NAME		Class	

ST ANDREW'S JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATIONS

Chemistry

Higher 2 **9729/01**

Paper 1 Multiple Choice **18 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, glue or correction fluid.

Write your name on the Answer Sheet in the spaces provided.

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

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

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

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

This document consists of **19** printed pages and **1** blank page.

1 During a laboratory practical exercise, a student tried to determine the concentration of $Fe^{2+}(aq)$ and $Fe^{3+}(aq)$ in a given mixture through two different experiments.

1. 25.0 cm^3 aliquot of the $Fe^{2+}(aq)$ and $Fe^{3+}(aq)$ mixture solution required 15.00 cm^3 of 0.1 mol dm^{-3} of acidified $KMnO_4$ solution for complete oxidation.
2. Using another 25.0 cm^3 aliquot, all the $Fe^{3+}(aq)$ was first reduced to $Fe^{2+}(aq)$ using zinc metal before requiring 34.20 cm^3 of the same $KMnO_4$ solution for complete oxidation.

What is the concentration of $Fe^{2+}(aq)$ and $Fe^{3+}(aq)$ in the given mixture?

A 0.012 mol dm^{-3} $Fe^{2+}(aq)$ and 0.0154 mol dm^{-3} $Fe^{3+}(aq)$

B 0.180 mol dm^{-3} $Fe^{2+}(aq)$ and 0.230 mol dm^{-3} $Fe^{3+}(aq)$

C 0.300 mol dm^{-3} $Fe^{2+}(aq)$ and 0.384 mol dm^{-3} $Fe^{3+}(aq)$

D 0.300 mol dm^{-3} $Fe^{2+}(aq)$ and 0.684 mol dm^{-3} $Fe^{3+}(aq)$

2 A number of elements in the actinoid series are radioactive and undergo decay to other elements. The following equation is an example of such decay.

$$^{241}_{94}Pu \rightarrow \text{element } \mathbf{A} + 9\,^{4}_{2}He + 5\,^{0}_{-1}e$$

Which of the following gives the identity of element **A**?

	Mass number	Atomic number
A	205	81
B	205	86
C	223	81
D	237	90

3 Which of the following shows an increase in the bond angle of the compound from left to right?

A NH_3 H_2S SiH_4

B PH_3 NH_3 $AlCl_3$

C PH_3 PF_3 PCl_3

D XeF_4 SCl_6 CCl_4

4 In which of the following does Statement **II** give a correct explanation for Statement **I**?

	Statement **I**	Statement **II**
1	Magnesium has a higher melting point than sodium.	Magnesium has more delocalised valence electrons which results in stronger metallic bonds.
2	Glycine, H_2NCH_2COOH, has a higher melting point than 2–hydroxyethanoic acid, $HOCH_2COOH$.	Glycine can form stronger hydrogen bonds than 2–hydroxyethanoic acid.
3	Chloromethane undergoes nucleophilic substitution more easily than fluoromethane.	The C–Cl bond in chloromethane is weaker than the C–F bond in fluoromethane.

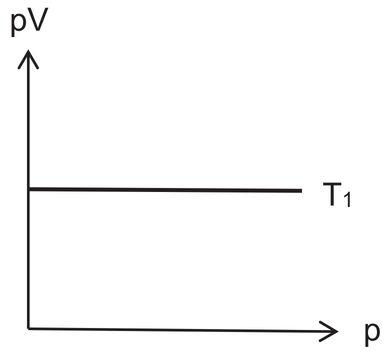
A 2 and 3

B 1 and 2

C 1 and 3

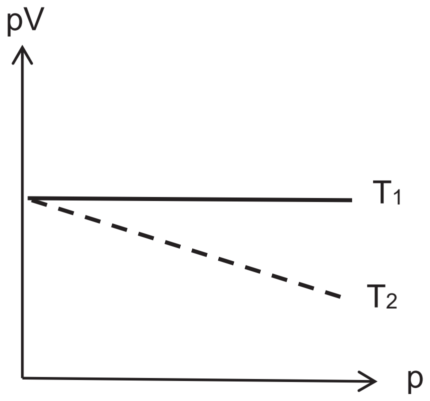
D 1, 2, and 3

5 The graph of pV against p is plotted for an ideal gas at constant temperature for a fixed mass of gas at T_1.

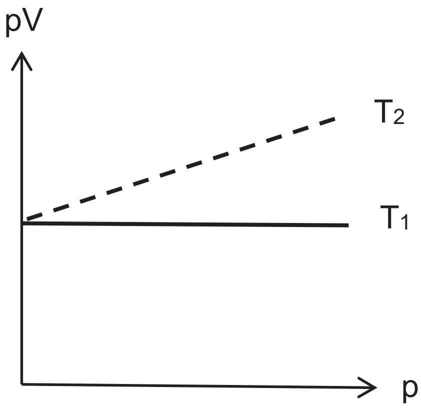


Which diagram shows the new graph at a lower temperature at T_2?

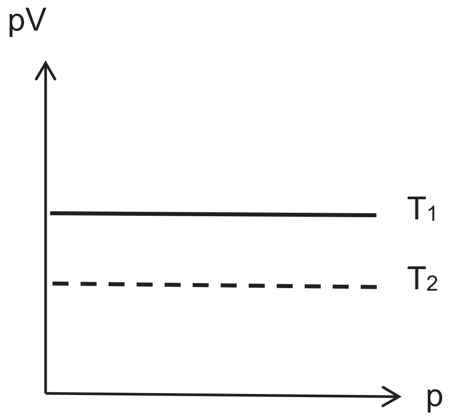
A



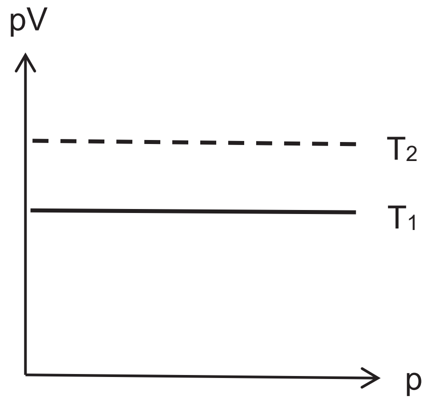
B



C



D



6 The enthalpy change of formation of carbon monoxide and carbon dioxide are given below.

ΔH_f (CO)= –110 kJ mol^{-1}

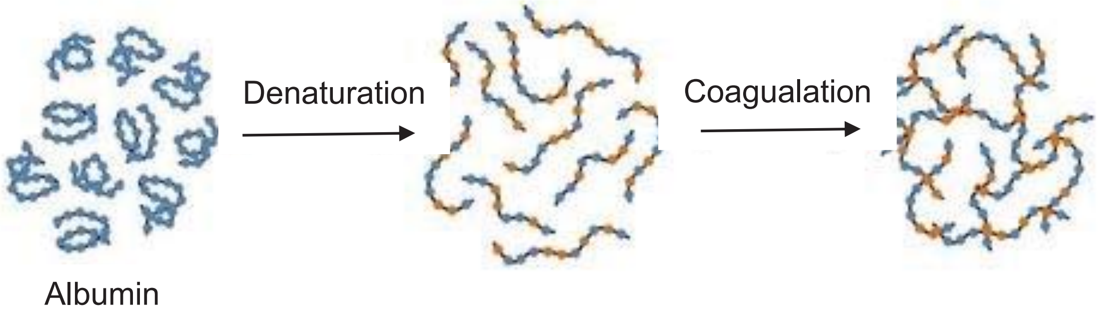
ΔH_f (CO$_2$)= –393 kJ mol^{-1}

Which of these statements are correct?

1 Carbon dioxide is energetically more stable than carbon monoxide.
2 The enthalpy change of combustion of carbon is –283 kJ mol^{-1}.
3 ΔH_f (CO$_2$) – ΔH_c (CO) has the same value as enthalpy change of formation of CO.

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

7 A raw egg white contains the protein, albumin, which is made of chains of amino acids that fold into specific and stable three-dimensional structure.
Heating the protein in an egg white causes the intermolecular forces to break and "unfold" the protein. In this state, albumin is denatured and will readily coagulate to form an extensive protein network.

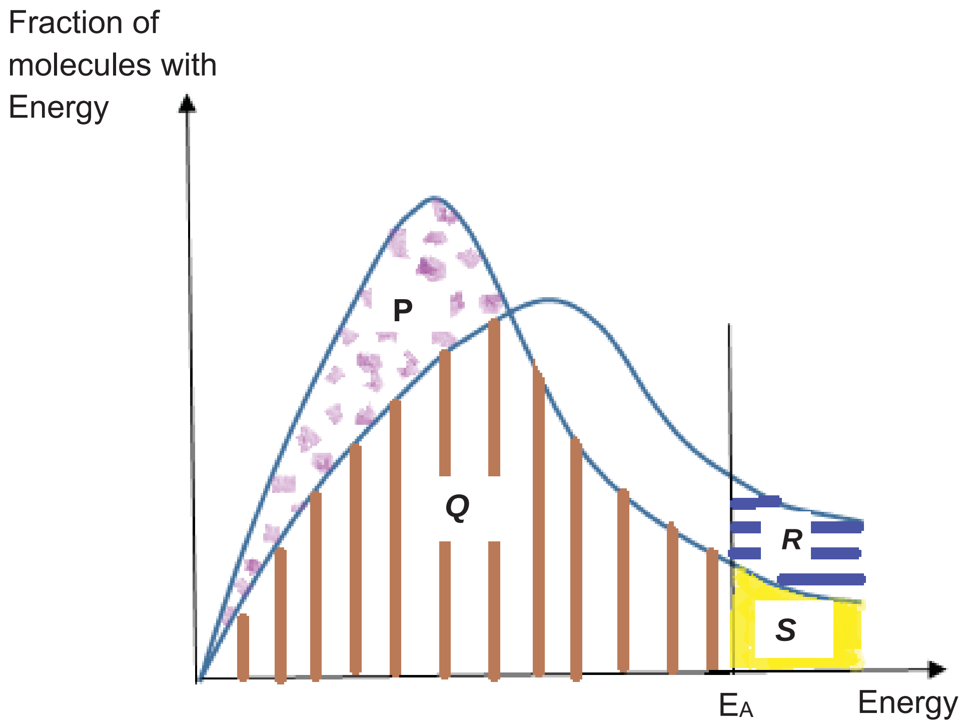


What are the correct signs of ΔS, ΔH, and ΔG for denaturation of albumin during cooking?

	ΔS	ΔH	ΔG
A	+	+	–
B	+	+	+
C	–	–	+
D	–	+	–

8 The diagram shows the Maxwell–Boltzmann energy distribution curves for air molecules at room temperature and inside the car engines where it is being combusted. The letters ***P***, ***Q***, ***R*** *and* ***S*** refer to the separate areas.

Which expression gives the fraction of the air molecules present inside the car engine?



A $\frac{S}{P}$ **B** $\frac{R+S}{P+Q+S}$ **C** $\frac{S}{P+Q+S}$ **D** $\frac{S}{P+Q}$

9 An experiment was carried out to investigate the kinetics of the reaction between ammonium peroxodisulfate, $(NH_4)_2S_2O_8$, an oxidising agent, and potassium iodide, KI, in the presence of a little starch.

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

The volume of the $(NH_4)_2S_2O_8$ and KI solutions in the mixture, together with the time taken for the mixture to darken for the various experimental runs are given below:

Experiment	Volume used / cm^3			Time / s
	1.0 mol dm^{-3} KI	0.040 mol dm^{-3} $(NH_4)_2S_2O_8$	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	20.0	0.0	?

Which of the following statements about the reaction is false?

A The reaction can be catalysed by $Fe(NO_3)_2(aq)$.

B The reaction involves the formation of an intermediate.

C The time taken for the mixture to darken in Experiment 4 is 40.5 s.

D The slow step involves the reaction between 1 mole of $(NH_4)_2S_2O_8$ and 1 mole of KI.

10 Silver chloride establishes an equilibrium with the relatively stable complex ion, $[Ag(NH_3)_2]^+$

$$AgCl(s) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq) + Cl^-(aq)$$

Which of the following statements is correct?

A When acid is slowly added to the mixture, a white precipitate is observed.

B The K_c expression is $K_c = \frac{[[Ag(NH_3)_2]^+]\,[Cl^-]}{[AgCl]\,[NH_3]^2}$

C Added more NH_3 to the solution when equilibrium is established will decrease its K_c value.

D Removal of some $AgCl(s)$ causes the position of equilibrium to shift left.

11 At a total pressure of 1.2 atm, sulfur trioxide is 50% dissociated according to the following equation at 150 K.

$$2SO_3\,(g) \rightleftharpoons 2SO_2\,(g) + O_2(g)$$

What is the mole fraction of oxygen in this equilibrium mixture?

