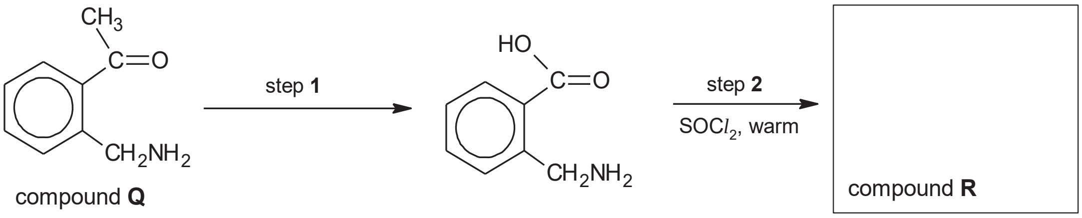
The phenylamine group in compound **P** is 2,4-directing.
Hence in **(a)(iv)**, 3 bromine atoms are substituted for 3 hydrogen atoms at 2, 4, and 6 position wrt to -NH_2 group attached to benzene ring.
Thus, the -CH_3 and the -$COCH_3$ groups will be at positions 3 or 5.

…………………………………………………………………………………………[2]

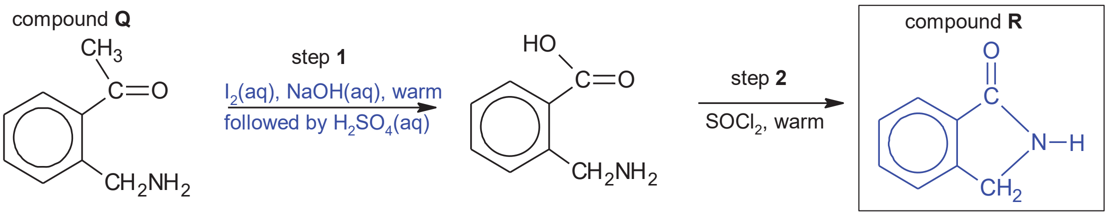
(b) Compound **Q**, $C_9H_{11}ON$, is a structural isomer of compound **P**.

The diagram below shows a possible reaction scheme for converting compound **Q** to form compound **R,** C_8H_7NO.

(i) Complete the diagram by suggesting the reagents and conditions for step **1**, and give the structural formula of compound **R**.



[2]



(ii) It was found that the yield of compound **R** was low. Suggest a reason for this. [1]

Acid in step 1 protonates basic amine OR
Intramolecular acid base reaction between acidic –COOH and basic –CH_2NH_2 group in intermediate compound formed in step 1

(c) The table below shows the pK_b values of two organic nitrogen compounds in aqueous solutions.

Compound	**pK_b**
methylamine, CH_3NH_2	3.36
trimethylamine, $(CH_3)_3N$	4.19

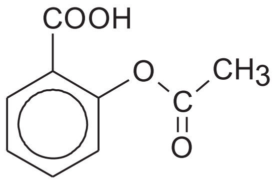
Using the data provided in the table above, suggest an explanation on the relative basicities of these two compounds.

[3]

Methylamine is more basic than trimethylamine.
The basicity of an organic nitrogen compound depends on the availability of the lone pair of electrons on the nitrogen atom to accept a proton.
Either explanation is acceptable:
1) Steric Factor:
The presence of 3 alkyl groups in trimethylamine (compared to 1 alkyl group in methylamine) results in steric hindrance, which hinders/makes it more difficult for the lone pair on nitrogen to accept the proton.
OR
2) Hydration Factor:
Hydration effect refers to the stabilisation of the protonated amine by water molecules. The water molecules form hydrogen bonds with the protonated amine and release energy called hydration energy, stabilising the protonated alkylamine.
Hydration due to hydrogen bonding is greater in protonated methylamine, and hence it is the most basic.

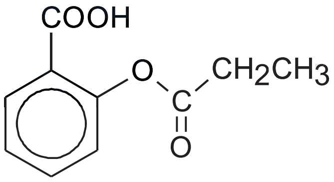
[Total:13]

6 **(a)** Acetylsalicylic acid (ASA), which is extracted from the leaves of the willow tree, has been used for its health effects for at least 2,400 years. It is an important medication that is used to treat pain, fever, and inflammation.



Acetylsalicylic acid

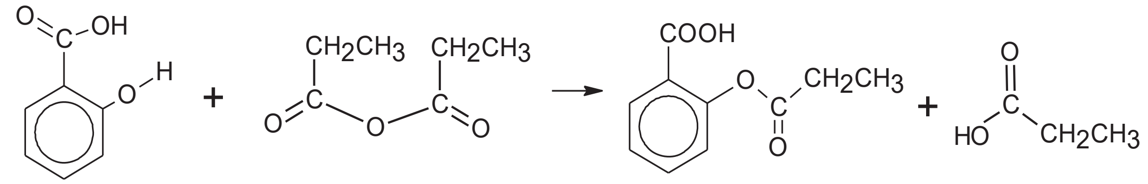
A chemist wanted to form a derivative of ASA, compound **T** below:



Compound **T**

One method to form compound **T** was to react 2-hydroxybenzoic acid and propanoic anhydride in reaction **1** below.

Reaction **1**



2-hydroxybenzoic acid propanoic anhydride compound **T**

(i) State the type of reaction that has occurred in the formation of compound **T** in reaction **1**.

Nucleophilic acyl substitution

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

The mechanism of reaction **1** consists of three steps and is described below:

Step 1:

The phenol group on 2-hydroxybenzoic acid acts as a nucleophile and attacks one of the reactive carbons in propanoic anhydride to form only one intermediate **W**. The intermediate **W** contains both a cationic oxygen and an anionic oxygen.

Step 2:

A proton is released from intermediate **W** to form intermediate **X**.

Step 3:

From intermediate **X**, a carboxylate anion is expelled as a leaving group, and an ester **Y** is formed as the other product.

Step 4:

Protonation of the carboxylate anion formed in step 3 produces a carboxylic acid.

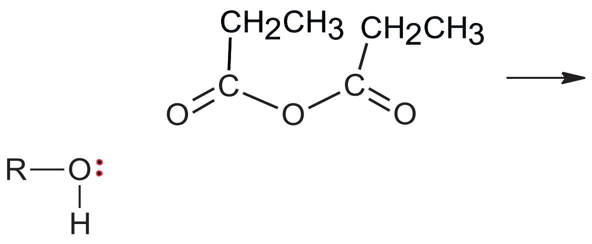
(ii) Draw all four steps in the full mechanism for the reaction between 2-hydroxybenzoic acid and propanoic anhydride.

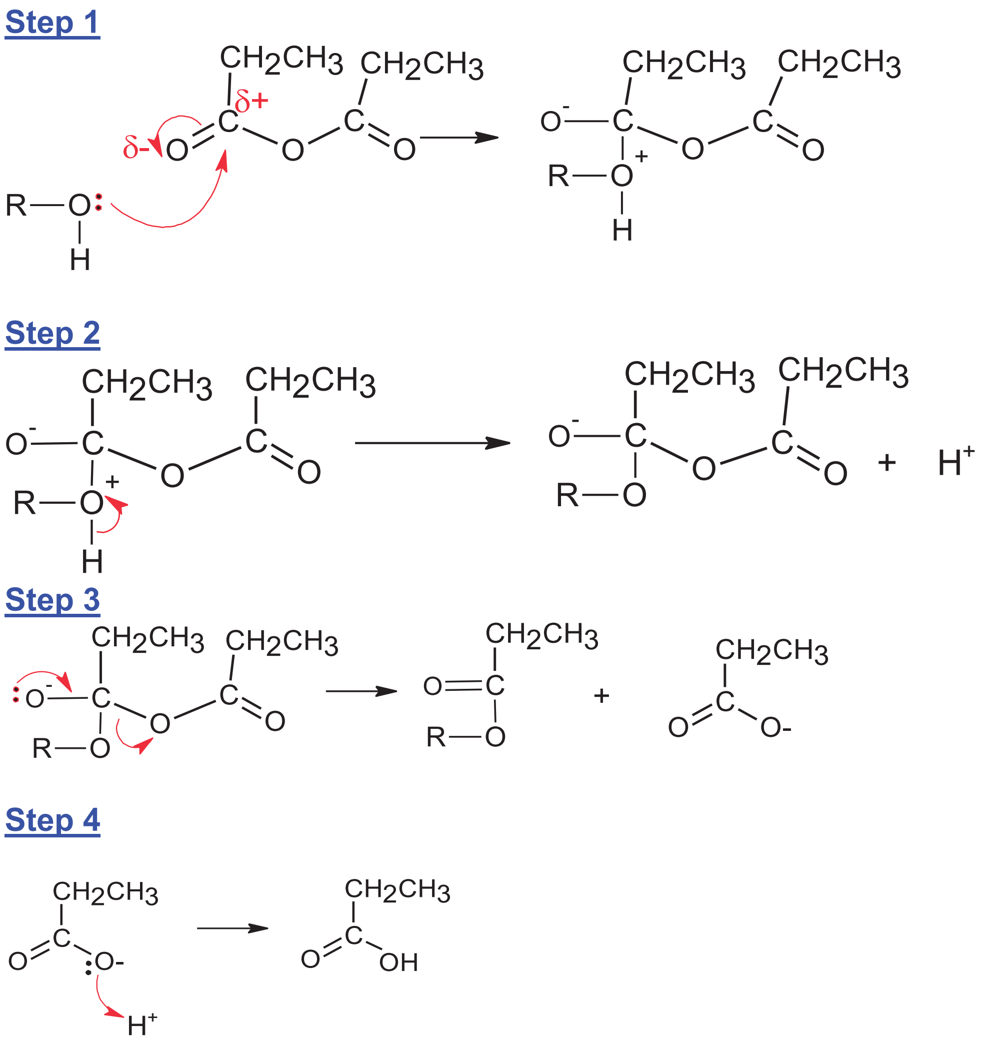
(you may use ROH to represent 2-hydroxybenzoic acid in your answer.)

For the first step of the mechanism, *complete* the diagram shown below and draw the remaining three steps of the mechanism in the space given below each step. Show all intermediates, relevant charges, lone pairs of electrons and indicate the movement of electron pairs with curly arrows in all the steps.

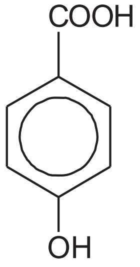
<u>Step 1</u>

Let R–O–H represents 2-hydroxybenzoic acid.



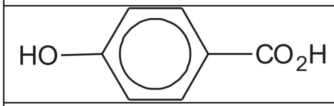
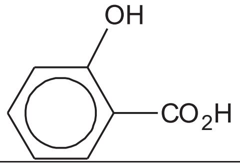


(iii) An isomer of 2-hydroxybenzoic acid is shown below:



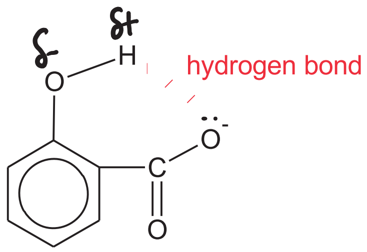
4-hydroxybenzoic acid

Both 2-hydroxybenzoic acid and 4-hydroxybenzoic acid are dibasic acids that ionises in two stages. The acid dissociation constant, pK_1, for the first stage of dissociation is given below.

	pK_1
	4.54
	2.97

With the aid of a diagram, explain why 2-hydroxybenzoic acid has a lower pK_1.

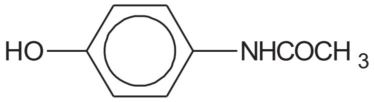
2-hydroxybenzoic acid has lower pK_1 thus it is a stronger acid than 4-hydroxybenzoic acid.



Due to the close proximity of the –COO⁻ and -OH groups in 2-hydroxybenzoate ion, the anion is stabilised by intramolecular hydrogen bonding.
As such, the equilibrium position for the dissociation of 2-hydroxybenzoic acid will lie more towards the right, releasing more H^+, and hence, stronger acid.

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

(b) Another medicine that is used widely to treat fever and pain is paracetamol, or commonly known as panadol.



Paracetamol

Some information on paracetamol is provided in Table 1 below.

Data on paracetamol	
Molecular Formula	$C_8H_9NO_2$
Density	1.263 g/cm^3
Melting Point	169°C
Boiling Point	420°C
Solubility in water	14 mg/ml
Bioavailability*	75% (oral) 100% (intravenous)
Biological half-life**	2 hours

Table 1

**Bioavailability refers to the percentage of a drug which enters the blood circulation when introduced into the body and hence able to have an active and effective effect.*

***Biological half-life of a drug is the time taken for the drug to reduce to half its original amount in the body.*

(i) Paracetamol can be produced from the reaction between 4-aminophenol and ethanoic anhydride as shown below.

C_6H_7NO	+	$C_4H_6O_3$	→	$C_8H_9NO_2$	+	$C_2H_4O_2$
4-aminophenol		ethanoic anhydride		paracetamol		
(M_r : 109)		(M_r : 102)		(M_r : 151)		

It is known that the yield of this reaction is only 60%. Calculate the minimum masses of the reactants that are required to produce 10 g of paracetamol.

Mass of 4-aminophenol required = $\frac{10}{151}\times\frac{100}{60}\times 109$ = 12.0 g

Mass of ethanoic anhydride required = $\frac{10}{151}\times\frac{100}{60}\times 102$ = 11.3 g

(ii) A doctor wishes to prescribe oral medication for one of his patients suffering from headache. In order for the medicine to be effective, the patient requires a recommended dosage of 560 mg of paracetamol in her body.

How many 250 mg paracetamol tablets should the patient take each time?

Mass of paracetamol that must be in the patient’s body = 560 mg
Mass of paracetamol that must be taken orally by patient
= 560 / (75 /100)
= 747 mg
Number of 250 mg paracetamol tablets that the patient should take
= 747 / 250 = 2.99 ≈ <u>3 tablets</u>

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

(iii) A patient suffering from acute dental pain is advised to consume orally, four 250 mg paracetamol tablets.

To effectively alleviate his pain, at any point of time, the amount of paracetamol in his body **must not** drop below 93 mg.

With reference to relevant data from Table 1, and the use of suitable calculations, determine the maximum number of hours that the oral medication prescribed above remains effective, and show clearly whether the doctor should advise the patient to take four tablets of paracetamol once in every 4 hours, 6 hours, or 8 hours. [2]

Mass of paracetamol in 4 x 250 mg tablets = 1000 mg
Mass of paracetamol that will be useful and effective = 75% x 1000 = 750 mg
Since biological half-life of paracetamol is 2 hours,

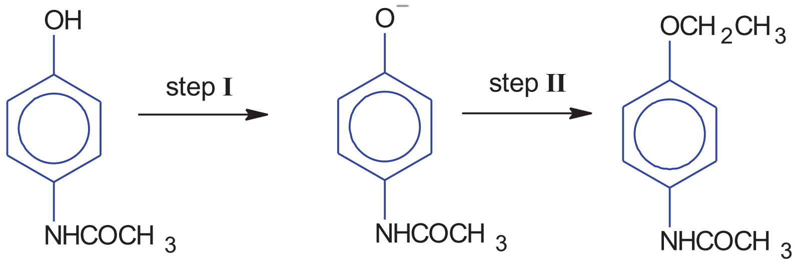
$$750\text{ mg} \xrightarrow{\text{2 hours}} 375\text{ mg} \xrightarrow{\text{2 hours}} 187.5\text{ mg} \xrightarrow{\text{2 hours}} 93.75\text{ mg}$$

It takes 2x3 = 6 hours for oral medication to remain effective, for the amount of paracetamol in his body to be at least **must not** drop below 93 mg

From the above calculation, it can be seen that the patient should take 4 tablets of paracetamol <u>once every 6 hours</u>.

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

(c) **(i)** Phenacetin was once used as an analgesic (pain killing drug). It can be synthesised from paracetamol below.



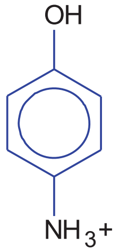
paracetamol

phenacetin

Suggest reagents and conditions for step **I** and **II**.

step **I** : NaOH(aq) (reject heat) or Na
step **II**: CH_3CH_2Br, heat

(ii) A student added aqueous sulfuric acid to paracetamol and heated it. Suggest the products obtained.



+ CH_3COOH

[Total:17]

End of paper

H

PIONEER JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION
HIGHER 2

CANDIDATE NAME

CT GROUP	1	6			

INDEX NUMBER				

CHEMISTRY

9729/03

Paper 3 Free Response

15 September 2017

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Data Booklet
Cover Page

READ THESE INSTRUCTIONS FIRST

Write your name, index number and CT group on all work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough workings.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question.

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

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

This document consists of **17** printed pages.

Section A

Answer all questions in this section.

1 Compounds containing halogens form a large class of chemicals, which are of industrial importance and are synthesised in huge quantities worldwide.

(a) Phosgene, $COCl_2$, is a gas which was produced during World War I, and was used as a chemical weapon. One method to produce phosgene from trichloromethane is as shown below.

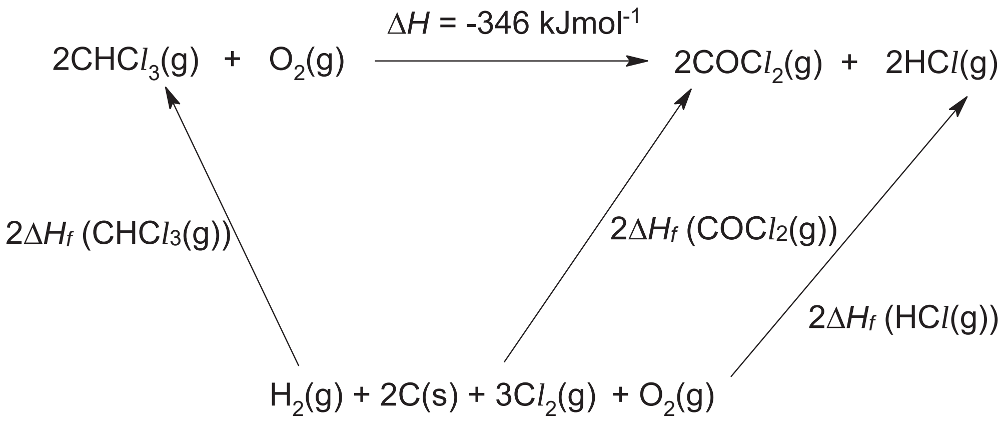
$$2CHCl_3(g) + O_2(g) \rightarrow 2COCl_2(g) + 2HCl(g) \qquad \Delta H = -346 \text{ kJ mol}^{-1}$$

Using the data below, calculate the standard enthalpy change of formation of $HCl(g)$.

standard enthalpy change of formation of $CHCl_3(g)$	-103 kJ mol^{-1}
standard enthalpy change of formation of $COCl_2(g)$	-184 kJ mol^{-1}

[1]

no need cycle



By Hess' Law,
$2\Delta H_f (CHCl_3(g)) + \Delta H = 2\Delta H_f (COCl_2(g)) + 2\Delta H_f (HCl(g))$
$2(-103) + (-346) = 2(-184) + 2\Delta H_f (HCl(g))$
$\Delta H_f (HCl(g))$= **-92.0 kJ mol^{-1}**

(b) Aqueous hydrochloric acid is another chemical with many industrial uses. It can be obtained by reacting hydrogen gas and chlorine gas in the presence of UV light, followed by dissolving the hydrogen chloride gas in water.

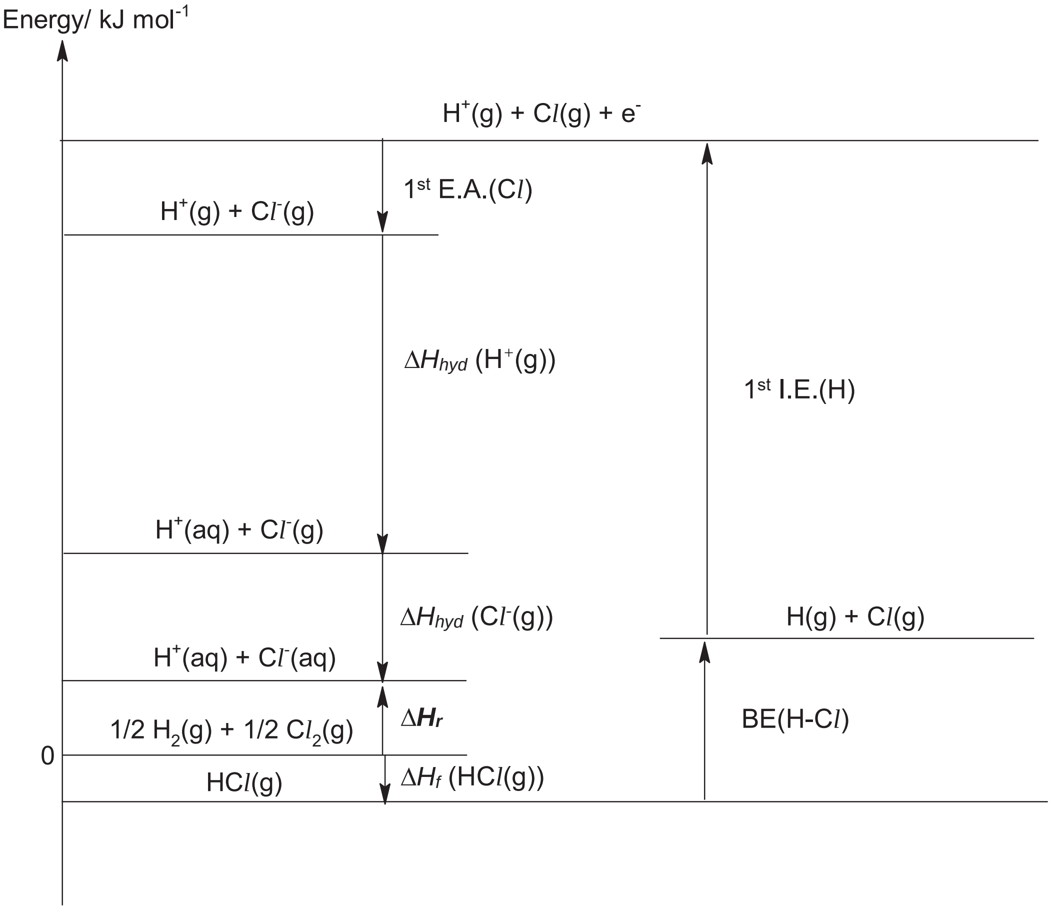
The equation for this reaction is as shown below.