A 0.60 **B** 0.20 **C** 0.30 **D** 0.24

12 Which of the following mixtures when dissolved in large amount of water could act as buffer solutions?

1 2 mol of HI and 1 mol of $CH_3CH_2NH_2$
2 2 mol of CH_3COCl and 3 mol of NaOH
3 2 mol of $CH_3CH_2NH_2$ and 1 mol of H_2SO_4

A 2 only
B 2 and 3
C 1 and 3
D None of the above

13 The solubility of 2 sparingly soluble solids MX_2 and LY is being determined experimentally.

Which of the following statements is always true?

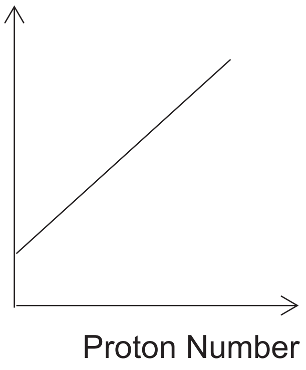
A The solubility product of MX_2 increases with increasing temperature.

B MX_2 will always be more soluble than LY if MX_2 has a higher K_{sp} value.

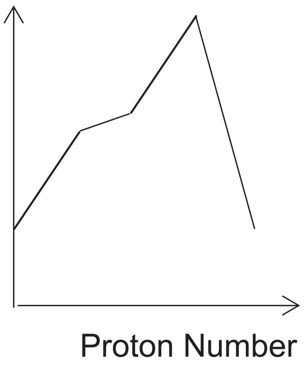
C The K_{sp} value of LY can be calculated from any concentration of L^+ and Y^-.

D Given that the solubility of LY is exothermic, the K_{sp} of LY will only change when temperature changes.

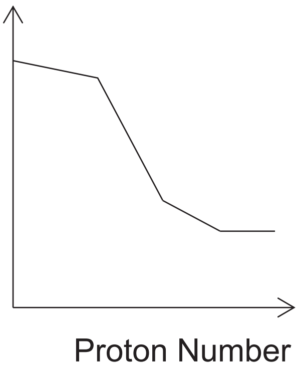
14 The following graphs show the variation of a property of the elements Na to P.



Graph 1



Graph 2



Graph 3

Which of the following correctly describes the property of the graphs?

	Graph 1	**Graph 2**	**Graph 3**
A	Electronegativity	Melting point of oxide	pH of oxide
B	Ionic radius	Melting point of element	pH of oxide
C	Covalent character	Melting point of chlorides	pH of chloride
D	Electronegativity	Melting point of element	pH of chloride

15 1.0 mol dm^{-3} aqueous solutions of three elements in Group 17 of the Periodic Table have standard electrode potentials as follows.

$X_2(aq) + 2e^- \rightleftharpoons 2X^-(aq)$ $E^\ominus = +1.36$ V

$Y_2(aq) + 2e^- \rightleftharpoons 2Y^-(aq)$ $E^\ominus = +1.07$ V

$Z_2(aq) + 2e^- \rightleftharpoons 2Z^-(aq)$ $E^\ominus = +0.54$ V

Which statements are correct?

1 There is an increase in oxidising power in the sequence X_2, Y_2, Z_2.

2 The reaction $X_2(aq) + 2Z^-(aq) \longrightarrow 2X^-(aq) + Z_2(aq)$ is spontaneous under standard conditions.

3 Z has the lowest electron affinity.

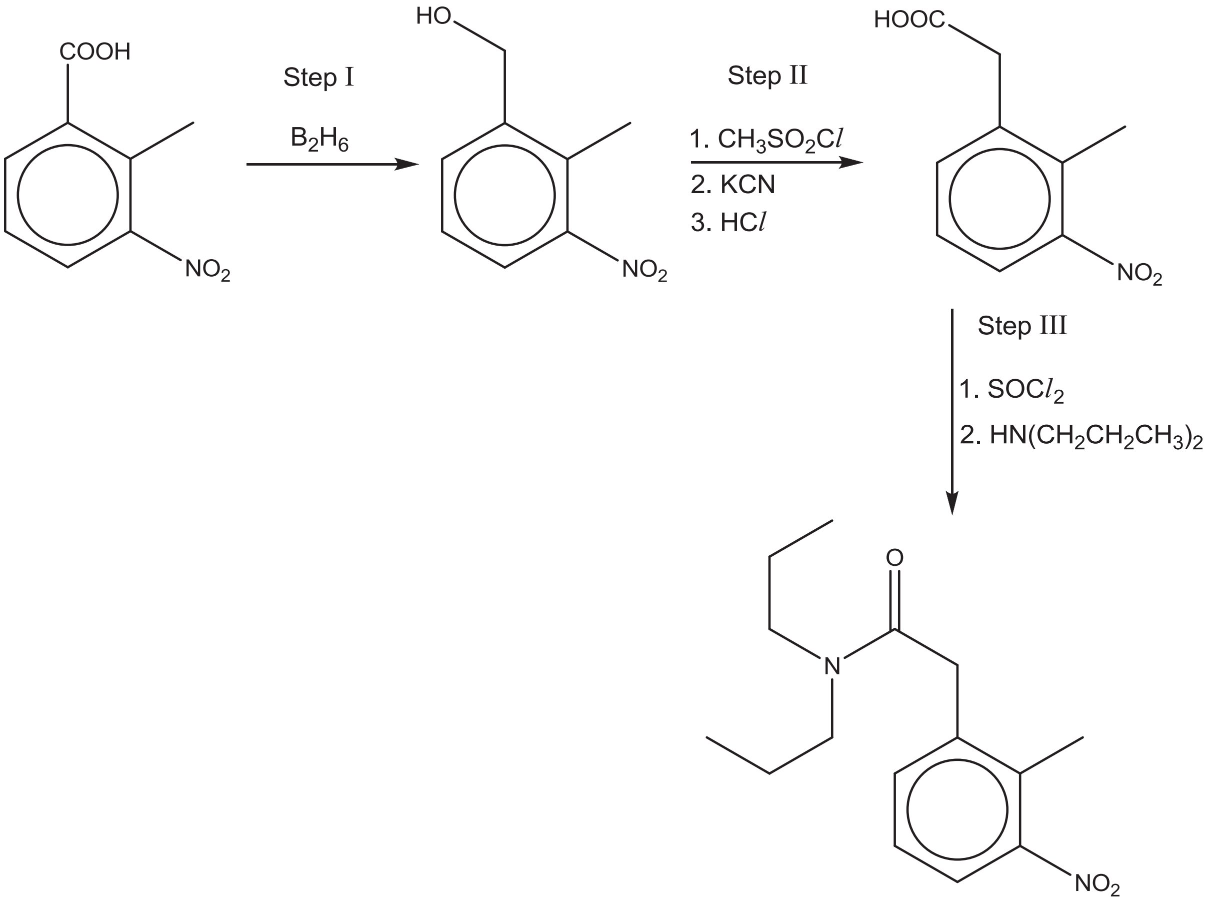
A 1 and 2

B 1 and 3

C 2 and 3

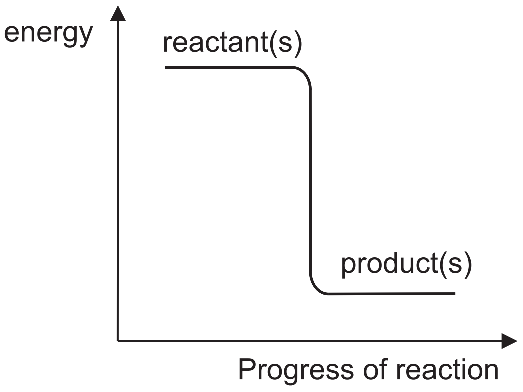
D 1, 2 and 3

16 Which of the following shows the correct type of reaction(s) occurring for each step of the synthesis?



	Step I	Step II	Step III
A	Oxidation	Substitution followed by condensation	Condensation
B	Oxidation	Acid base reaction followed by oxidation	Substitution followed by condensation
C	Reduction	Substitution followed by hydrolysis	Substitution followed by condensation
D	Reduction	Hydrolysis followed by oxidation	Condensation

17 An energy level diagram for a single reaction step is shown below.



To which of the following steps in the reaction of ethane with bromine in the presence of light does this diagram apply?

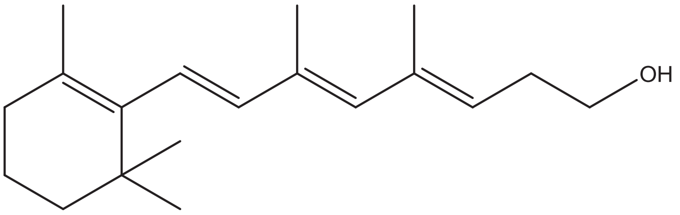
A $Br_2 \longrightarrow Br\bullet + Br\bullet$

B $CH_3CH_3 + Br\bullet \longrightarrow CH_3CH_2\bullet + HBr$

C $CH_3CH_2\bullet + Br_2 \longrightarrow CH_3CH_2Br + Br\bullet$

D $CH_3CH_2\bullet + CH_3CH_2\bullet \longrightarrow CH_3CH_2CH_2CH_3$

18 The structure of Vitamin A is shown below.



Vitamin A

Which of the following statements about Vitamin A is true?

A White fumes is observed when it is treated with excess ethanoyl chloride.

B When it reacts completely with $LiAlH_4$ in dry ether, a saturated compound that contains 4 chiral carbon centres is produced.

C Effervescence is observed when it reacts with hot alkaline potassium manganate(VII) solution.

D 1 mol of Vitamin A reacts with excess sodium metal to produce 22.7 dm^3 of hydrogen gas at 273 K and 1 bar.

19 An optically active sample of 2–chlorobutane, $CH_3CH_2CHC\mathit{l}CH_3$, was heated under reflux with aqueous sodium hydroxide to produce compound **Q**, which rotates plane of polarised light.

Which of the following statements about the reaction are correct?

1 The reaction occurred via a S_N1 mechanism.

2 $CH_3CH_2CH_2OCH_3$ is a functional group isomer of **Q**.

3 The rate of reaction increases when the sample is replaced with 2–bromobutane.

4 **Q** reacts with concentrated sulfuric acid at $170\ ^{o}C$ to give a mixture of three isomeric alkenes.

A 1 and 3 only

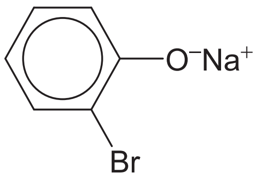
B 2 and 3 only

C 2 and 4 only

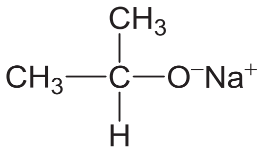
D 2, 3 and 4 only

20 Which of the following salts has the smallest $p\mathit{K}_b$?

A

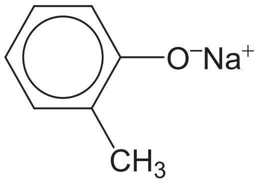


B

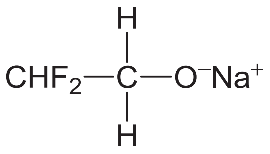


$CH_3-\overset{CH_3}{\underset{H}{C}}-O^-Na^+$

C



D



$CHF_2-\overset{H}{\underset{H}{C}}-O^-Na^+$

21 The uncatalysed reaction between propanal and HCN proceeds via two steps and the rate equation for the formation of cyanohydrin is as follows.

$$\text{Rate} = k[CH_3CH_2CHO][CN^-]$$

Which of the following statements is correct?

A The intermediate formed in this reaction is planar.

B Only one product is obtained since this is an addition reaction.

C The uncatalysed reaction between propanone and HCN occurs at a faster rate than that of propanal.

D The same product can be obtained by heating 1–chloropropan–1–ol with ethanolic NaCN.

22 ^{18}O is an isotope of oxygen.

When butylethanoate is hydrolysed with dilute sulfuric acid in the presence of $H_2{}^{18}O$, a mixture of 2 products is formed. Which of the following pairs gives the correct structures of the two products?