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g) \rightarrow H^+(aq) + Cl^-(aq) \qquad \Delta H_r$$

Using the Data Booklet, the data in the table below, and your answer in **(a)**, construct an appropriate energy-level diagram to calculate ΔH_r.

	$\Delta H^{\ominus}$/ kJ mol^{-1}
First ionisation energy of H(g)	+1310
First electron affinity of C*l*(g)	– 364
Standard enthalpy change of hydration of Cl^- (g)	– 381
Standard enthalpy change of hydration of H^+(g)	– 1130

[4]



By Hess' Law,

$\Delta H_r = \Delta H_f$ (HC*l*(g)) + BE(H-C*l*) + 1st I.E.(H) + 1st E.A.(C*l*) + ΔH_{hyd} (H^+(g)) + ΔH_{hyd} (Cl^-(g))

ΔH_r = (-92) + 431 + (+1310) + (– 364) + (– 1130) + (– 381)

BE(H-C*l*) = **-226 kJ mol^{-1}**

Elements should be clearly placed at ground state of energy = 0.

(c) When heated, Group 17 hydrides, HX, undergo thermal decomposition.

$$HX \longrightarrow \frac{1}{2} H_2 + \frac{1}{2} X_2$$

Using the data on bond energies of the various H-X bonds given below, predict and explain how the thermal stability of the hydrides varies down the Group 17.

Bonds	Bond energies/ kJ mol^{-1}
H-C*l*	+431
H-Br	+366
H-I	+299

[2]

The thermal stability of Group 17 hydrides **decreases** down the group.

Down the group, the **atomic radii of the halogen increases**, which resulted in the less effective overlap due to the bigger orbitals involved. The **H-X bond length increases,** resulting in decreasing bond energy and lesser energy is required to break the weaker H-X bond for decomposition and the thermal stability decreases.

(d) Seawater is an important source of ionic halides like sodium chloride, sodium bromide and sodium iodide.

When silver nitrate is added to separate test-tubes containing aqueous sodium chloride, sodium bromide and sodium iodide, the various AgX (X = C*l*, Br and I) precipitates were observed. The solubilities of these precipitates upon addition of dilute NH_3 and concentrated aqueous NH_3, are recorded below.

	NaC*l*	**NaBr**	**NaI**
To NaX(aq), add $AgNO_3$(aq)	white ppt observed	cream ppt observed	yellow ppt observed
To the resulting mixture, add dilute NH_3(aq)	soluble	insoluble	Insoluble
To the resulting mixture, add excess concentrated NH_3(aq)	soluble	soluble	Insoluble

(i) Write the balanced ionic equation for the formation of the cream precipitate from adding silver nitrate to sodium bromide.

[1]

$Br^-(aq) + Ag^+(aq) \rightarrow AgBr(s)$

State symbols must be given as it is ionic equation.

(ii) Explain the effect of adding aqueous ammonia to each of the resulting mixture and clearly account for any difference in the observation. [3]

$AgX(s) \rightleftharpoons Ag^+(aq) + X^-(aq)$

$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq)$ **reaction 2**

The **solubility product, K_{sp}, of the silver halides decreases down Group 17** (i.e. K_{sp} of AgC*l* > AgBr > AgI).

When aqueous ammonia solution is added, based on reaction **(2)**, the small amount of $Ag^+(aq)$ ions present in the resulting mixture is used up to form $[Ag(NH_3)_2]^+(aq)$ complex. This **decreases the concentration of $Ag^+(aq)$ ions** as a result and **the ionic product of the silver halide decreases** .

Since silver chloride has the largest K_{sp}, the **ionic product** drops below ***K**_{sp}* **of AgC*l*** and hence silver chloride dissolves when NH_3(aq) solution is added.

In contrast, silver bromide and sodium iodide has smaller K_{sp}. Hence, even though ionic product decreases, the **ionic products of both silver bromide and silver iodide are still larger than their respective K_{sp} values** and the precipitates remained insoluble when dilute NH_3(aq) solution is added.

However, with concentrated aqueous ammonia, the formation of diamminesilver(I) complex is sufficient to decrease the [Ag^+], thus causing the ionic product of AgBr to fall below its K_{sp} value thus ppt dissolves. This explains why AgBr(s) is soluble in concentrated NH_3(aq) but insoluble in dilute NH_3(aq).

For AgI:
The formation of diamminesilver(I) complex in both dilute and concentrated aqueous ammonia is not sufficient to cause the ionic product of AgI to fall below its K_{sp} value (as the K_{sp} value of AgI is extremely low). Therefore, AgI(s) is insoluble in both dilute and concentrated NH_3(aq).

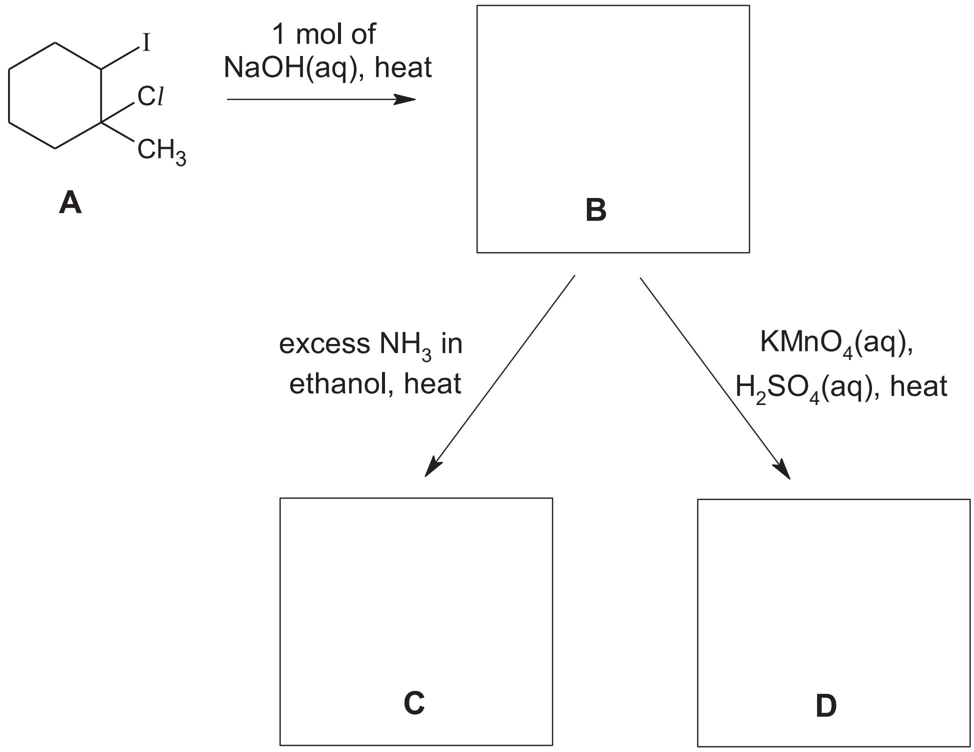
(e) Halogenoalkanes are widely synthesised by reacting halogens with alkenes. In turn, halogenoalkanes can undergo nucleophilic substitution using sodium hydroxide to form alcohols commercially.

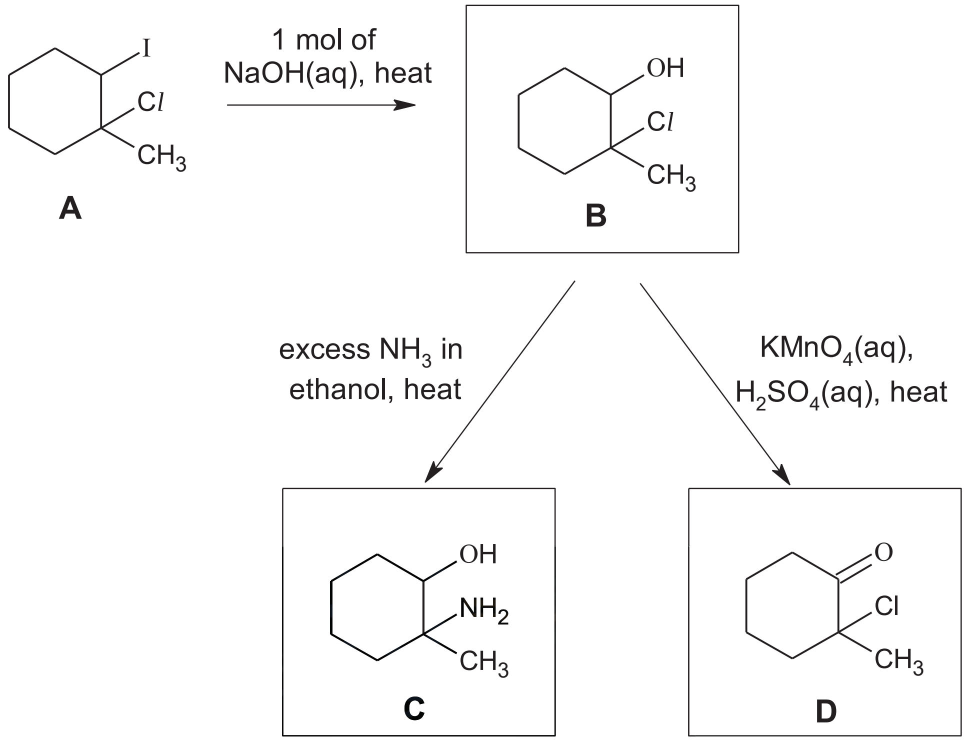
(i) Give one reason why iodoalkanes are more reactive towards nucleophilic substitution with aqueous NaOH than the corresponding chloroalkanes.

[1]

The bond energy of C–I is lower / C–I bond weaker than C– C*l*. C–I bond is more easily broken.
OR
C*l*$^-$ is also a weaker leaving group than I$^-$ as C*l*$^-$ is a stronger base than I$^-$.

(ii) A sequence of reactions, starting from compound **A**, a dihalogeno compound, is shown below.



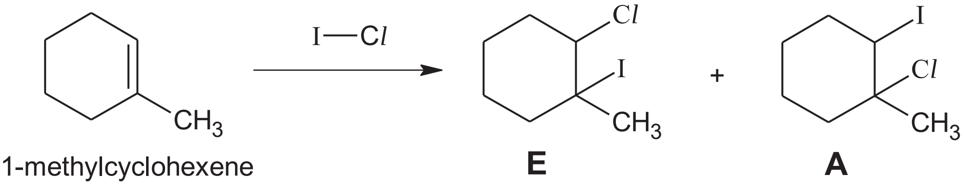


Draw the structures of compounds **B**, **C** and **D**.

[3]

(iii) The halogens form many interhalogen compounds, one such example is IC*l*, commonly known as Wijs' reagent.

Wijs' reagent can react with 1-methylcyclohexene to form a mixture of compound **E** and **A**. Explain why **A** is the major product for this reaction.



[2]

The alkene functional group of 1-methylcyclohexene will **attack the iodine atom** of the ICl molecule **first as iodine atoms are more delta positive** than Cl, to form a new C- I bond. The major product will have the new ICl bond formed on the carbon number 2, as this will result in a **more stable carbocation with the positive charge on the first carbon** which had an additional **electron-donating methyl group**. OR form more stable carbocation

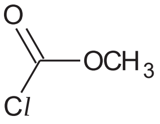
(f) **(i)** Below outlines a reaction scheme of phosgene with NaOH(aq) in two stages.

$$COCl_2 \xrightarrow[\text{stage 1}]{OH^-} COCl(OH) \xrightarrow[\text{stage 2}]{} CO_2 + HCl$$

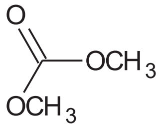
State the types of reaction occurring in stage 1, and stage 2. [2]

Stage 1: Nucleophilic acyl substitution (*for carboxylic acids and derivatives*)
Stage 2: Elimination

(ii) In order to remove any phosgene present in a bottle of chloroform, a small amount of methanol is added. use the information in **(f)(i)** to suggest the structural formula of the organic compound formed when phosgene reacts with methanol. [1]



or



[Total:20]

2 **(a)** Carbon monoxide reacts with steam over a copper / zinc catalyst, to form a mixture of carbon dioxide and hydrogen gas.

Reaction 1: $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$

When an equimolar mixture of hydrogen and carbon dioxide at an initial total pressure of 4 atm is allowed to reach equilibrium at 1000 K, the percentage of steam in the mixture of gases is found to be 15%.

(i) Calculate K_p of the system in **reaction 1** at 1000 K. [2]

	$CO(g)$	$H_2O(g)$	$\rightleftharpoons$	$CO_2(g)$	+	$H_2(g)$
Initial pressure / atm	0	0		2		2
Change in pressure / atm	+x	+x		-x		-x
Eqm pressure / atm	x	x		2-x		2-x

P_{H2O} = x / 4 = 0.15
Thus, x = P_{H2O} = P_{CO} = 0.60 atm
P_{CO2} = P_{H2} = 1.40 atm
$K_p = (1.40)^2 / (0.60)^2 = 5.44$

(ii) Suggest, with a reason, whether or not a higher pressure would favour the formation of steam. [1]

No because same number of moles of gas on right and left side

(b) Sodium ethanoate can be used to prepare ethane by an electrochemical reaction, which is known as the Kolbe electrolysis reaction. Ethane is formed at the anode by the following reaction:

$$2CH_3CO_2^- \rightarrow C_2H_6 + 2CO_2 + 2e^-$$

A student investigated the electrolysis of aqueous solution of sodium ethanoate, using graphite electrodes in a litmus solution.

(i) Give the equation for the reaction occurring at the cathode, and state the final colour expected at the cathode.

Construct an equation for the **overall** reaction. [2]

At the cathode:

- Equation at cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
- The product OH^- turns the litmus solution blue.

- Overall reaction:

$$2\,CH_3CO_2^- + 2H_2O \rightarrow C_2H_6 + 2CO_2 + H_2 + 2OH^-$$

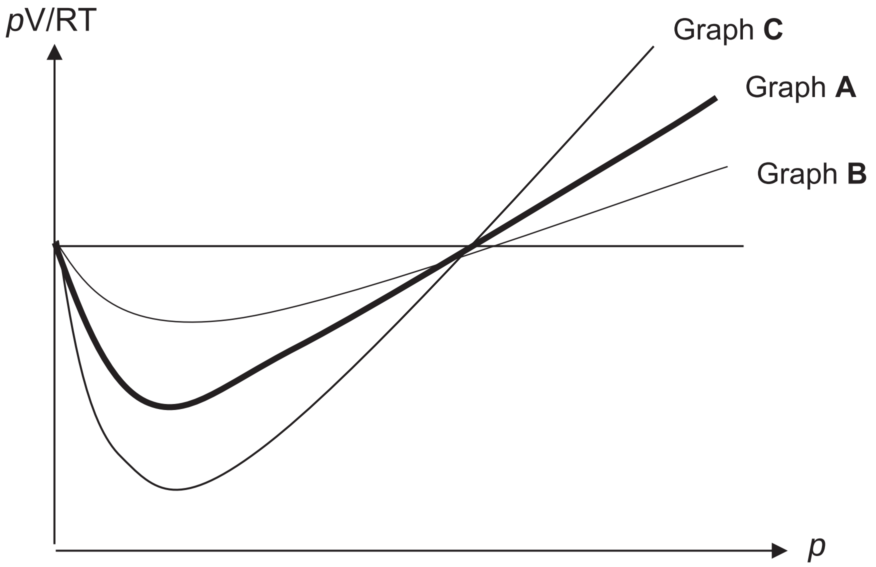
(ii) Calculate the time, in minutes, needed by the student to pass a current of 5.0 A through a solution of sodium ethanoate, to produce 1.50 g of ethane. [2]

No of moles of ethane = 1.5/30 = 0.0500 mol
No of moles of electrons = 0.05 x 2 = 0.100 mol

$$\text{time} = Q/I = \frac{0.1\times96500}{5\times60} = 32.2 \text{ min}$$

(c) **(i)** The value of pV/RT is plotted against p for the following three gases, where p is the pressure and V is the volume of the gas.
Given that graph **A** represents 1 mol of CO_2 at 298 K.

Identify which of the following graphs, **B** or **C,** represent 1 mol of CO_2 at 500 K.



[2]

Graph **B** is CO_2 at 500 K
CO_2 at 500 K deviates less than CO_2 at 298 K. At higher temperature, CO_2 molecules possess higher average kinetic energy and are more able to overcome forces of attraction between the molecules.

(ii) Sulfur dioxide is used by the Romans in winemaking, when they discovered that burning sulfur candles inside empty wine vessels keeps them fresh and free from vinegar smell.

One such cylinder of sulfur dioxide has an internal volume of 2.5 dm^3, and a mass of 2.3 kg.

Calculate the pressure (in pascals) that the sulfur dioxide would exert inside the cylinder at room temperature. [1]

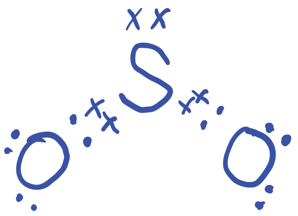
Pls take note: Room temperature is now 293K!
$pV = nRT$
$p = (2.3 \times 10^3 / 64.1)(8.31)(293) / (2.5 \times 10^{-3})$
$= 3.49 \times 10^4$ kPa

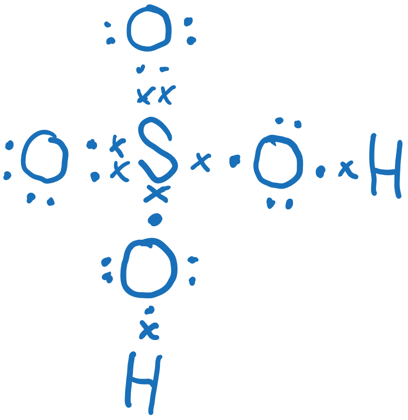
(d) Sulfuric acid is used in many industrial processes of major importance.

The process used to produce sulfuric acid involves a three–stage process. The first stage is to pass air over burning sulfur. The emerging gas is then passed over a catalyst, V_2O_5, which is maintained at 450-550ºC in the reaction chamber.

Stage **I**: $S(s) + O_2(g) \rightarrow SO_2(g)$
Stage **II**: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
Stage **III**: $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(l)$

(i) Draw dot-and-cross diagrams to show the bonding in SO_2 and H_2SO_4. State the bond angle, with respect to sulfur atom, in each of them. [4]





Accept between 110° and 120° 109.5°

(ii) The boiling points of sulfur trioxide and sulfur dioxide are 45°C and -10°C respectively.

Account for the difference in boiling points for both compounds, in terms of structure and bonding. [2]

- Both compounds have **simple covalent structures/ simple molecular structures**.
- However, SO_3 has a higher boiling point than SO_2 because SO_3 has **stronger (intermolecular) instantaneous dipole-induced dipole attractions** due to its
- **larger electron cloud size / more electrons being polarised.**

(SO_2 has weaker intermolecular permanent dipole-dipole attractions.)

- Hence, **more energy** is required to overcome the bonding in SO_3.

(e) For each of the following pairs of compounds, suggest **one** simple chemical test to distinguish them from each other. State the reagents and conditions needed and give the expected observations for each compound.

(i) $CH_2=CHCH_2CH(CH_3)OH$ $CH_2=CHC(CH_3)_2OH$

J **K**

Test: Add **$K_2Cr_2O_7$(aq), H_2SO_4(aq) and heat** to both compounds**.**

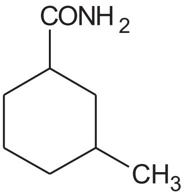
Observation: The solution of **A** will change from **orange to green** while the solution of **B** will **remain orange**.

OR

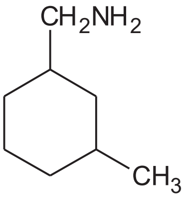
Test: Add **I_2(aq), NaOH(aq) and warm** to both compounds.

Observation: The solution of **J** will decolourise brown iodine and give a **yellow ppt** while solution of **K** **will not**.

(ii)



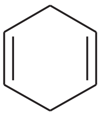
L



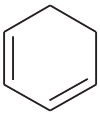
M

Test: Add NaOH(aq) and heat to both compounds.
Observation: **L** will give pungent gas (NH_3) that turns **moist red paper blue** while **M will not**.

(iii)



P



Q

Add $KMnO_4$(aq), H_2SO_4(aq) and heat to both compounds.
Observation: The solution of **P and Q** will change from **purple to colourless** but the solution of **Q** will **produce** bubbles of CO_2 that form white ppt with limewater

[Total:22]

3 Nitrous oxide, N_2O, is commonly known as laughing gas due to the euphoric effects of inhaling it. At a temperature of 1000 K, in the presence of chlorine catalyst, N_2O decomposes to its elements according to the following equation:

$$2N_2O(g) \rightarrow 2N_2(g) + O_2(g)$$

The experimental rate equation for this reaction is Rate = $kP^{a}_{N_2O}\,P^{b}_{Cl_2}$

where P_{N_2O} and P_{Cl_2} are the partial pressures of N_2O and Cl_2 respectively and a and b are non-zero constants.

The rate of decomposition of pure N_2O may be followed at constant temperature, by measuring the total pressure of the system with time.

The data below refers to a reaction in which pure N_2O decomposes in the presence of chlorine catalyst, Cl_2, (at partial pressure of 47 kPa).