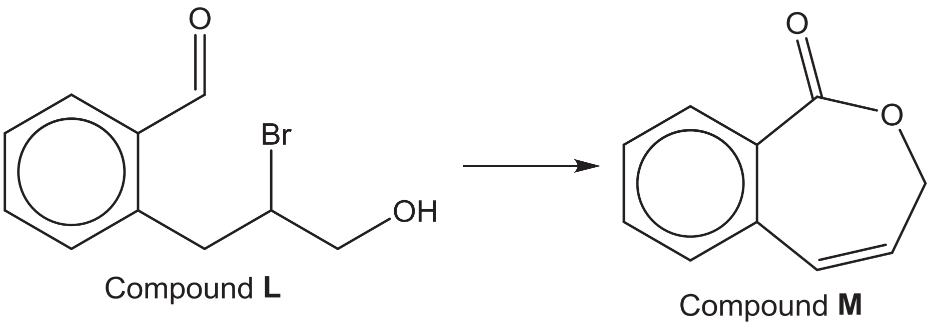
A $CH_3CH_2CH_2CH_2OH$ and $CH_3CO^{18}OH$

B $CH_3CH_2CH_2CH_2{}^{18}OH$ and CH_3CO_2H

C CH_3CH_2OH and $CH_3CH_2CH_2CO^{18}OH$

D $CH_3CH_2{}^{18}OH$ and $CH_3CH_2CH_2COOH$

23



Which of the following sequence of reagents and conditions can be used to carry out the conversion above?

	Stage 1	**Stage 2**	**Stage 3**
A	warm with ammonical silver nitrate solution	hot NaOH(aq)	heat in the presence of concentrated H_2SO_4
B	warm with Fehling's solution	heat in the presence of concentrated H_2SO_4	hot NaOH(aq)
C	warm with ammonical silver nitrate solution	hot NaOH(alc)	heat in the presence of concentrated H_2SO_4
D	warm with Fehling's solution	heat in the presence of concentrated H_2SO_4	hot NaOH(alc)

24 Compound **W** has the following properties :

- Empirical formula : C_3H_7N
- Decolourises aqueous bromine
- Reacts with hot acidified $KMnO_4$ to form an α–amino acid

Which of the following could be compound **W**?

1 $CH_2{=}CHCH_2NH_2$

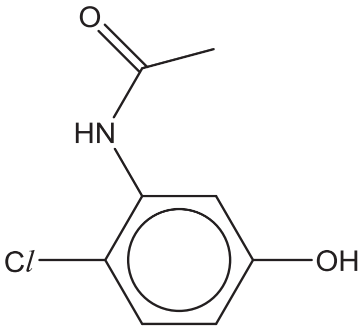
2 $CH_3CH{=}CHNH_2$

3 $CH_2(NH_2)CH_2CH{=}CHCH_2CH_2NH_2$

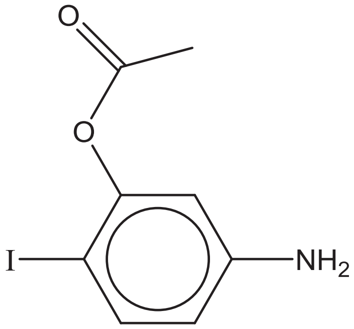
4 $CH_2(NH_2)CH_2CH_2CH{=}CHCH_2NH_2$

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

25 Which of the following reagents would give different observations when added to both compounds in separate test–tubes?



Compound **Y**



Compound **Z**

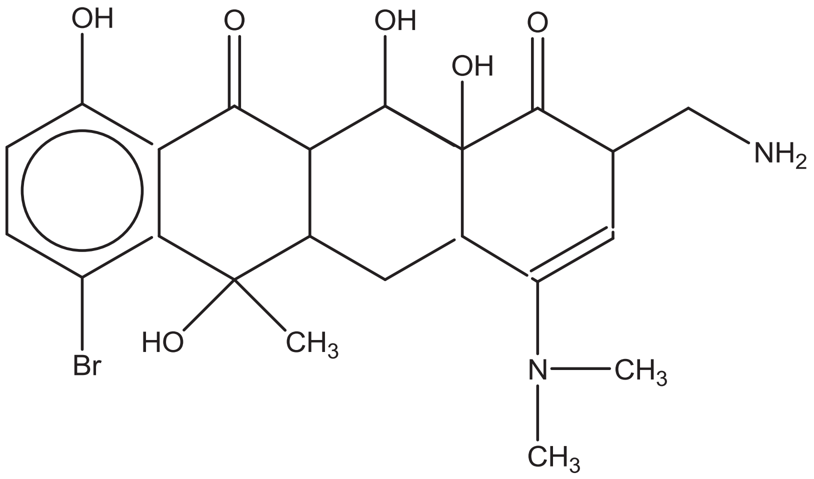
A aqueous bromine

B 2,4–dinitrophenylhydrazine

C $LiAlH_4$ in dry ether, followed by hot acidified $KMnO_4$

D ethanolic silver nitrate

26 Compound **X** is an isomer of the antibiotic *Aureomycin*.



Compound **X**

Which of the following statements are true for compound **X**?

1 1 mole of **X** reacts with 5 moles of propanoyl chloride.

2 1 mole of compound **X** reacts with 3 moles of hydrogen gas in the presence of Ni catalyst at 150 ^{0}C.

3 1 mole of compound **X** reacts with 6 moles of HBr(g) at room temperature.

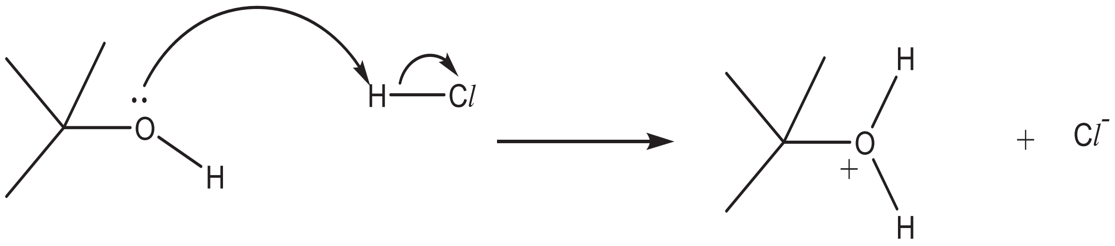
A 1 only

B 1 and 2

C 2 and 3

D 1, 2 and 3

27 Alkyl halides can be prepared from alcohol. The first step in the mechanism involves the following:



What is the role of the alcohol in the above step?

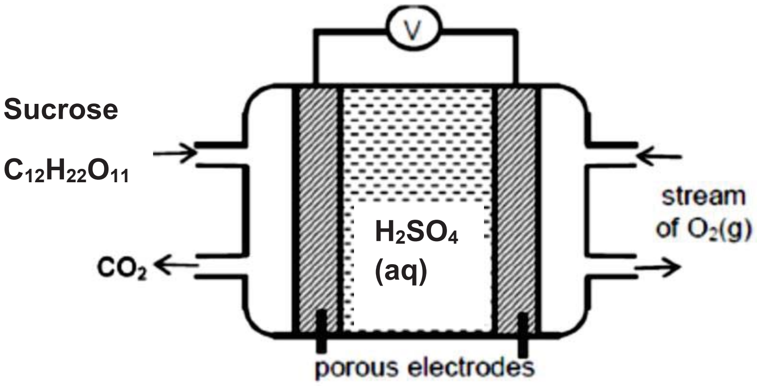
A Brønsted–Lowry acid

B Lewis base

C Ligand

D Electrophile

28 A microbial fuel cell (MFC) is a bio–electrochemical system that drives an electric current by using bacteria and mimicking bacterial interactions found in nature. An example of an MFC is as shown below with $E^{\theta}_{cell} = +1.25$ V.



Which of the following statements about the above MFC is **not** correct?

A Electrons flow from the right electrode to the left electrode.

B H^+ is produced at the anode.

C Sucrose is oxidised in this reaction.

D $E^{\theta}_{(anode)}$ is –0.02 V.

29 0.0170 mol of chromium(III) iodide reacts with excess ammonia to form compound **Y** which has a coordination number of 6. When a solution of **Y** is treated with an excess of aqueous silver nitrate, 0.0340 mol of solid is precipitated.

What is the formula of compound **Y**?

A $Cr(NH_3)_3I_3$

B $Cr(NH_3)_4I_3$

C $Cr(NH_3)_5I_3$

D $Cr(NH_3)_6I_3$

30 The table shows the electronic configuration of three elements in the Periodic Table. (The elements are represented by letters which are not their symbols.)

Element	Electronic configuration
P	$[Ar]4s^1$
Q	$[Ar]3d^74s^2$
R	$[Ar]3d^{10}4s^1$

Which of the following statements are correct?

1 $\mathbf{Q}_2O_3$ is likely to exist.

2 First ionisation energy of **P** is lower than that of **R**.

3 The compound **R**I is a white solid.

A 1 only

B 1 and 2

C 2 and 3

D 1, 2 and 3

NAME		**Class**	

ST ANDREW'S JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION

Chemistry (9729) **11 September 2017**

Paper 2 Structured Questions **2 hours**

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS:

Write in dark blue or black pen.

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

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

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

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

A Data Booklet is provided.

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

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

For Examiner's use:

Question	**1**	**2**	**3**	**4**	**5**	**6**	**Total**
Marks	/ **17**	/ **5**	/ **10**	/ **16**	/ **6**	/ **21**	/ **75**

This document consists of **19** printed pages (including this page).

Turn Over

Answer **all** the questions

1 Sulfur is a common element on Earth that forms many important chemical compounds.

One of these compounds is sodium thiosulfate, $Na_2S_2O_3$, an ionic compound used to treat several medical conditions, such as cyanide poisoning and fungal growths.

(a) **(i)** Draw a dot-and-cross diagram for sodium thiosulfate, $Na_2S_2O_3$. State the shape and bond angle in the thiosulfate ion.

[2]

(ii) Below are the melting points of sodium thiosulfate and sulfur.

Compound	**Melting point / °C**
Sodium thiosulfate	49
Sulfur, S_8	115

Explain why sulfur has a higher melting point than sodium thiosulfate.

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(b) Another important sulfur compound is sulfuric acid, H_2SO_4. Before the Contact Process was discovered, concentrated sulfuric acid for industrial purposes was produced by the following method.

The mineral pyrite, FeS_2, was first heated in air and oxidised to solid $Fe_2(SO_4)_3$ and sulfur dioxide gas.

$Fe_2(SO_4)_3$ decomposes at 480 °C to form iron(III) oxide and sulfur trioxide gas. The sulfur trioxide gas could be mixed with any volume of water to produce sulfuric acid of the desired concentration. However, this process was expensive and not efficient.

(i) Write a balanced equation, with state symbols for the reaction between pyrite, FeS_2, and oxygen to form $Fe_2(SO_4)_3$.

……………………………………………………………………………………..[1]

(ii) With the aid of an equation, define the term standard enthalpy change of formation of gaseous sulfur trioxide, SO_3.

…………………………………………………………………………………......

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……………………………………………………………………………………..[2]

(iii) Given the following information, determine the enthalpy change of formation of gaseous sulfur trioxide SO_3.

$Fe_2(SO_4)_3(s) \rightarrow Fe_2O_3(s) + 3SO_3(g)$ $\Delta H_{rxn} = +95$ kJ mol^{-1}

Substance	**ΔH_f / kJ mol^{-1}**
$Fe_2(SO_4)_3(s)$	–2107
$Fe_2O_3(s)$	–824

[3]

(iv) Use the appropriate bond energies given in the *Data Booklet* and the data below to calculate another value for the standard enthalpy change of formation of gaseous sulfur trioxide SO_3.

$\frac{1}{8}S_8(s) + O_2(g) \rightarrow SO_2(g)$ $\Delta H_f = -297$ kJ mol^{-1}

[3]

(v) Suggest a reason for the discrepancy between the values in **(b)(iii)** and **(b)(iv)**.

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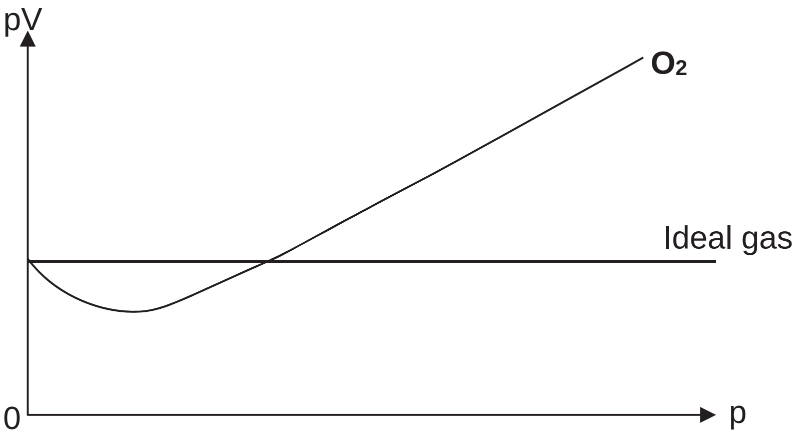
…………………………………………………………………………………………..[1]

(c) The value of pV is plotted against p for 1 mol of oxygen O_2, where p is the pressure and V is the volume of the gas at 300 K.