Experiment 1:

time / s	0	40	80	140	240
P_{total} / kPa	87.0	91.3	93.0	98.0	102.2
P_{N_2O}	40	31. 4	25	18	9.6

(a) **(i)** Show that the partial pressure of N_2O at any instant is given by
$P_{N_2O} = 214 - 2P_{total}$ [2]

Let x = pressure of N_2O that dissociated

	$2N_2O(g)$	→ $2N_2(g)$	+ $O_2(g)$

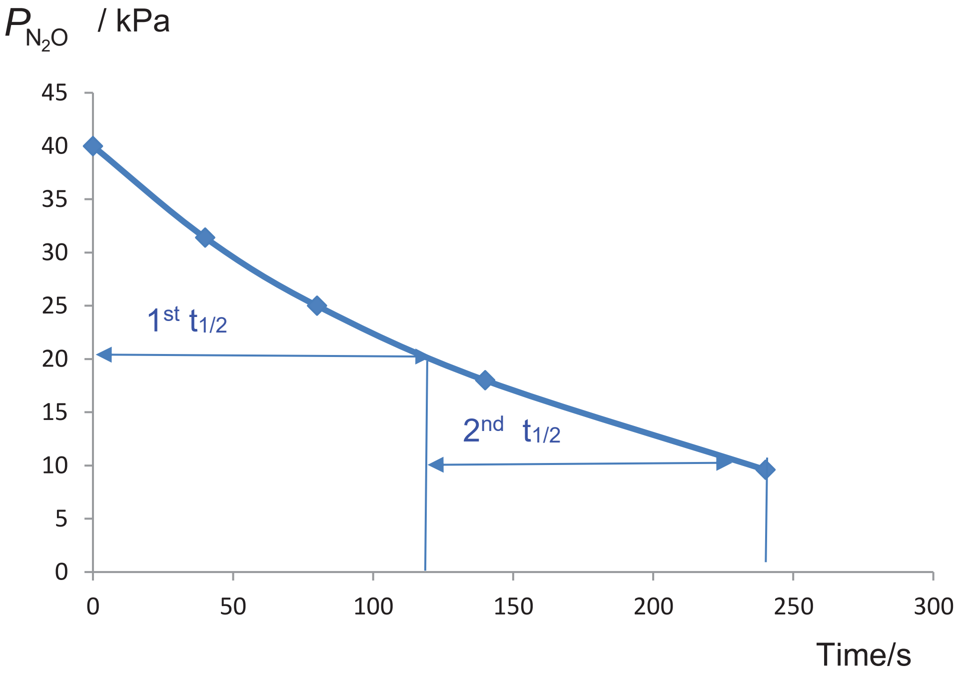
Initial P / kPa	40	0	0
Change in P/ kPa	-2x	+2x	+1x
Final P / kPa	40-2x	2x	X

P_{total} = 40-2x + 2x + x +47 = 87+x

X = P_{total} - 87

P_{N_2O} = 40-2x = 40 -2(P_{total} – 87) = 214 -2P_{tot} (shown)

(ii) Use the given data provided in the table above to plot a graph of P_{N_2O} against time on suitable axes. Showing all your working and drawing clearly any construction lines on your graph, use your graph to determine the value of a, the order of reaction with respect to N_2O.



-Axes, correct labelled (with units)
-Correct plotting of points
-Correctly draw grid lines to show the two $t_{1/2}$ (range of half-life ±10%) $t_{1/2}$ is about 121s
-Conclude first order from constant half lives construction lines for the 2 half-lives [4]

(iii) Two additional experiments, experiments 2 and 3 were carried out and the following results were obtained.

	P_{N_2O} / kPa	P_{Cl_2} / kPa	Initial rate/ kPa s^{-1}
experiment 2	70	35	0.306
experiment 3	70	70	0.613

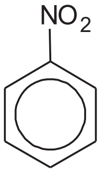
Determine b, the order of reaction with respect to chlorine. Explain your reasoning. [1]

Compare experiments 2 and 3, keeping P_{N_2O} constant, when P_{Cl_2} doubled, initial rate doubled. Order with respect to chlorine =1

(iv) Hence write the rate equation for the reaction. [1]

Rate = $kP_{N_2O}\,P_{Cl_2}$ give ecf based on students' orders from (e)(ii) and (iii)

(b) Nitrobenzene is an organic compound used to mask unpleasant odors in shoe and leather dressings.



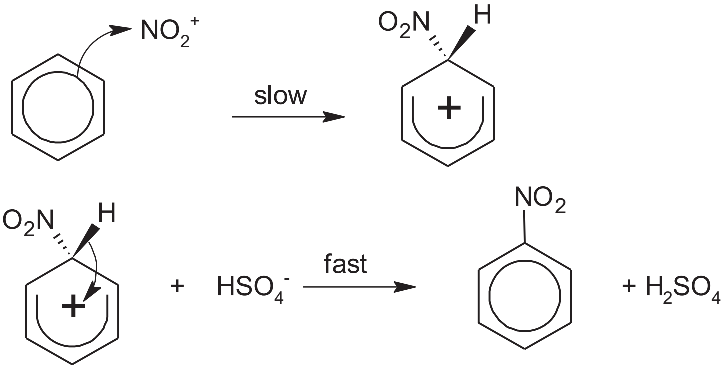
(i) Suggest the type of hybridisation of N in nitrobenzene. [1]

sp^2 hybridisation

(ii) Nitrobenzene can be formed from reacting benzene with concentrated nitric acid and sulfuric acid. Name and outline the mechanism of the nitration of benzene. Indicate the rate-determining step and draw the formula of the organic intermediate. [3]

Electrophilic substitution

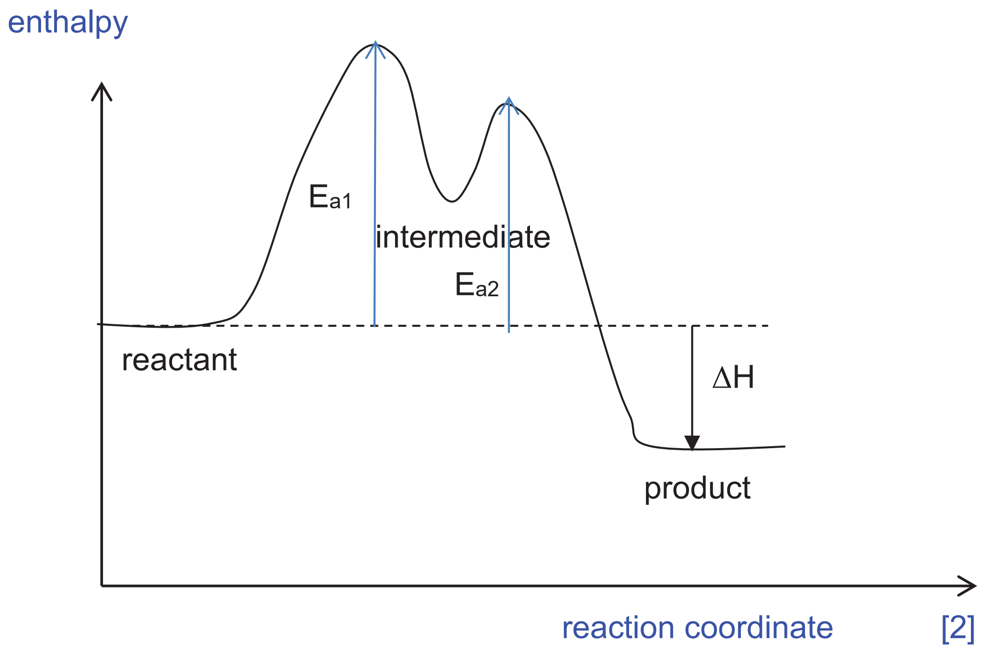
$2H_2SO_4 + HNO_3 \rightleftharpoons 2HSO_4^- + NO_2^+ + H_3O^+$



Deduct one mark if any of these are missing below

- Correctly drawn curly arrows for step 1
- Correctly drawn curly arrows for step 2
- Label **slow (rate-determining)** step
- correct intermediate (no need to show dashed and bold lines)
- Regeneration of catalyst, $\mathbf{H_2SO_4}$

(iii) Given that the nitration of benzene is exothermic, sketch the reaction pathway diagram of the reaction, labelling clearly the reactant, intermediate and product on your diagram.



[2]

- Axes clearly labelled
- Relative energy level of reactants and product (lower)
- Show 2 ‘humps’, and Ea1 > Ea2
- Label reactant,
- Label intermediate and
- Label product

(c) To investigate the mechanism of nitration of benzene, every hydrogen atom on benzene is replaced by its isotope, deuterium, to form C_6D_6.

Carbon–deuterium (C-D) bond has higher bond energy than a carbon–hydrogen (C-H) bond.

If the rate-determining step involves the breaking of a C–H bond, replacing the C–H bond with a C–D bond will change the rate constant, *k*, of the reaction. This is known as the deuterium isotope effect.

Deuterium isotope effect = $\frac{k_H}{k_D}$

k_H = rate constant for nitration of C_6H_6

k_D = rate constant for nitration of C_6D_6

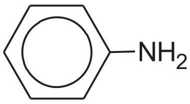
If $\frac{k_H}{k_D} = 1$, it is said that the deuterium isotope effect is absent.

If $\frac{k_H}{k_D} >> 1$, it is said that the deuterium isotope effect is present.

Predict with reasoning, if the deuterium isotope effect would be present in the nitration of benzene. [1]

As the rate-determining step does not involve the breaking of a C-H bond / the C-H bond is only broken in the fast step of the mechanism, there is no deuterium isotope effect present in nitration of benzene.

(d) **(i)** Nitrobenzene can be converted to phenylamine, which is used in the synthesis of polyurethane, a polymer used in making tyres.



phenylamine

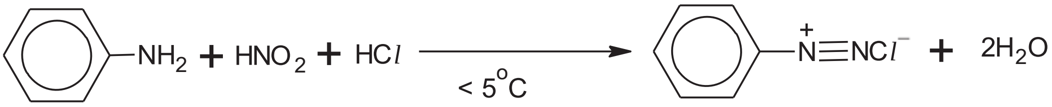
Suggest the reagents and conditions to convert nitrobenzene to phenylamine. [1]

Sn, concentrated HCl, heat
Followed by NaOH(aq)

(ii) The following equations illustrate the formation of phenol from phenylamine, in two steps:

In step 1, phenylamine reacts with cold nitrous acid, HNO_2, and hydrochloric acid, HC*l*, to form phenyldiazonium chloride.

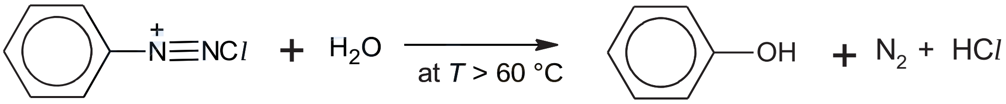
Step **1**



phenyldiazonium chloride

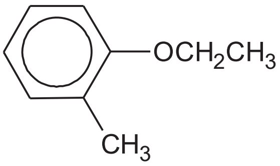
In step 2, phenyldiazonium chloride can react with water upon heating to give phenol.

Step **2**



phenyldiazonium chloride

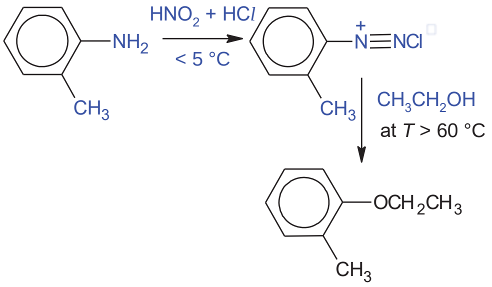
Propose a two-step synthetic pathway for the conversion of 2-methylphenylamine to compound **S** below.



Compound **S**

[2]

Answers:



[Total:18]

Section **B**

Answer **one** question from this section.

4 **(a)** A blood test can detect abnormally high levels of an amino acid which is one of the signs of the disease phenylketonuria, a rare condition in which a person is unable to properly break down amino acids such as phenylalanine.

In acidic solution, phenylalanine is completely protonated and exists as $H_3N^+CHRCO_2H$, where R is $–CH_2C_6H_5$.

Protonated phenylalanine, $H_3N^+CHRCO_2H$, acts as a dibasic acid that ionises in stages.

$H_3N^+CHRCO_2H \rightleftharpoons H_3N^+CHRCO_2^- + H^+$ $\quad pK_1 = 1.83$

$H_3N^+CHRCO_2^- \rightleftharpoons H_2NCHRCO_2^- + H^+$ $\quad pK_2 = 9.13$

(i) Calculate the pH of a 0.80 mol dm^{-3} solution of protonated phenlyalanine (ignore the effect of pK_2 on the pH).

Let $[H_3O^+] = [H_3N^+CHRCO_2^-] = x$ mol dm^{-3} at equilibrium

	$H_3N^+CHRCO_2H$	$+ H_2O \rightleftharpoons$	H_3O^+	$+ H_3N^+CHRCO_2^-$
Initial conc	0.80		-	-
Change in conc	-x		+x	+x
Eqm conc	0.80-x		x	x

$$K_a = \frac{[H_3O^+][H_3N^+CHRCO_2^-]}{[H_3N^+CHRCO_2H]} = \frac{x^2}{0.80 - x}$$

Since protonated phenylalanine is a weak acid, extent of dissociation is small.

⇒ Hence x is negligible compared to 0.80 mol dm^{-3}.

Therefore, $(0.80 – x) \approx 0.80$

$$K_a = \frac{x^2}{0.80} = 10^{-1.83}$$

Solving, x $= 0.10878$ mol dm^{-3}

Hence, initial pH = $-\lg [H^+ (aq)]$ = 0.963 (3sf)

(ii) An amphiprotic species is one that can act as a Bronsted-Lowry acid or base. The pH of a solution containing an amphiprotic species is given by the following expression.

$$pH = ½(pK_1 + pK_2)$$

In the titration of protonated phenylalanine with NaOH, an amphiprotic species is formed.

Identify the amphiprotic species formed and calculate the pH of the solution.

Amphiprotic species formed = $H_3N^+CHRCO_2^-$

pH at 1st equivalence point= (1.83 + 9.13)/2 = 5.48

(iii) Sketch the titration curve when 25.0 cm^3 of protonated form of phenylalanine is being titrated with 70 cm^3 of NaOH(aq) of the same concentration. On your sketch, clearly mark the two pK_a values and the points you have calculated in **(i)** and **(ii)**.

- Label both axes
- Label initial pH = 0.963
- Sketch shape correctly 2 sharp changes in pH at correct equivalence volumes 25.0 cm^3 & 50.0 cm^3
- Label pK_1 = 1.83 at 12.5 cm^3
- Label pK_2 = 9.13 at 27.5 cm^3
- pH at 1st equivalence point = 5.48

(iv) Suggest a suitable indicator from the following table to be used to detect the first equivalence point and state the colour change of the solution at this equivalence point.

indicator	**pH range**	**acid solution**	**basic solution**
Thymol Blue	1 – 3	Red	yellow
Methyl Red	5 – 6	yellow	Red
Phenol red	7 – 8	yellow	Red
Phenolphthalein	8 – 10	colourless	red

1st equivalence point pH = 5.48 (region of sharp pH change), methyl red is a suitable indicator.
The colour will change **from yellow to orange**.

(b) "Acidity regulators" are food additives that have a buffering action on the pH of food. A mixture of citric acid, $C_5H_7O_4CO_2H$, and its sodium salt is often used for this purpose.

You may assume that citric acid behaves as a monobasic weak acid.

$C_5H_7O_4CO_2H \rightleftharpoons C_5H_7O_4CO_2^- + H^+$; $K_a = 7.4 \times 10^{-4}$ mol dm^{-3}

(i) A citric acid / sodium citrate buffer mixture is prepared by mixing 40.0 cm^3 of 0.100 mol dm^{-3} citric acid and 60.0 cm^3 of 0.200 mol dm^{-3} sodium citrate.

Calculate the pH of the buffer solution. [1]

Amount of HA = 4×10^{-3} mol
Amount of A^- 0.012 mol

pH = pKa + log $[A^-]/[HA]$

= 3.13 + log (3) = 3.63

(ii) Write equations to show how this mixture of citric acid and sodium citrate regulates the acidity on addition of H^+ ions and OH^- ions. [2]

On addition of H^+,

$C_5H_7O_4CO_2^- + H^+ \longrightarrow C_5H_7O_4CO_2H$

On addition of OH^-,

$C_5H_7O_4CO_2H + OH^- \longrightarrow C_5H_7O_4CO_2^- + H_2O$

Full forward arrows

(c) **(i)** Describe the conditions needed to hydrolyse a protein non-enzymatically. [1]

Heat under reflux with H_2SO_4(aq) or NaOH(aq) for several hours.

(ii) Histidine decarboxylase undergoes enzymatic hydrolysis. Upon hydrolysis, the polypeptide fragments of the enzyme's active site are isolated as shown below.

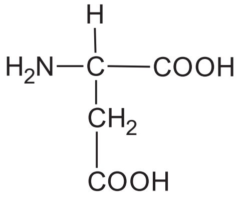
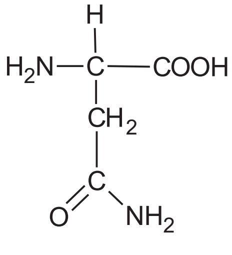
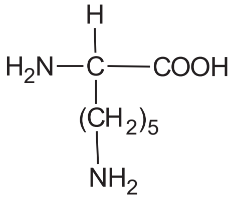
- Ala-Cys-Phe
- Gly-Gly
- Lys-Asp-Asp-Gly-Gly
- Phe-Arg-Lys

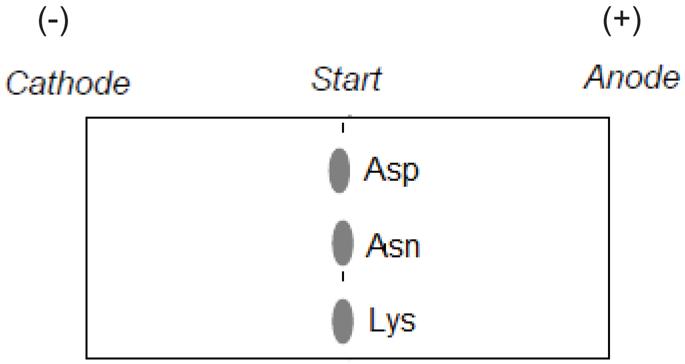
Deduce the sequence of the 9 amino acid residues of the enzyme's active site. [2]

Working
Ala-Cys-Phe
Phe-Arg-Lys
Lys-Asp-Asp-Gly-Gly
Gly-Gly must show working for stacking

Ala-Cys-Phe-Arg-Lys-Asp-Asp-Gly-Gly

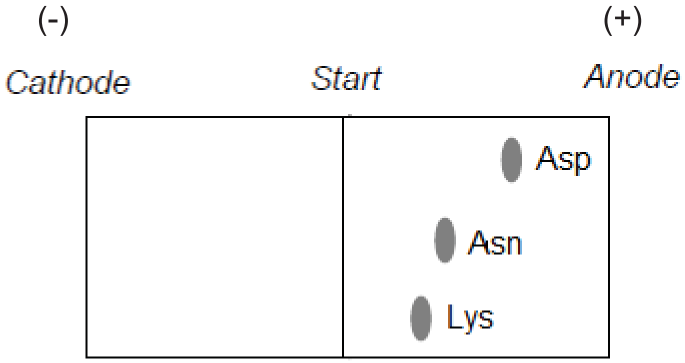
(iii) A different segment of tripeptide, Asp-Asn-Lys, was subjected briefly to acidic hydrolysis which produced individual amino acids as well as various peptides. The resulting mixture buffered at pH 13 was separated in an electric field using electrophoresis.

Amino acid			
Abbreviation	Asp	Asn	Lys



Using the above template sketch and label the position of the three amino acids after the separation. State one factor that affect the rate at which the charged particles move during electrophoresis.

[3]

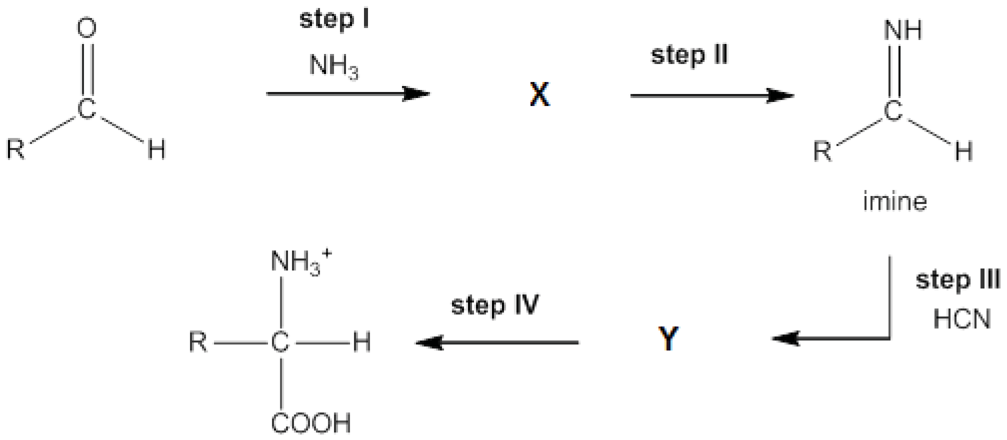


One factor: Mass or charge density of species

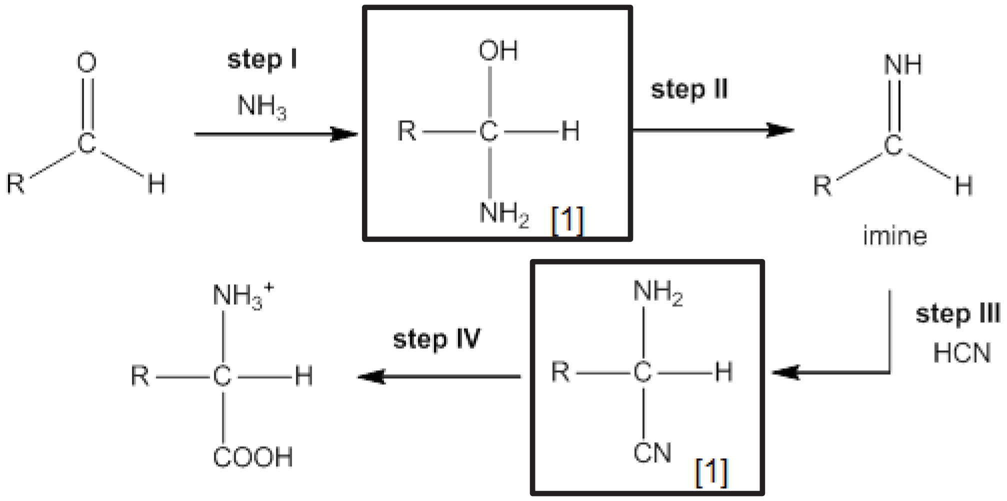
(d) The Strecker synthesis assembles an α-amino acid from the amine precursor and an aldehyde.