(i) On the diagram above, draw and label the graph of pV against p for SO_3 at 300 K. [1]

(ii) Explain the difference between the graph of SO_3 and the graph of O_2.

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

[Total: 17]

2 Transition elements show typical properties that distinguish them from s-block elements, such as calcium. These include variable oxidation states in their compounds, and the formation of coloured complex ions.

(a) An ion of manganese has 3 electrons in its 3d subshell. Suggest the oxidation state of this manganese ion.

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

(b) The following table gives data about some physical properties of the elements calcium, chromium, and manganese.

Property	**Ca**	**Cr**	**Mn**
Atomic radius (metallic) / nm	0.197	0.129	0.132
Ionic radius (2+) / nm	0.099	0.073	0.083
Melting point / K	1112	1907	1246
Density / g cm^{-3}	1.54	7.19	7.43
Electrical conductivity / x 10^6 S cm^{-1}	0.298	0.0774	0.00695

(i) Explain why the atomic radii of chromium and manganese are similar to each other.

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(ii) Explain why the density of manganese is significantly greater than that of calcium, using relevant data from the table and the *Data Booklet*. (No calculations are required.)

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[Total: 5]

3 A student investigated the thermal decomposition of two carbonates, calcium carbonate and barium carbonate in the following way to determine its exact composition. He used the same amount, in moles, of each carbonate.

$\boldsymbol{M}CO_3\,(s) \rightarrow \boldsymbol{M}O(s) + CO_2\,(g)$ **M** is Ca or Ba

He heated the carbonates separately for 5 minutes. The solid obtained after heating was then shaken with distilled water to form an alkaline solution. A portion of the solid remained insoluble and was filtered. A sample of the alkaline filtrate was titrated with hydrochloric acid. No effervescence was observed during the titration.

(a) **(i)** Suggest which carbonate is less likely to decompose completely. Explain your answer.

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……………………………………………………………………………………[2]

(ii) It was observed that the volume of acid used in the titration was smaller for the carbonate which did not decompose completely.

Explain how the incomplete decomposition can result in a lower volume of acid used in the titration.

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……………………………………………………………………………………….[2]

(b) Explain the difference between the magnitude of the lattice energies of calcium carbonate and calcium oxide.

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

(c) Given that the decomposition of calcium carbonate is an endothermic reaction.

$$\Delta H = +178 \text{ kJ mol}^{-1} \text{ and } \Delta S = +159 \text{ J K}^{-1} \text{ mol}^{-1}$$

Calculate the minimum temperature at which this reaction becomes spontaneous.

[2]

(d) Beryllium oxide can react with sodium hydroxide.

$$BeO + 2NaOH \rightarrow Na_2BeO_2 + H_2O$$

Explain this behaviour despite Be being a Group 2 element.

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[Total: 10]

4 Gaseous phosphorus(V) chloride dissociates according to the following equation.

$$PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$$

Different amounts of the three gases were placed in a closed container and allowed to come to equilibrium at 200 °C. The experiment was repeated at 425 °C.

The equilibrium partial pressure of the three gases at each temperature are given in the table below.

	Partial pressure / x 10^{-3} N m^{-2}		
temperature/°C	PCl_5	PCl_3	Cl_2
200	1.46	11.8	2.77
425	7.61	0.211	0.368

(a) **(i)** Write the expression for the equilibrium constant, K_p, for this reaction. Give the units.

Expression……………………………………………………………………………......

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

(ii) Calculate the value of K_p at each of the temperatures given.

[2]

(iii) Is the forward reaction exothermic or endothermic? Explain your answer.

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

(b) What will be the effect on the equilibrium partial pressure of PCl_5 when the following changes are carried out on this new equilibrium? Explain your answers clearly.

(i) The pressure of the system is halved at constant temperature.

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……………………………………………………………………………………[2]

(ii) Helium gas is added at constant volume and temperature.

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……………………………………………………………………………………[2]

Chloroethane can be made by reacting PCl_3 with ethanol, via nucleophilic substitution mechanism.

$$PCl_3 + CH_3CH_2OH \rightarrow CH_3CH_2Cl + HOPCl_2$$

(c) Outline a simple chemical test that can be carried out to see if chloroethane is produced in the mixture after reacting with PCl_3.

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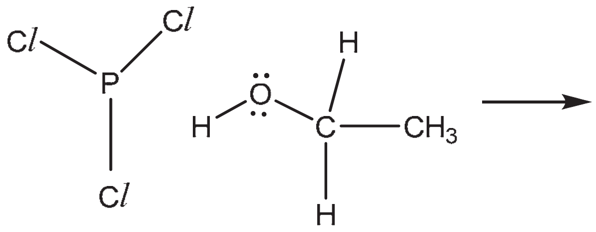
……………………………………………………………………………………[2]

(d) The mechanism is thought to involve these steps.

- The first step is where P-C*l* bond breaks. P is electron deficient and reacts with alcoholic O to form a protonated oxygen intermediate.
- The C-O bond is broken. C*l*⁻ act as a nucleophile.

Complete the diagram to suggest a mechanism to show how chloroethane is formed. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows.



[3]

(e) Explain why chlorobenzene cannot be made in the same way using phenol and PCl_3.

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

[Total: 16]

5 Bromine reacts with organic compounds in different ways.

(a) When butane reacts with gaseous bromine in the presence of ultraviolet light, the major product was 2-bromobutane instead of 1-bromobutane. Using the stability of the intermediates, explain the observation.

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

(b) A solution of 2-bromobut-2-ene, upon heating with ethanolic silver nitrate solution, does not form a cream precipitate.

Upon addition of concentrated sulfuric acid in the cold and followed by heating with ethanolic silver nitrate, 2-bromobut-2-ene formed a cream precipitate.

Explain the above observations.

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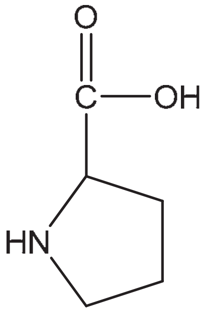
[Total: 6]

Turn Over

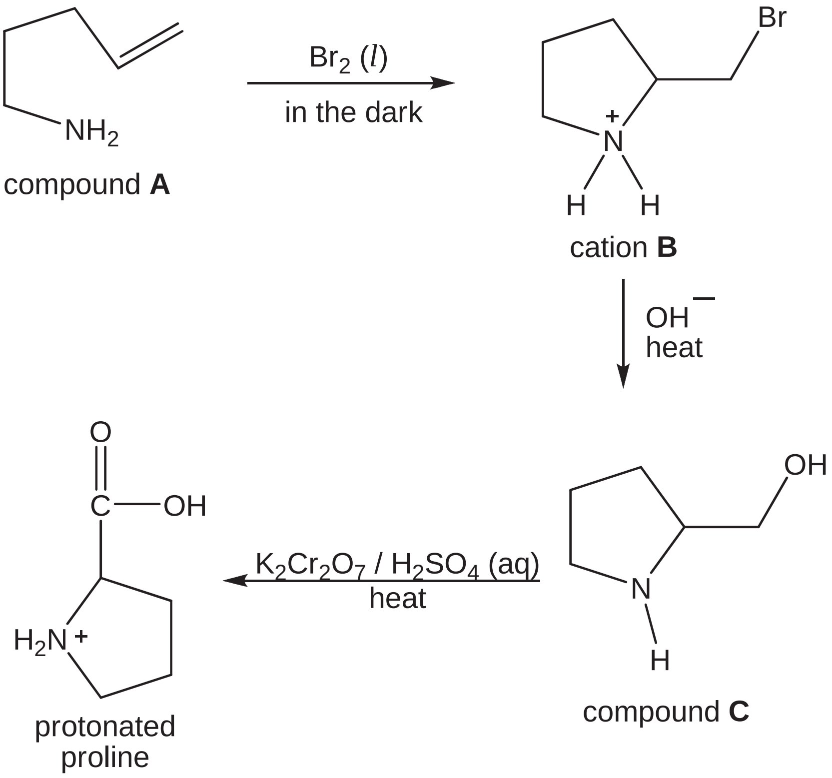
6 Proteins, found within the human body, are formed by amino acids. These amino acids are classified as either essential (cannot be synthesised by the human body) or non-essential (can be synthesised by the human body) amino acids.

(a)



Proline

Proline, one of the non-essential amino acids, is associated with the production of collagen which promotes healthy skin and heart muscle. Protonated proline can potentially be synthesised in the following manner.



The reaction of compound **A** with liquid bromine occurs via a two-step mechanism.

- compound **A** reacts with bromine to form a carbocation intermediate in the first step.
- the ammonium ion is formed in the second step.

(i) Name and suggest the mechanism for this reaction. Show any relevant lone pairs, dipoles and charges, and indicate the movement of electron pairs with curly arrows.

[3]

(ii) This synthesis also produces another organic compound (molecular formula $C_5H_{10}NO_3Br$). Suggest the skeletal formula of the cation.

[1]

(iii) Compound **C** was extracted and reacted with 1 mole of ethanoyl chloride to form a neutral compound **D** with molecular formula $C_7H_{13}NO_2$. Draw the structure of compound **D**. Explain why this product is formed.

Structure

Explanation……………………………………………………………………………..

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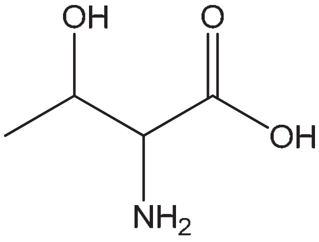
(b)



Threonine

Threonine, one of the essential amino acids, maintains protein balance within the human body and supports the cardiovascular, liver, central nervous and immune system functions.

In the laboratory, threonine could be synthesised from but-2-enoic acid.

(i) State the type of isomerism exhibited by but-2-enoic acid.

……………………………………………………………………………………[1]

(ii) Suggest a 2-step synthesis for the formation of threonine from but-2-enoic acid, showing the intermediate clearly in your answer.

[3]

(iii) By considering the stereoisomers of threonine, suggest why only 25% of the synthesised threonine could be used in the human body.

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

…………………………………………………………………………………….[2]

(c) **(i)** Suggest whether threonine or proline has the more basic amine group. Explain your answer.

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…………………………………………………………………………………….[2]

(ii) Explain, in terms of their structures, the higher solubility of threonine in water as compared to benzoic acid in water.

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……………………………………………………………………………………..[2]

(d) According to dieticians, a teenager requires approximately 1.00 g of calcium each day. This particular mineral is found predominantly in milk, cheeses and yogurts, which most individuals consume in the morning.

(i) Procedure to extract calcium ions is stated as follows :

1. A cup of milk (300 ml) was first filtered to remove impurities before excess amounts of sodium carbonate was added to form $CaCO_3$.
2. The mixture was then refiltered and the white residue (assumed to be solely calcium carbonate) was washed once again with deionised water and filtered again.
3. The white residue was then dissolved in 0.500 dm^3 of 0.160 mol dm^{-3} hydrochloric acid. 25.0 cm^3 of this resulting solution was then titrated against 0.125 mol dm^{-3} sodium hydroxide. The titre volume was found to be 26.45 cm^3.

What is the recommended number of cups of milk each day a teenager should consume to meet the daily requirements?

[3]

(ii)

Compound	Amount per serving
Vitamin A	5000 IU
Vitamin C	300 mg
Vitamin D	600 IU
Vitamin E	30 IU
Vitamin K	80 mcg
Thiamin (Vitamin B-1)	50 mcg
Riboflavin (Vitamin B-2)	50 mg
Vitamin B-12 (as Cyanocobalamin)	50 mcg
Calcium (as in calcium carbonate)	200 mg
Magnesium (as magnesium oxide)	50 mg
Zinc (as zinc oxide)	25 mg
Selenium (as L-Selenomethionate)	200 mcg
Molybdenum (as sodium molybdate)	75 mcg

A typical multivitamin dietary supplement tablet would have the above composition. Given that the teenager does not consume any form of dairy products, how many tablets would a teenager need to take to achieve the daily requirement of calcium?

[1]

(iii) A student wants to test the validity of the composition of calcium in this tablet and decided to follow the steps mentioned in **(d)(i)**.

State 1 possible problem that the student would face.

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…………………………………………………………………………………….[1]

[Total: 21]

~END OF PAPER~

Turn Over

NAME		Class	

ST ANDREW'S JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION

Chemistry (9729) **15 September 2017**

Paper 3 Free Response **2 hours**

Additional Materials: Data Booklet, Writing Paper

READ THESE INSTRUCTIONS:

Write in dark blue or black pen.

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

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

Section A

Answer **all** questions. Marks [60]

Section B

Answer **one** question. Marks [20]

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 **14** printed pages (including this page).