- Step **I** is a nucleophilic addition reaction.
- Step **II** involves the elimination of water from **X** to form an imine**.**
- Step **III** is similar to the formation of cyanohydrin when the imine undergoes nucleophilic addition with HCN and forms an α-amino nitrile, **Y**.
- Step **IV** is the hydrolysis of **Y** to form the carboxylic acid functional group.

In the following reaction flow scheme, draw the intermediate compounds **X** and **Y** and suggest the reagent and condition for the step **IV** in the scheme.



[3]



Step IV: H_2SO_4 (aq) heat or HC*l* (aq) heat (accept dilute in place of aq)

[Total:20]

5 Copper is an important transition element that can readily form complex ions with *ligands*. Copper forms a large variety of compounds, usually with variable oxidation states. Copper compounds also act as useful *homogeneous catalysts*, commonly used in many industrial operations.

(a) Define the terms *ligand* and *homogeneous catalyst*. [2]

Ligand is a neutral molecule or anion which contains at least **1 lone pair of electrons** available for forming **dative bonds** with the available **empty orbitals** on the central metal ion/atom.

Homogeneous catalysts **increase the rate of reaction** by providing an alternative pathway with **lower activation energy**. *Homogeneous catalysts* are in the **same phase as the reactants** in the reaction.

(b) In recent years, horseshoe crabs have generated great interest amongst scientists due to its blood with remarkable antibacterial properties. An unusual aspect of the blood is that it is bright blue, a consequence of using copper-based haemocyanin to transport oxygen.

Haemocyanin (Hc) contains two copper atoms that reversibly bind a single oxygen molecule, O_2, to form oxyhaemocyanin, HcO_2, according to the following equation:

$$2Hc(aq) + O_2(aq) \rightleftharpoons 2HcO_2(aq) \quad \textit{equilibrium 1}$$

Oxygenation causes a color change between Cu(I) deoxygenated form and the Cu(II) oxygenated form.

(i) By considering *equilibrium 1*, comment on how the crab cells receive oxygen from the air in the lungs. Check TYS haemoglobin
Hint: Consider the level of oxygen in the lungs

[2]

In the lungs, $[O_2]$ is high. This results in the **position of equilibrium shifting to the right**, favouring the formation of the oxyhaemocyanin HcO_2.

In the cells, $[O_2]$ is low. The position of equilibrium will hence **shift to the left**, favouring the release of O_2.

(ii) Indicate the color change from Cu(II) oxygenated form to Cu(I) deoxygenated form. Hence explain why both copper complex ions exhibit different colours.

[5]

From blue to colourless

oxyhaemocyanin contains Cu^{2+}: [Ar] $3d^9$
Cu(II) has partially filled 3d-orbitals.
In presence of ligands, the originally degenerate 3d orbitals split into 2 sets of different energy levels, separated by a small energy gap (ΔE).

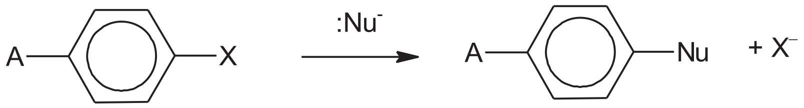
ΔE corresponds to the energy of visible light. An electron from the lower energy d orbital absorbs a specific wavelength of visible light and is promoted to a half-filled, higher energy 3d orbital. d-to-d transition can take place and colour observed is complementary to the colour absorbed.

deoxygenated haemocyanin contains Cu^{+}: [Ar] $3d^{10}$
Cu(I) has fully filled 3 d-orbitals ($3d^{10}$). Hence, d-to-d electron transition cannot occur, and no visible light is absorbed, which accounts for it being colourless.

(c) Most aromatic compounds undergo electrophilic substitution.

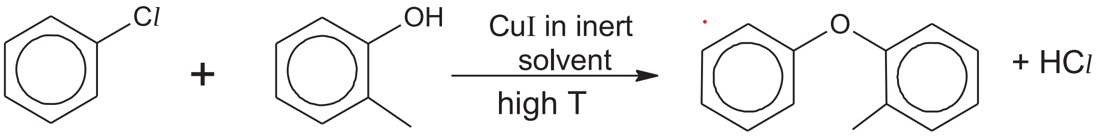
However it is possible for aryl halides to undergo a limited number of nucleophilic substitution reactions with strong nucleophiles.

An example of a reaction is as follows:



An example of an aryl nucleophilic substitution is the *Ullmann coupling* reaction where hydrocarbons fragments are coupled, using copper compounds as a catalyst.

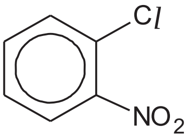
An example is indicated in reaction **1** below.



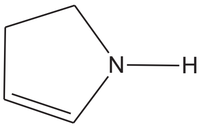
reaction **1**

(i) The conditions for the *Ullmann coupling* reactions are usually harsh conditions, and yet give low yield.

In a similar reaction under the same temperature and pressure, the two compounds below were reacted together:

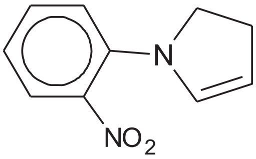


and



.

Deduce and draw the structure of the product for the above reaction. [1]



(ii) Predict, with reasoning, if the above reaction in **(c)(i)** will result in a higher or lower yield compared to reaction **1**. [2]

The presence of the electron-withdrawing NO_2 group on the benzene increase the δ+ on the carbon which attracts nucleophile more strongly

As such, the above reaction will result in a higher yield.

(iii) Like copper(I) iodide, aqueous Fe^{2+} is a good homogeneous catalyst used in the decomposition of aqueous hydrogen peroxide as indicated below.

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

With reference to relevant data in the *Data Booklet*, suggest a mechanism for the catalysis of the above reaction by aqueous Fe^{2+}. [3]

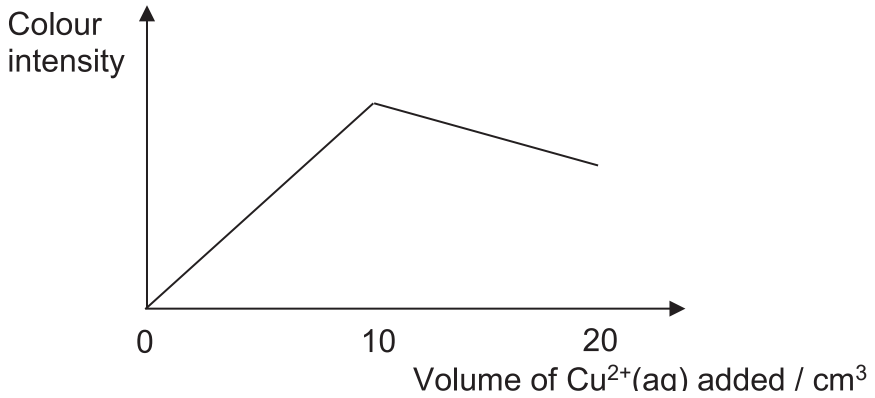
$H_2O_2 + 2H^+ + 2e \rightarrow 2H_2O$ $E^\theta = +1.77V$
$Fe^{2+} \rightarrow Fe^{3+} + e$ $E^\theta = -0.77V$
Step 1 Overall: $H_2O_2 + 2H^+ + 2\,Fe^{2} \rightarrow 2H_2O + 2Fe^{3+}$ $E^\theta_{cell} = +1.00V$
mark for calculating E^θ_{cell}]

$H_2O_2 \rightarrow O_2 + 2H^+ + 2e$ $E^\theta = +0.68V$
$Fe^{3+} + e \rightarrow Fe^{2+}$ $E^\theta = +0.77V$
Step 2 Overall: $H_2O_2 + 2\,Fe^{3+} \rightarrow O_2 + 2Fe^{3+}\ 2H^+$ $E^\theta_{cell} = +0.09V$

(d) Copper(II) species can have various coordination numbers, though tetracoordinated copper(II) species are not as common as hexacoordinated ones.

The formula of a methylamine-copper complex ion, $[Cu(CH_3NH_2)_x(H_2O)_2]^{2+}$, can be determined using a colorimeter.

In an experiment, a solution of 0.050 mol dm^{-3} of $Cu^{2+}(aq)$ was added 1 cm^3 at a time to 20 cm^3 of 0.100 mol dm^{-3} of aqueous CH_3NH_2. The colour intensity of the resultant solution after each addition was measured using a colorimeter. The following graph was obtained.

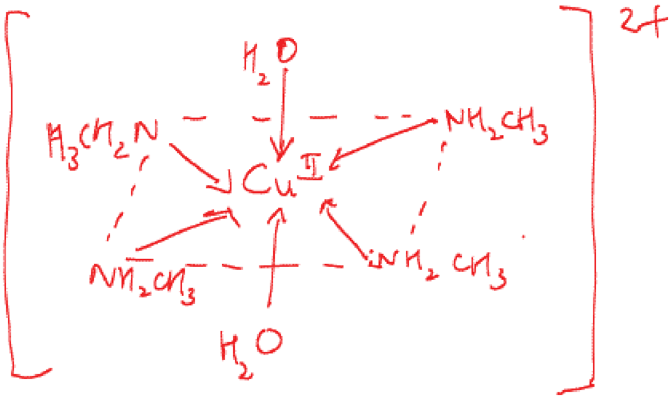


(i) Using the graph, determine the value of ***x.*** [2]

No. of mol of Cu^{2+} = (0.10/1000) x 0.05 = 5x10^{-4}
No. of mol of CH_3NH_2 = (20/1000) x 0.1 = 2 x 10^{-3}

$1/x = (5\times10^{-4})/(2 \times 10^{-3})$
$x = 4$

(ii) Draw the structure of the methylamine-copper complex ion. [1]



(e) Mercury is poisonous as it can cause many health problems ranging from neurological, respiratory to cardiovascular problems. One possible treatment for mercury poisoning involves administering a solution of $EDTA^{4-}$, a common hexadentate ligand which forms complexes with many metal ions.

Copper and calcium ions are essential minerals required by the body. Using relevant data from below, comment on the use of $EDTA^{4-}$ as a treatment for mercury poisoning and comment on its effect on the concentrations of copper and calcium ions in the body.

Equilibrium	K_c /mol^{-1} dm^3
$Ca^{2+} + EDTA^{4-} \rightleftharpoons [Ca(EDTA)]^{2-}$	6×10^{10}
$Cu^{2+} + EDTA^{4-} \rightleftharpoons [Cu(EDTA)]^{2-}$	5×10^{18}
$Hg^{2+} + EDTA^{4-} \rightleftharpoons [Hg(EDTA)]^{2-}$	6.3×10^{21}

[2]

As K_c of $[Hg(edta)]^{2-}$ is higher than that of $[Ca(edta)]^{2-}$ and $[Cu(edta)]^{2-}$, Hg^{2+} will be **removed first** in preference of Cu^{2+} when edta is used. As such, it is useful in the removal of heavy metals (such as Hg) from the body.

However, when a high dosage of EDTA is added, Cu^{2+}, which are essential for health, will also be removed due to the shifting of the position of equilibrium to the right, favoring the formation of the complexes. (as K_c of $[Hg(edta)]^{2-}$ $[Cu(edta)]^{2-}$ are closer in magnitude)

Hence, limited amount of edta should be administered to prevent the loss of Ca^{2+} and Cu^{2+}.

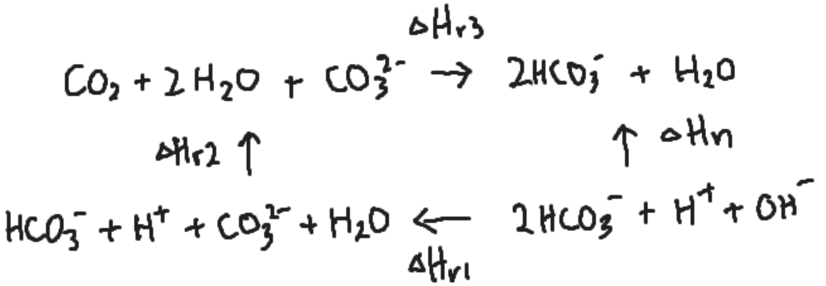
[Total:20]

End of Paper

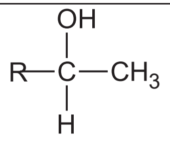
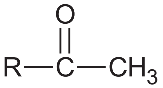
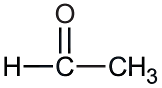
MYE Practical Exam Mark Scheme

Qn	Skills assessed	Marking scheme	Mark	Mark ref
1(a)(i)	PDO Layout **P1**	Tabulates temperature and volume of FA 2 added in the table. Table has correct headers and units.	1	**1**
	PDO Record **P2**	All the volumes are recorded to the nearest 0.05 cm^3 and temperature to 0.1 °C	1	**2**
(a)(ii)	PDO Layout **P3**	Axes correct way round + correct labels + units + scale. Sensible linear scale must be chosen so that the plotted points occupy at least half the graph grid in both x and y directions.	1	**3**
	PDO Layout **P4**	All points correctly plotted to within ±1/2 small square. Checks all points and put ticks if correct.	1	**4**
	PDO Mani **P5**	Graph line must be best fit-lines. Lines should be extrapolated until they cross. Do not allow mark if clearly anomalous points are included or it the lines do not cross each other	1	**5**
(a)(iii)	PDO Mani **P6**	Correct reading to within ±1/2 small square of $T_{maximum}$. Correct calculation of $\Delta T_{maximum}$. Correct reading of $V_{equivalence}$.	1	**6**
	MMO Quality **M1** **M2**	Award MR 7 based on the difference, $\Delta T_{maximum}$, between student's and supervisor's $\Delta T_{maximum}$ value. Give 1 mark if this difference is ≤ 0.3 °C Award MR 8 based on the difference, $V_{equivalence}$, between student's and supervisor's $V_{equivalence}$ value. Give 1 mark if this difference is ≤ 0.75 cm^3 Shift 1: Jessie 10.75 cm^3 and 5.1 °C, Kelly 10.40 cm^3 and 4.88 °C Shift 2: Joseph 10.33 cm^3 and 5.3 °C, Russell 10.00 cm^3 and 5.7 °C (Physics) Shift 3: Jessie 12.40 cm^3 and 4.85 °C (Biology), Russell 12.00 cm^3 and 6.7 °C (Physics)	1 1	**7** **8**

(b)(i)	ACE Interpret **A1**	Calculates percentage error for 40 cm^3 of FA 1 using measuring cylinder and burette % error (measuring cylinder) = (0.5 / 40) x 100 % % error (burette) = [(2 x 0.05) / 40] x 100 %	1	**9**
(b)(ii)	ACE Interpret **A2**	States that the apparatus is burette and explains that $NaHCO_3$ is the limiting reagent thus accuracy is essential.	1	**10**
(b)(iii)	PDO Layout **P7**	Records T_{FA1}, T_{FA3} and $T_{mixture}$ to 0.1 °C.	1	**11**
(c)(i)	ACE Interpret **A3**	[NaOH] = $(25.0 \times 10^{-3} / V_{equivalence} \times 10^3) \times 1.00$	1	**12**
(c)(ii)	ACE Interpret **A4** **A5**	$Q = (V_{equivalence} + 25.0)(1.00)\ c\ \Delta T_{maximum}$ $n(NaHCO_3) = 1.00 \times 25.0/1000 = 0.025$ mol $\Delta H_{reaction1} = -q / n(NaHCO_3)$	1 1	**13** **14**
(d)	ACE Interpret **A6** **A7**	$\Delta T_{maximum2} = \mid T_{mixture} - T_{average} \mid$ $q = (V_{FA\ 1} + V_{FA3}) \times 4.18 \times \Delta T_{maximum2}$ $\Delta H_{reaction2} = +q / 40.0 \times 10^{-3}$	 1 1	 **15** **16**
	PDO Display **P8**	Shows working in all calculations in 1(a), 1(b), 1(c) and 1(d) All calculations must be relevant although they may not be complete or correct	1	**17**
	PDO Display **P9**	Shows appropriate significant figures (3 or 4) in all final answers in 1(a), 1(b), 1(c) and 1(d)	1	**18**
	PDO Display **P10**	Shows appropriate units in all final answers in 1(a), 1(b), 1(c) and 1(d)	1	**19**

(e)	ACE Interpret **A8** **A9** **A10**	 Each part of cycle not balanced deduct 1 mark $\Delta H_{\text{reaction3}}$ = (-57.1) + (-**(c)(ii)**) + (-**(d)**)	2 1	**20** **21** **22**
2(a)	PDO Layout **P11**	Tabulates volume of **FA 6**, water and time taken for blue colour to appear in the table. All the volumes are recorded to 1 d.p. and time to nearest 0.1 s.	1	**21**
	ACE Interpret **A11**	Adds volume of water to maintain a constant total volume of 71 cm^3.	1	**22**
	ACE Interpret **A12**	Correctly calculates V_{FA6} x t and V_{FA6}^2 x t.	1	**23**
(b)(i)	ACE Interpret **A13**	Explains that the same volume of $S_2O_3^{2-}$ is used in each experiment, thus same amount, thus amount of I_2 reacted is the same which gives a constant concentration of I_2.	1	**24**
(b)(ii)	ACE Conclusion **A15**	Explains that V_{FA6} x t is constant for experiment 1 to 3, n = 1. Thus, order of reaction w.r.t bromate(V) is 1.	1	**25**
(c)	ACE Interpret **A16**	Correctly calculates V_{FA5} x t and V_{FA5}^2 x t and correctly deduces the order of reaction with respect to H^+.	1	**26**
	ACE Conclusion **A17**	Explains that V_{FA5}^2 x t is constant for experiment 1 to 3, n = 2. Thus, order of reaction w.r.t H^+ is 2.	1	**28**
(d)	ACE Conclusion	States that is the statement is not valid and explains that to calculate half-life, concentration of sulfuric acid concentration of	1	**29**

	A19	bromate(V) is not in large excess (x10).		
(e)	ACE Interpret **A20**	States that excess I_2 left in the flask will react with the $S_2O_3^{2-}$ in the new experiment. As there is lesser $S_2O_3^{2-}$ for the new experiment, less I_2 is reacted, the time taken to produce the I_2 will be shorter in the second experiment and hence observe the blue colour faster. or State that the excess chemicals (H^+, BrO_3^-, I^-) left in the flask will increase the concentrations of (H^+, BrO_3^-, I^-) in the next reaction. This will cause the rate of reaction to increase and the time taken to produce the I_2 will be shorter and hence observe the blue colour faster.	1	**30**
(f)(i)	Plan **Pl 1** **Pl 2**	Suggest appropriate volumes of H^+, $KBrO_3$ and KI to make a mixture of total volume 250 cm^3. Ensures that [KI] is at least 10x lesser than [H^+] and [$KBrO_3$].	1 1	**31** **32**
(ii)	ACE Interpret **A21** **A22**	States that colour is blue and/or purple Explains that since the observed colour of iodine is yellow-orange, the complimentary colour is absorbed.	1 1	**33** **34**
(iii)	PDO Layout **P8** ACE Interpret **A23**	Axes correct way round + correct labels + units + scale + labeling of 50, 75 and 100% [I_2]. 1st order product time graph with 2 constant consecutive half-lives.	1 1	**35** **36**
	ACE Conclusion **A24**	States that the order of reaction with respect to [I^-] will have constant half-lives.	1	**37**
3(a)(i)	MMO/ PDO Collecting	7 observation points – 2 with negative results Observations		

	M4 **M5**	6-7 = 3 4-5 = 2 2-3 = 1 0-1 = 0	3	**38** **39** **40**
(ii)	ACE Conclusion **A25** **A26**	Argues for **FA 8** is ethanal as it is the only one to form a silver mirror as it is oxidised by Tollens' reagent or the only one to form brick red precipitate as it is oxidised by Fehling's solution. Argues for **FA 9** is propan-2-ol as it is oxidised to decolourise potassium manganate(VII) or oxidised to form a yellow precipitate by aqueous iodoine but not oxidised by Tollens' or Fehling's.	1 1	**41** **42**
(b)(i)	ACE Interpret **A27**	Correctly identifies the structural feature as  $R-CH(OH)-CH_3$ and/or  $R-CO-CH_3$ where R = H or alkyl group. Labelling of R is optional.	1	**43**
(b)(ii)	ACE Interpret **A28**	Give the correct structural formula  $H-CO-CH_3$	1	**44**
(c)(i)	ACE Conclusion **A29**	Suggests Al^{3+}, Ba^{2+}, Mg^{2+}, Zn^{2+} (Ca^{2+} and Mn^{2+}) as cations that may be present.	1	**45**
(c)(ii)	Plan **Pl 3**	Selects NaOH(aq) and NH_3(aq) for identification of cation.	1	**46**
	MMO/ PDO Collecting **M6** **M7**	Gives observation of NaOH(aq) with cation. White precipitate with NaOH(aq) dropwise for Al^{3+}, Mg^{2+} and Zn^{2+}. White precipitate dissolves in excess NaOH(aq) for Al^{3+} and Zn^{2+}. [1] Gives observation of NH_3(aq) with cation. White precipitate with NH_3(aq) dropwise for Al^{3+} and Zn^{2+}. White precipitate dissolves in excess NH_3(aq) for Zn^{2+} but not Al^{3+} [1]	1 1	**47** **48**
	ACE	Concludes that **FA 10** contains Zn^{2+}	1	**49**

	Conclusion **A30**			
3(d)	Plan	Tests include (a) adding Br_2(aq), $Br_2(l)$ or cold dilute alkaline $KMnO_4$ (b) $AgNO_3$(aq) (c) hot acidified $K_2Cr_2O_7$ (d) heat with NaOH(aq), cool, HNO_3(aq), followed by $AgNO_3$(aq)		
	PI 4	Selects reagents that would unambiguously identify 2 compounds with positive tests for each. [1] **or**	3	**50**
	PI 5	Selects reagents that would unambiguously identify 3 compounds with positive tests for each. [2] **or**		**51**
	PI 6	Selects reagents that would unambiguously identify 4 compounds with positive tests for each. [3]		**52**
	PI 7	Outlines a logical sequence/order of testing; doesn't test compounds already identified [1]	1	**53**
	PI 8	Some ambiguity in links etc, but worthy of credit [1] or	2	**54**
	PI 9	Clearly and unambiguously links the testing sequence with the compounds to be identified [2]		**55**