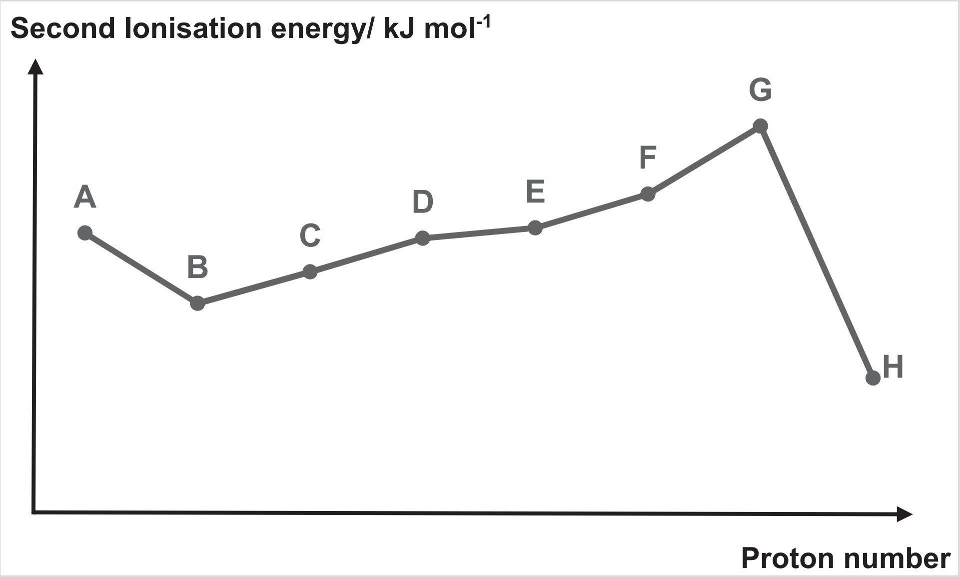
Section A

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

1 **(a)** Iodine is a lustrous purple-black solid at standard conditions that sublimes readily to form a violet gas.

(i) Give the equation that represents the *second ionisation energy* of *iodine*. [1]

(ii) The graph below shows the second ionisation energies of eight elements with consecutive atomic number. [2]



Which of the above elements, **A** to **H**, is iodine? Explain your answer.

(iii) Explain the trend in second ionisation energies from elements **A** to **G**, including the irregularity for element **B**. [4]

(iv) Suggest, with reason, which of the above elements, **A** to **H**, can form an amphoteric oxide. [2]

Hence, write an equation to show the reaction of this amphoteric oxide with hydrochloric acid. (You are not required to provide the identity of the element in the equation.)

1 **(b)** Hydrogen peroxide reacts with acidified iodide ions to liberate iodine, according to the following equation:

$$H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \rightarrow 2H_2O(l) + I_2(aq)$$

The rate of reaction can be measured by the increase in the concentration of iodine formed over time. The reaction was determined to be zero order with respect to $[H^+]$.

The following results were obtained by varying the concentrations of hydrogen peroxide and iodide ions.

Expt	Initial $[H_2O_2(aq)]$ / mol dm^{-3}	Initial $[I^-(aq)]$ / mol dm^{-3}	Initial rate / mol dm^{-3} min^{-1}
1	0.020	0.040	1.2×10^{-4}
2	0.020	0.050	1.5×10^{-4}
3	0.050	0.040	3.0×10^{-4}
4	0.020	0.500	1.5×10^{-3}
5	0.050	1.000	7.5×10^{-3}

(i) What is understood by the terms *order of reaction* and *half-life*. [2]

(ii) Determine the order of the reaction with respect to $[H_2O_2]$ and $[I^-]$ and hence suggest the units of the rate constant of this reaction. [3]

(iii) The half-life of hydrogen peroxide in experiment 4 was 9.24 min. Predict the half-life of hydrogen peroxide in experiment 5. [1]

To investigate the rate of the above reaction, a teacher suggested titrating the iodine formed with sodium thiosulfate solution at specified time intervals.

(iv) Write an equation for the reaction between iodine and thiosulfate. [1]

1 **(b)** **(v)** Suggest how the reaction can be quenched at specified time intervals. [1]

(vi) With reference to the *Data Booklet*, explain why hydrochloric acid is not a suitable acid used for the reaction between hydrogen peroxide and iodide. [2]

[Total:19]

2 Metals have been used widely since ancient times.

(a) An electrochemical cell is constructed using solutions of $NaHSO_4$, H_2SO_3, and $MnSO_4$ with suitable electrodes.

The relevant half reactions are:

$HSO_4^-(aq) + 3H^+(aq) + 2e^- \rightleftharpoons H_2SO_3(aq) + H_2O$ $E^\ominus = +0.17\ V$

$Mn^{2+}(aq) + 2e^- \rightleftharpoons Mn(s)$ $E^\ominus = -1.18\ V$

(i) Draw a fully labelled diagram of the above electrochemical cell to measure the cell potential under standard conditions, indicating clearly the direction of the electron flow in the external circuit. [3]

(ii) Write a balanced equation for the reaction that would take place if the electrodes of the cell were connected together by an external circuit. [1]

(iii) Calculate the standard cell potential for this cell [1]

(iv) Calculate the standard Gibbs free energy change, $\Delta G^\ominus$, for the cell above. [1]

(v) Suggest, with reasons, what happens to the $E^\ominus_{cell}$ when the following are done to the electrochemical cell above. [4]

1) The pH of the HSO_4^-/H_2SO_3 half−cell is increased.

2) A solution of sodium hydroxide to the Mn^{2+}/Mn half−cell.

2 **(b)** In an electrolytic cell, a current of 0.250 A is passed through a concentrated solution of a chloride of iron, producing iron metal and gas, **Y**.

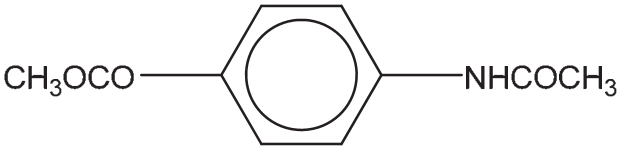
(i) Write the equation for the half-reaction take occurs at the anode. [1]

(ii) When the cell operates for 2 hours, 0.521 g of iron is deposited at one of the electrodes. Determine the formula of the chloride of iron in the original solution. [2]

(iii) Write a balanced equation for the overall reaction that occurs in the cell. [1]

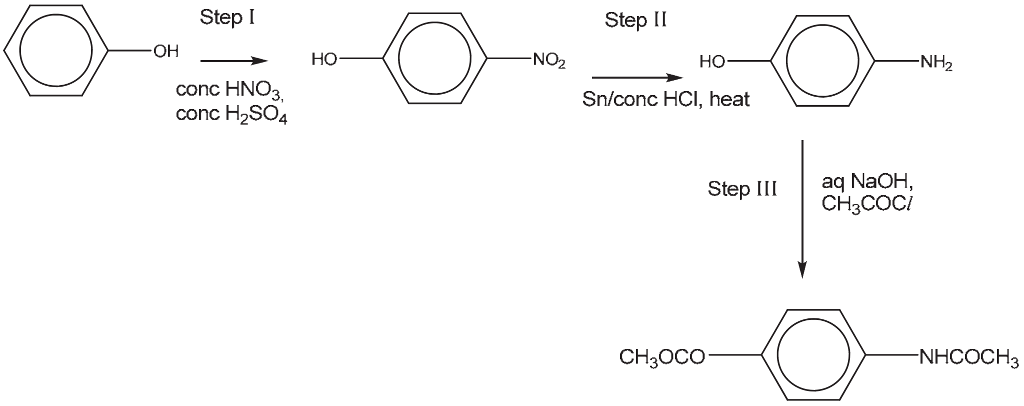
(iv) Calculate the current that would produce the gas **Y** from the solution at a rate of 2.50 g per hour. [2]

(c) Metals are also used as catalysts in organic synthesis. The derivative of acetaminophene is investigated for the treatment of headaches.

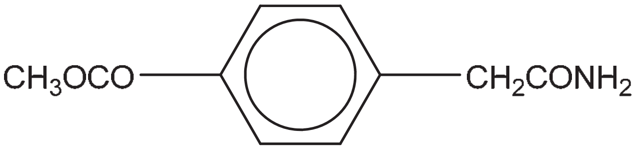


Derivative of acetaminophene

(i) A student suggested a flawed synthesis of the derivative of acetaminophene starting from phenol. Identify and explain the error in each step. [3]



2 **(c)** **(ii)** Compound **Z** is an isomer of the derivative of acetaminophene. Suggest a simple chemical test to distinguish between the derivative of acetaminophene and compound **Z**. [2]



compound **Z**

[Total:21]

3 **(a)** Blood obtains its colour from its respiratory proteins which occur as octahedral metal complexes. It is different in different organisms.

Protein	Source	Metal per subunit	De-oxygenated colour	Oxygenated colour
Haemoglobin	Mammals, birds, fish, reptiles, insects	1 Fe	red-purple	red
Haemocyanin	mollusks, crustaceans, spiders	2 Cu	colourless	blue

(i) Explain why oxygenated haemoglobin and haemocyanin are coloured. [3]

(ii) Using the Cartesian axes, like those shown in Figure 3.1, draw **fully labelled** diagrams of the following. [2]

- One of the d-orbitals at the lower energy level in an octahedral complex. Label the diagram “lower”.
- One of the d-orbtials at the upper energy level in an octahdral complex. Label this diagram “upper”.

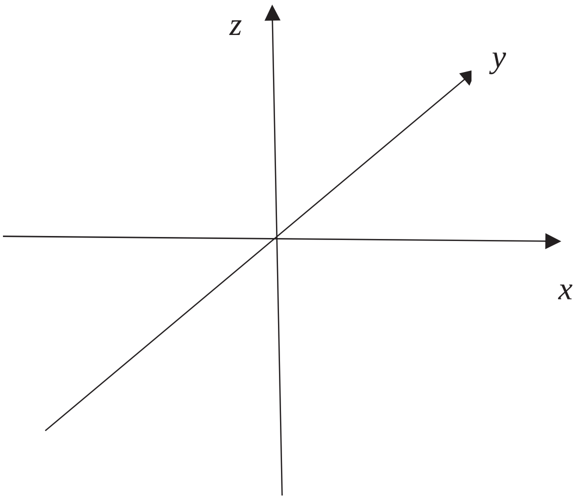
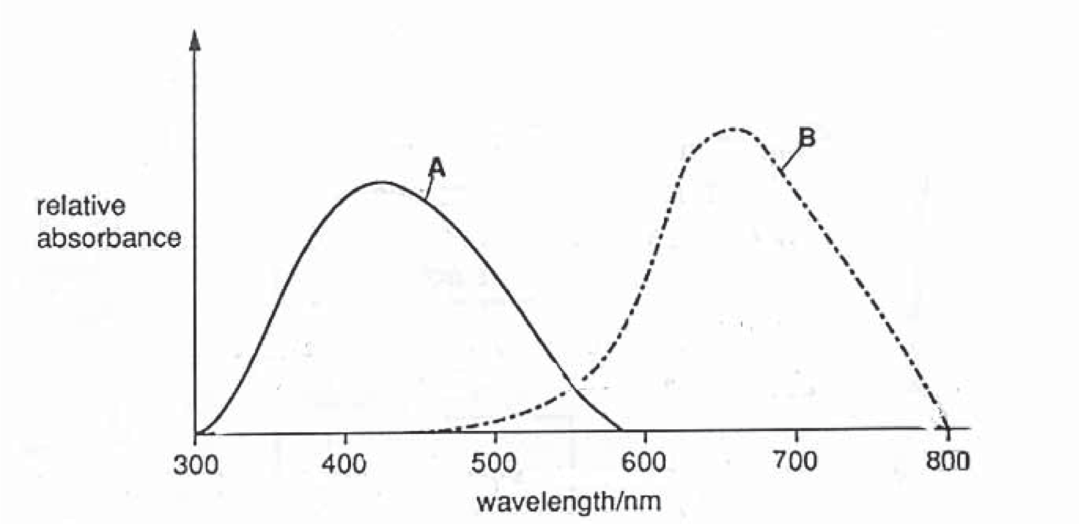


Figure 3.1

(iii) Explain why the splitting of the d subshell occurs in an octahedral complex using your answer in **(a)(ii)**. [2]

3 **(b)** Oxygenated haemoglobin and haemocyanin were analysed and the absorption spectrum was observed.



Colour	Wavelength (nm)	Colour	Wavelength (nm)
Violet	380 – 400	**Yellow**	560 – 580
Blue	400 – 490	**Orange**	580 – 620
Green	490 – 560	**Red**	620 – 800

(i) Which graph represents the absorption spectrum of oxygenated haemocyanin? Explain your answer. [2]

(ii) Which oxygenated blood (haemoglobin or haemocyanin) has a larger energy gap between the d subshells after splitting? Explain your answer. [2]

(iii) The deoxygenated haemocyanin has a Cu^+ central ion. State the electronic configuration of Cu^+. Hence, suggest why the deoxygenated haemocyanin is colourless? [2]

3 **(c)** Carbon monoxide, chlorine and phosgene are the best known toxic gases. Many of these gases are assigned an NFPA 704 health rating of 4 (may be lethal) or 3 (may cause serious or permanent injury).

Toxic Gas	Chemical formula	Colour	Odour	NFPA 704 Health Rating
carbon monoxide	CO	colourless	No	3
chlorine	Cl_2	green	Yes	4
phosgene	CCl_2O	colourless	No	4

(i) Describe, in terms of bonding, what happens when carbon monoxide is absorbed in the human blood and hence, explain why it is given a NFPA 704 health rating of 3. [2]

(ii) Chlorine was widely used as a chemical warfare in World War I. However, it was replaced by phosgene as a more effective chemical warfare. Suggest one possible reason why chlorine was replaced by phosgene. [1]

(d) Phosgene reacts with water to release hydrogen chloride and carbon dioxide gas.

$$CCl_2O + H_2O \rightarrow CO_2 + 2HCl \quad \text{------------Reaction } \mathbf{1}$$

(i) Draw the dot-and-cross diagram of phosgene and suggest its bond angle. [2]

(ii) Suggest the type of reaction involved in Reaction **1**. [1]

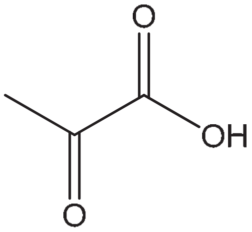
(iii) Gaseous spills of phosgene can be removed using ammonia. The reaction is similar to Reaction **1**. Suggest how phosgene reacts with ammonia, using a chemical equation . [1]

[Total:20]

Section B

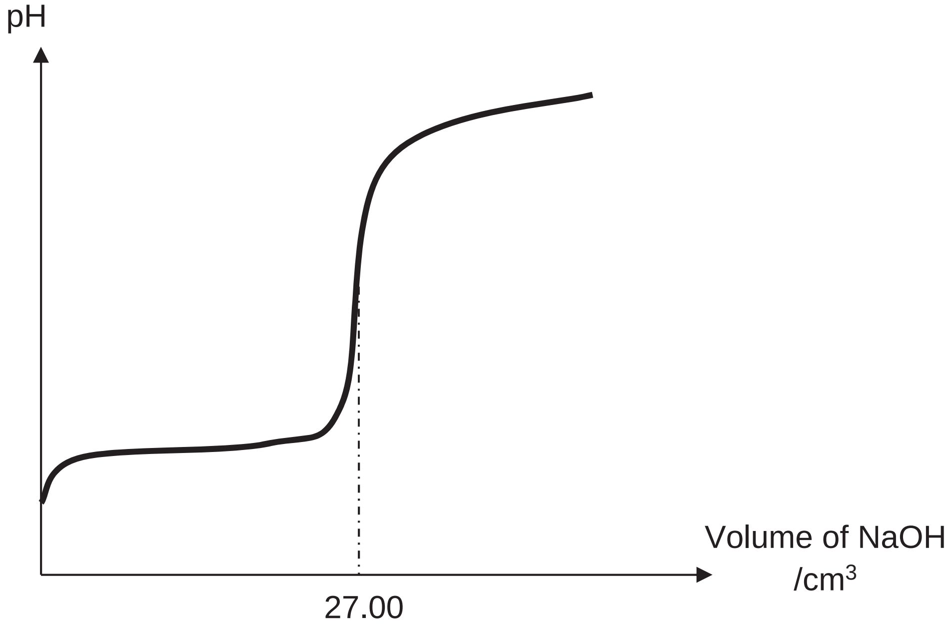
Answer **one** question from this section.

4. Pyruvic acid is an important component in the human body. It is involved in various processes such as the Krebs Cycle.



Pyruvic acid

(a) 30.0 cm^3 of pyruvic acid was titrated against 0.15 mol dm^{-3} of NaOH. The following titration curve was obtained.



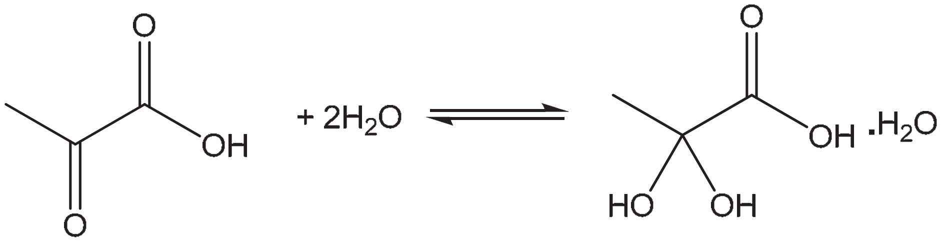
(i) Given that the solution of pyruvic acid is only 15.3 % dissociated, calculate the value of K_a for pyruvic acid, stating clearly its units. [2]

(ii) Calculate the volume of NaOH added to obtain a solution of pH 12. [2]

(iii) Suggest a suitable indicator for this titration. [1]

4 **(a)** **(iv)** Blood has a working pH of 7.35 to 7.45. Suggest why pyruvic acid is found in trace amounts in blood. Hence, draw the major species of pyruvic acid in blood. [2]

(b) An experiment to study the equilibrium between pyruvic acid and its hydrated form was done by Y. Pocker in 1969. The following data was obtained.



pyruvate hydrate

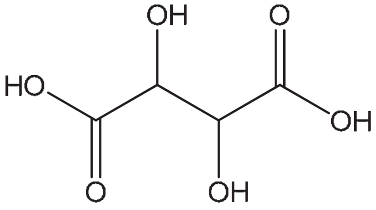
Temperature/ K	$\frac{\text{[pyruvate hydrate]}}{\text{[pyruvic acid]}}$
278	3.47
294	1.75
304	1.06
324	0.47

(i) Deduce whether the hydration of pyruvic acid is an endothermic or exothermic reaction. [2]

(ii) The pyruvate hydrate has a higher pK_a value than pyruvic acid. Explain. [2]

(c) Suggest a 2-step synthesis for the formation of carbon dioxide from pyruvic acid. [3]

4 **(d)** Pyruvic acid was first synthesised in the laboratory through the distillation of tartaric acid with potassium hydrogen sulfate. The structure of tartaric acid is shown below.



Tartaric acid

(i) Suggest why tartaric acid has a much higher melting point than pyruvic acid. [2]

(ii) There are three stereoisomers present in tartaric acid. Two of them rotate plane of polarised light in opposite direction, whereas one has no effect on plane of polarised light. [4]

Draw **all** the stereoisomers of tartaric acid and explain why one of the stereoisomers does not rotate the plane of polarised light.

[Total: 20]

5 **(a)** Thallium(I) chromate, Tl_2CrO_4, has a solubility product of 8.67×10^{-13} $mol^3\ dm^{-9}$ at 25 °C.

(i) Calculate the solubility of Tl_2CrO_4 in 0.05 mol dm^{-3} K_2CrO_4. [2]

(ii) Given that the numerical K_{sp} value of $BaCrO_4$ is 1.17×10^{-10}, deduce which precipitate will be formed first if K_2CrO_4 was added slowly into a solution containing 0.015 mol dm^{-3} of Ba^{2+} and 0.015 mol dm^{-3} Tl^+. [2]

(b) Transition elements are known to form coloured complexes. Chromium is one of the common transition element used today.

(i) An equilibrium exists between chromate(VI) ion and dichromate(VI) ions. [2]

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

Explain why changes in pH will cause changes in the colour of the solution.

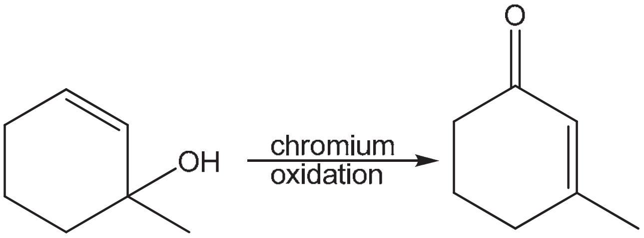
(ii) When gallium, Ga, is added to an acidified $Na_2Cr_2O_7$ solution, a series of colour changes takes place until a blue solution is obtained. [3]

Using relevant data from the *Data Booklet* and the data given below, explain the observation of the colour changes.

$$Ga^{3+} + 3e^- \rightleftharpoons Ga \qquad E^{\ominus} = -0.53V$$

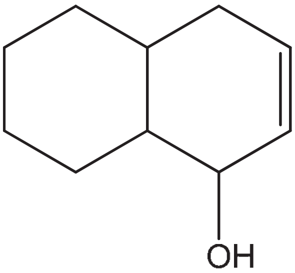
(iii) Suggest why the blue solution slowly changes to a green solution when it is left standing in air. [1]

(c) Chromium oxidation is a special type of reaction in which oxidation and a rearrangement takes place. An example of a chromium oxidation is as shown.



1-methylcyclohex-2-enol 3-methylcyclohex-2-enone

(i) Draw the structure of the product when the following compound undergoes chromium oxidation. [1]



(ii) Suggest a simple chemical test to distinguish between 1-methylcyclohex-2-enol and 3-methylcyclohex-2-enone. [2]

5 **(d)** Compound **F**, $C_4H_9O_3N$, is a neutral and chiral compound which is soluble in water. When compound **F** is heated with dilute sulfuric acid and potassium dichromate(VI), compound **G**, $C_4H_6O_5$, is formed. 1 mol of compound **G** reacts with aqueous sodium carbonate to produce 1 mol of CO_2. If compound **F** is heated with concentrated sulfuric acid and potassium dichromate(VI), compound **H**, $C_4H_4O_4$, is formed instead. When compound **F** reacts with $LiAlH_4$ in dry ether, a compound **J** which is no longer neutral is formed. [7]

Deduce the structures of compounds **F**, **G** **H** and **J**, and explain the reactions involved.

[Total: 20]

~END OF PAPER~

Name:		**Shift:**	
Class:		**Laboratory:**	

ST ANDREW’S JUNIOR COLLEGE

PRELIMINARY PRACTICAL EXAMINATION

Chemistry **29 August 2017**

Higher 2 **2 hours 30 minutes**

Additional Materials: Qualitative Analysis notes

READ THESE INSTRUCTIONS FIRST.

Write your name and class on all the work you hand in.
Give details of the practical shift and laboratory in the boxes provided above.

Write in dark blue or black pen.

You may use a soft pencil for any diagrams or graphs.

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

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

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

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

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

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

Planning	Practical
14	41

This paper consists of **18** printed pages including this page and quantitative analysis notes.

1 Determination of the M_r of a hydrated ethandioate salt

Calcium ethanedioate is the major component of the most common type of human kidney stones. It is one of a series of salts formed from ethanedioic acid, $H_2C_2O_4$. Another of these salts can be represented by the formula $\mathbf{X}_2C_2O_4.H_2O$, where **X** is a Group 1 metal.

Solution **Q** contains 64.5 g dm^{-3} of $\mathbf{X}_2C_2O_4.H_2O$ in deionised water. You are not provided with **Q.**

FA 1 is a diluted solution of **Q**, in which 35.70 cm^3 of **Q** was made up to 250 cm^3 with deionised water in a graduated flask.

FA 2 is 0.0200 mol dm^{-3} potassium manganate(VII), $KMnO_4$.

FA 3 is 1.00 mol dm^{-3} sulfuric acid, H_2SO_4**.**

In this question, you will perform a titration. The data from this titration will be used to determine:

- the concentration of $C_2O_4^{2-}$ in **Q**,
- the M_r of $\mathbf{X}_2C_2O_4.H_2O$, and hence the identity of **X**.

(a) Titration of FA 1 against FA 2

In this titration, **FA 2** is run from the burette into the conical flask containing **FA 1** and **FA 3**. Initially, the colour of the **FA 2** will take some time to disappear.

After some **FA 2** has been added, sufficient Mn^{2+}(aq) ions will be present to allow the reaction to occur faster.

The end-point is reached when a permanent pale pink colour is obtained.

(i)
1. Fill the burette with **FA 2**.
2. Using a pipette, transfer 25.0 cm^3 of **FA 1** into the conical flask.
3. Using an appropriate measuring cylinder, transfer 50.0 cm^3 of **FA 3** to the same conical flask.
4. Heat this solution to about 65 °C.
5. Run **FA 2** from the burette into this flask until a **permanent** pale pink colour is obtained.
6. Record your titration results in the space provided on page 3. Make certain that your recorded results show the precision of your working.
7. Repeat points **1** to **6** as necessary until consistent results are obtained.
8. **Turn off your Bunsen burner**.

Results

[5]

(ii) From your titrations, obtain a suitable volume of **FA 2** to be used in your calculations.

Show clearly how you obtained this volume.

Volume of **FA 2** =………………………………….. **[1]**

(b) **(i)** The equation for the reaction between ethanedioate ions and manganate(VII) ions is shown below.

$5C_2O_4^{2-}(aq) + 2MnO_4^{-}(aq) + 16H^{+}(aq) \rightarrow 10CO_2(g) + 2Mn^{2+}(aq) + 8H_2O(l)$

Calculate the amount, in moles of ethanedioate ions, $C_2O_4^{2-}$ in 25.0 cm^3 of **FA 1**.

Amount of $C_2O_4^{2-}$ in 25 cm^3 of **FA 1** =……………………………… **[1]**

1 **(b)** **(ii)** Determine the concentration, in mol dm^{-3}, of $C_2O_4^{2-}$ in **Q**.

Concentration of $C_2O_4^{2-}$ in **Q** =……………………… **[2]**

(iii) Use your answer to **(b)(ii)** to calculate the M_r of the ethanedioate salt.

M_r of the ethanedioate salt = ……………………..

Hence, deduce the identity of **X**.
Show your working.

[A_r: C, 12.0; O, 16.0; H, 1.0; Li, 6.9; Na, 23.0; K, 39.1; Rb, 85.5; Cs, 132.9; Fr. 223.0]

[3]

X is …………………..

1 **(c)** A student performed the experiment in **(a)(i)** using a sample of another ethanedioate salt. The student obtained a mean titre value of 22.20 cm^3. The teacher calculated that the volume of **FA 2** required should have been 22.40 cm^3. The teacher told the student that the total percentage error from the apparatus in the experiment was 0.4 %.

Calculate the error in the student's result, based on these data. State **and** explain whether or not the student's result is accurate.

…………………………………………………………………………………………………

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

[Total: 14]

2 **Evaluation of the reliability of a gas collection method in determining a value for the *M*$_r$ of the ethanedioate salt.**

In this experiment, you will react the ethanedioate salt with potassium manganate(VII), in the presence of a small amount of manganese(II) ions. You will measure the volume of CO_2 gas produced at timed intervals and determine the maximum volume of CO_2 gas produced.

FA 4 is a solution containing manganese(II) ions, Mn^{2+}.

You will need access to the **FA 1**, **FA 2** and **FA 3** solutions you used earlier.

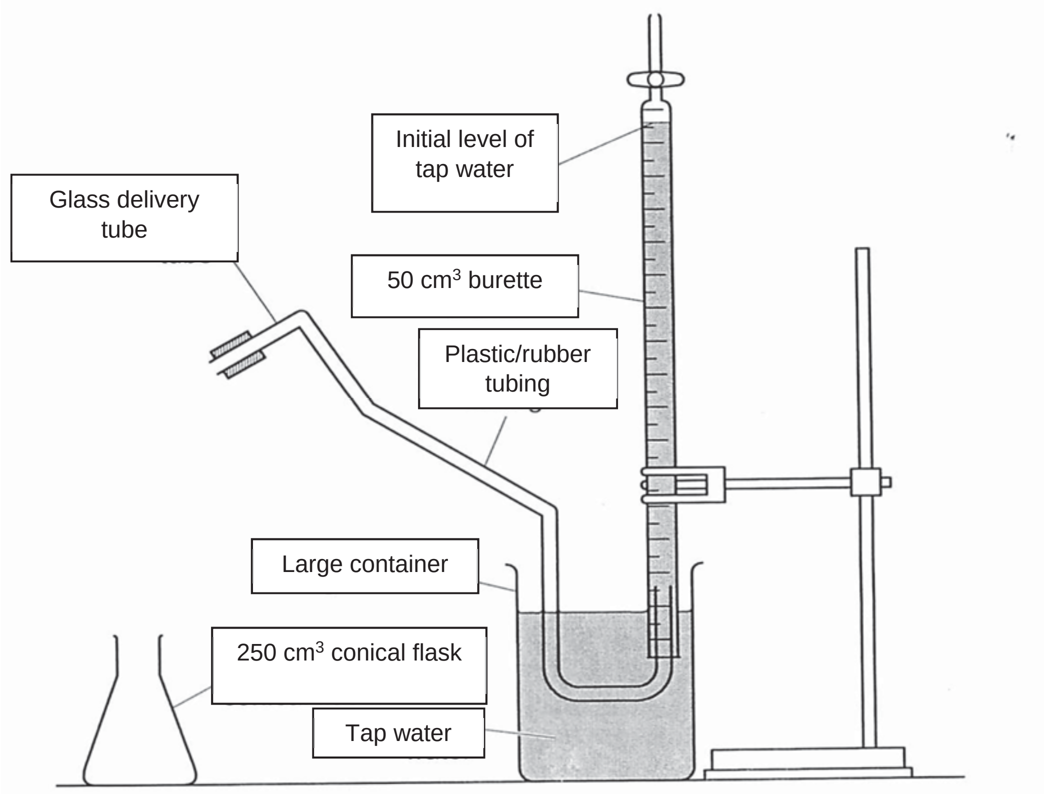


Fig. 2.1

You will measure the level of water in the burette at timed intervals.

In an appropriate format in the space provided on page 7, prepare a table in which you may record each burette reading and the time it was taken.

In addition, your table will need to show the total volume of CO_2 collected up to that time, recorded to one decimal place.

1. Set up the apparatus as shown in Fig. 2.1. You should insert the plastic/rubber tubing to a sufficient depth so that it will not subsequently shake loose.
2. Adjust the water level in the burette until it is between 48.0 cm^3 and 50.0 cm^3. You may find it helpful to use an empty dropping pipette to introduce small amounts of air from the bottom of the burette tube.
3. Use appropriate measuring cylinders to add to the 250 cm^3 conical flask.
    - 20.0 cm^3 of **FA 1**
    - 50.0 cm^3 of **FA 3**
4. Using a dropping pipette, add about 1 cm^3 of **FA 4** to the conical flask.
5. Using an appropriate measuring cylinder, measure out 30.0 cm^3 of **FA 2.**
6. Transfer the **FA 2** into the conical flask and insert the bung into the conical flask.
7. Allow any bubbles created in the burette when the bung was inserted in the conical flask to rise to the top. Start the stopwatch, read and record the initial water level in the burette.
8. Note: Once you have started the stopwatch, allow it to continue running for the duration of the experiment. You must not stop the stopwatch until the reaction is complete.
9. Check that the plastic/rubber tubing is securely positioned in the burette.
10. Hold the flask by its neck and gently swirl it continuously.
11. At t = 0.5 min, read and record the water level in the burette, to 1 decimal place, together with the time it was measured, in your table.
12. Continue to gently swirl the flask. Read and record the water level in the burette every half minute, until the reaction is complete.

(a) (i) Experimental Results

[3]

2 **(a)** **(ii)** Plot on the grid below, a graph of the volume of CO_2 on the y-axis, against time, *t,* on the x-axis.

Draw the most appropriate line, taking into account all of your points.

[4]

2 **(a)** **(iii)** The equation for the reaction between ethanedioate ions and manganate(VII) ions is shown below.

$5C_2O_4^{2-}(aq) + 2MnO_4^{-}(aq) + 16H^{+}(aq) \rightarrow 10CO_2(g) + 2Mn^{2+}(aq) + 8H_2O(l)$

Use this equation, and appropriate data from your graph, to calculate a value for the amount, in moles of ethanedioate ions, $C_2O_4^{2-}$, present in 20.0 cm^3 of **FA 1**.

[molar volume of gas = 24.0 $dm^3\ mol^{-1}$ at r.t.p.]

[1]

Amount of ethanedioate ions, $C_2O_4^{2-}$, in 20.0 cm^3 of **FA 1** = …………………..

(b) **(i)** Using your answer to question **1(b)(i)**, calculate the amount of ethanedioate ions in 20.0 cm^3 of **FA 1**. Hence, determine the maximum volume of CO_2 at r.t.p. that could have been produced from 20.0 cm^3 of **FA 1**.

maximum volume of CO_2 produced from 20.0 cm^3 of **FA 1** =…………..

[4]

(ii) Suggest a reason for the difference between the total volume of CO_2 you collected and the maximum volume of CO_2 calculated in **2(b)(i).**

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

(iii) Suggest an improvement to this experiment that would overcome this problem.

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

2 **(b)** **(iv)** In Question **1** you calculated a value for the M_r of the ethanedioate salt. The total volume of CO_2 collected in **2(a)(i)** could also be used to calculate a value for the M_r of the ethanedioate salt.

Suggest which of these two *Mr* values would be higher. Explain your answer.

……………………………………………………………………………………

……………………………………………………………………………………

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

(c) The presence of Mn^{2+} ions, which are produced in the reaction between MnO_4^- ions and $C_2O_4^{2-}$ ions, is thought to catalyse this reaction.

(i) A student performed the experiment you performed in **2(a)(i)** but forgot to add **FA 4** to the mixture of **FA 1** and **FA 3** before adding the **FA 2**.

The student performed the experiment at the same temperature as your experiment and obtained the graph shown in **Fig. 2.2**.

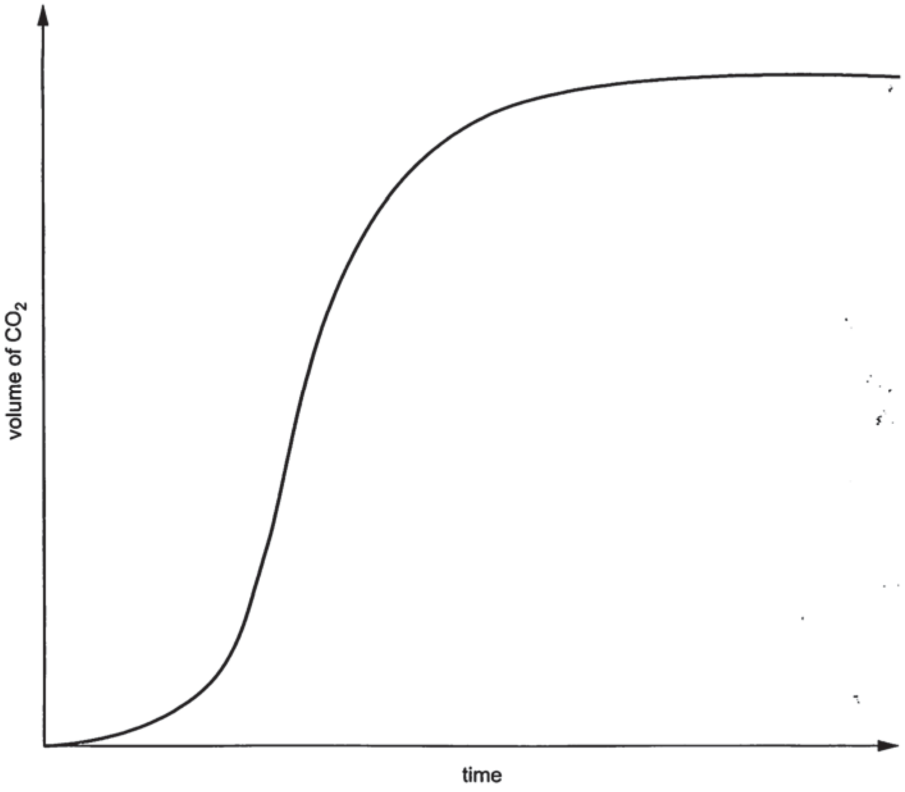


Fig. 2.2

2 **(c)** **(i)** Consider the **shape** of the graph in **Fig 2.2** and your graph in **2(a)(ii)**.

Describe one major difference between the shapes. Suggest an explanation for your answer.

Difference ……………………………………………………………………………

……………………………………………………………………………………..

Explanation …………………………………………………………………………

………………………………………………………………………………………

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

(ii) For the titration in **1(a)(i)** between ethanedioate ions, $C_2O_4^{2-}$, and manganate(VII) ions, MnO_4^-, the solution needs to be at about 65 °C at the start. As cold **FA 2** is added, the temperature of the mixture decreases. However, this decrease in temperature does not cause the rate of reaction between $C_2O_4^{2-}$ ions and MnO_4^- ions added from the burette to decrease.

Suggest an explanation for this.

………………………………………………………………………………………

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………………………………………………………………………………………

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

2 **(d)** **Planning**

The oxidation of iodide ions, I^-, by peroxodisulfate ions, $S_2O_8^{2-}$, is known to be catalysed by Fe^{2+} or Fe^{3+} ions.

A similar reaction, shown below, in which ethanedioate ions, $C_2O_4^{2-}$, are oxidised by peroxodisulfate ions, $S_2O_8^{2-}$, may be catalysed by Cu^{2+} ions and by Ag^+ ions.

$$S_2O_8^{2-} + C_2O_4^{2-} \rightarrow 2\ SO_4^{2-} + 2\ CO_2$$

(i) Suggest an explanation why both of these reactions are slow when performed in the absence of a catalyst.

……………………………………………………………………………………………

……………………………………………………………………………………………

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

(ii) Plan an investigation to test how well, **if at all**, Cu^{2+} ions and by Ag^+ ions catalyse the reaction between $C_2O_4^{2-}$ ions and $S_2O_8^{2-}$ ions.

In your plan, you should include details of:

- the reactants and conditions that you would use,
- the apparatus you would use and the procedure you would follow,
- the measurements you would take,
- an outline of how you would use your results to compare the effectiveness of each ion as a potential catalyst.

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…………………………………………………………………………………………… **[7]**

[Total: 26]

3 You are provided with the solid **K12** which contains one cation given in the Qualitative Analysis Notes.

You are to perform the tests below to identify the cation present in **K12** and suggest the nature of **K12.** Record your observations in the spaces provided. Your answers should include

- Details of colour changes and precipitates formed,
- The names of any gases evolved and details of the test used to identify each one.

You should indicate clearly at what stage in a test a change occurs.

Marks are **not** given for chemical equations.

No additional or confirmatory tests for ions present should be attempted.

Tests	**Observations and Deductions**
1 Heat **K12** alone.	
2 Warm **K12** with dilute hydrochloric acid. Keep the solution.	
3 To the solution from test **2**, add dilute nitric acid and barium nitrate(V) solution	
4 Warm **K12** with a freshly made solution of iron(II) sulfate solution.	
5 Dissolve **K12** in dilute nitric acid. Add manganese(II) sulfate solution and two drops of silver nitrate(V) solution to act as a catalyst. Boil the mixture.	
6 Warm **K12** with sodium hydroxide solution.	

Nature of **K12:** ______________________________

Cation it contains: ______________________________ **[9]**

[Total: 9]

4 Planning

You are provided with 3 unlabelled bottles and each bottle contains one of the following organic compounds,

- Butanamide
- Lactic acid, $CH_3CH(OH)CO_2H$
- Pyruvic acid, CH_3COCO_2H

(a) Outline a sequence of simple chemical tests to identify each of the above organic substances. You may use any other common laboratory chemical reagents and apparatus, if necessary. You are **not** allowed to identify the substances by elimination. You are reminded that most of the compounds listed are *flammable* liquids. **[3]**

Test	**Expected Observations & Deductions**

(b) Suggest a safety measure that you would consider in carrying out your plan.

[1]

(c) State the required reagents and conditions. Draw a set-up of the apparatus for the synthesis of pyruvic acid from lactic acid.

[2]

[Total: 6]

The End

2017 SAJC H2 Chemistry Preliminary Practical Examination
PREPARATION LIST

Apparatus List:

- 2 × burettes
- 1 × 25.0 cm^3 pipette
- 1 × pipette filler
- 1 × retort stand and clamp
- 2 × funnels
- 2 × 250 cm^3 conical flasks
- 2 x 50 cm^3 measuring cylinders
- 1 × 25 cm^3 measuring cylinder
- 2 × dropping pipettes
- 1 × white tile
- 1 x thermometer
- 1 x stopwatch, reading to at least 0.1 s
- 1 × 250 cm^3 conical flask complete with rubber bung and glass delivery tube with at least 35 cm of plastic/ rubber tubing attached

- 1 x large container (water trough)
- 1 x wash bottle (deionised water)
- 1 x test-tube rack
- 7 x test tubes
- 1 x test tube brush;
- 1 x spatula
- 1 x test-tube holder;
- 1 x Bunsen burner
- 1 x tripod stand
- 1 x wire gauze
- 1 x delivery tube
- 1 x glass rod
- 1 x wooden splinter
- 1 x marker
- 1 x goggles

Communal:

- filter paper
- filter paper/ litmus box

- toilet roll
- lighter

Chemical List:

Chemical basket:

- **FA1**
- **FA2**
- **FA3**
- **FA4**

Communal:

K12

Reagent Rack

- aqueous sodium hydroxide
- aqueous ammonia
- aqueous silver nitrate(V) solution
- aqueous nitric acid
- aqueous sulfuric acid
- aqueous hydrochloric acid
- aqueous barium nitrate (V) solution
- aqueous potassium manganate (VII)
- aqueous calcium hydroxide
- iron (II) sulfate solid
- aqueous manganese(II) sulfate

Q1 and Q2

hazard	label	per candidate	identity	Notes (hazards given in this column are for the raw materials)
	FA 1	150 cm^3	0.0500 mol dm^{-3} potassium ethanedioate	Dissolve 9.21 g of $K_2C_2O_4.H_2O$ **[HH]** in deionised water and make up the solution to 1 dm^3.
	FA2	150 cm^3	0.0200 mol dm^{-3} potassium manganate(VII)	Dissolve 3.16 g of $KMnO_4$ **[O][MH][N]** in about 250 cm^3 of deionised water, then add deionised water to 1 dm^3.
[MH]	**FA3**	250 cm^3	1.0 moldm^{-3} sulfuric acid	Cautiously pour 55 cm^3 of concentrated (98%) sulfuric acid [C] into 500 cm^3 of deionised water with continuous stirring. Make the solution up to 1 dm^3 with deionised water. Care: *concentrated sulfuric acid is very corrosive.*
	FA4	5 cm^3	0.100 moldm^{-3} manganese(II) sulfate	Dissolve 16.9g of $MnSO_4.H_2O$ **[HH][N]** in each 1 dm^3 of solution.

Q3

Title	**Practical Inorganic Analysis** **Deduce the identities of the organic compounds K 12**		
Label Code	**Chemicals**	**Preparation**	**Per Student**
	$(NH_4)_2S_2O_8$	-	2-3 g/student
[MH]	1.0 mol dm^3 HCl (bench reagent)	Standard lab preparation	5cm^3 / student (bench reagent)
	Nitric acid		2cm^3/student
	Barium nitrate (V) solution		2cm^3/student
	Iron(II) sulfate crystal		2cm^3/student
	Manganese (II) sulfate solution		2cm^3/student
	Silver nitrate(V) solution		1cm^3/student (bench reagent)
aqueous sodium hydroxide [C]	2.0 mol dm^3 NaOH	Dissolve 80.0 g of NaOH **[C]** in each dm^3 of solution. **Care**: the process of solution is exothermic and any concentrated solution is very corrosive.	4 cm^3/student (bench reagent)

2017 H2 Chemistry Paper 1 Worked Solution

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

1 Amt of $KMnO_4$ used for first experiment = 0.1 x 15/1000 = 1.5×10^{-3} mol

$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$

Amt of Fe^{2+} present = $1.5 \times 10^{-3} \times 5 = 7.5 \times 10^{-3}$ mol

$[Fe^{2+}] = 7.5 \times 10^{-3} /(25/1000) = 0.3$ mol dm^{-3}

Amt of $KMnO_4$ used for second experiment =0.1 x 34.2/1000 = 3.42×10^{-3} mol

Amt of Fe^{2+} present = 0.0171 mol

Amt of Fe^{3+} originally in 25 cm^3 = $0.0171 - (7.5 \times 10^{-3}) = 9.6 \times 10^{-3}$ mol

$[Fe^{3+}] = 9.6 \times 10^{-3} / (25/1000) = 0.384$ mol dm^{-3}

Ans: C

2 9 x 4 = 36 nuclides were lost, hence the mass number of element A is now 241 – 36 = 205.

9 x 2 = 18 protons were lost, hence the atomic number of element A before accounting for the electrons is 94 – 76. However, the implication of ${}^{0}_{-1}e$ is that each electron lost increases the atomic number by 1, so 5 electrons means that the atomic number increases by 5. Hence 76 + 5 = 81.

Ans: A

3 A is not correct. From NH_3 to H_2S, the shape changes from trigonal pyramidal to bent, hence the bond angle actually decreases.

B is correct. PH_3 has a smaller bond angle than NH_3 as P is less electronegative than N, hence the bond pairs are further away from the central atom and experience less bond–pair–bond pair repulsion, hence leading to a smaller bond angle in PH_3. $AlCl_3$ has a larger bond angle than NH_3 as it is trigonal planar with a bond angle of 120 º.

C is not correct. From PH_3 to PF_3, H is less electronegative than F, hence the bonding electron pairs are closer to the central atom in PH_3, hence experience greater bond–pair–bond pair repulsion, hence leading to a greater bond angle in PH_3. From PH_3 to PF_3, there is a decrease in bond angle.

D is not correct. XeF_4 is square planar with bond angle of 90º. SCl_6 is also square planar with bond angle of 90º. Hence there is no increase in bond angle.

Ans: B

4 Glycine forms zwitterions and has an ionic lattice structure with strong electrostatic forces of attraction between the zwitterions, hence has a higher melting point than 2–hydroxyethanoic acid.

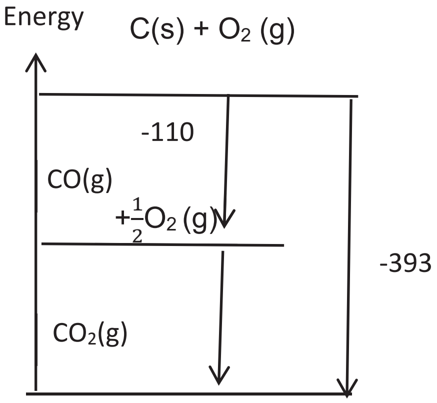
Ans: C

5 pV = nRT. For fixed mass of gas at constant T, pV α k. Hence graph should be horizontal line with gradient k.

At lower T, pV should be be lower than original.

Ans: C

6



Ans: A

7 $\Delta G = \Delta H - T\Delta S$

ΔH will be positive, because interactions in the protein are broken going to the unfolded state. ΔS will also be positive, because the unfolded state is more disordered with coil being more random. ΔG is negative as denaturation is spontaneous when egg is cooked.

Ans: A

8 At a higher temperature, the graph is skewed towards the right. Area under the graph represents the number of molecules with energy greater than or equal to $E_{A.}$

Ans: B

9 Since total vol is constant, [reactants] is α to its vol

Rate α 1/time

Comparing expt 1 & 2, when $[I^-]$ increases 1.5 times, rate increases 170/113 = 1.5 times. Hence 1st order wrt $[I^-]$

Comparing expt 2 and 3, $[S_2O_8^{2-}]$ increases 2 times, rate increases 113/56.5 = 2 times. Hence 1st order wrt $[S_2O_8^{2-}]$

⇨ Rate = k $[S_2O_8^{2-}][I^-]$

Comparing Expt 1 & 4, when $[I^-]$ increases 2 times and $[S_2O_8^{2-}]$ increases 4 times, rate should increase 8 times. Hence time in Expt 4 = 170/8 = 21.3 s.

Since Rate = k $[S_2O_8^{2-}][I^-]$, slow step should involve 1 mole of $(NH_4)_2S_2O_8$ and 1 mole of KI. Since overall eqn involves 2 moles of I^-, the reaction must have more than 1 step. Hence reaction should involve intermediates.

Fe^{2+} can act as homogenous catalyst in the reaction which is slow due to the reaction between two anions:

Step 1: $\underline{\mathbf{2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}}}$

$E^{\ominus}_{cell}$ = +2.01 – (+0.77) = + 1.24 V (> 0, reaction is feasible)

Step 2: $\underline{\mathbf{2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2}}$

$E^{\ominus}_{cell}$ = +0.77 – (+0.54) = + 0.23 V (> 0, reaction is feasible)

Ans: C

10 A: When acid is added, NH_3 is removed. Hence POE will shift left and white precipitate of $AgCl$ is formed.

B: K_c expression does not include solids.

C: K_c expression is not affected by concentration

D: Removing solid does not shift POE.

Ans: A

11

$$2SO_3\,(g) \rightleftharpoons 2SO_2\,(g) + O_2(g)$$

Initial/atm	x	0	0
Eqm/atm	0.5x	0.5x	0.25x

0.5x+0.5x+0.25x = 1.2

x = 0.96

Mole fraction of O_2 = 0.25(0.96) / 1.2 = 0.2

Alternatively,

$$2SO_3\,(g) \rightleftharpoons 2SO_2\,(g) + O_2(g)$$

Initial/mol	x	0	0
Eqm/mol	0.5x	0.5x	0.25x

Mole Fraction of O_2 = (0.25x)/ (0.5x+0.5x+0.25x) = 0.2

Ans: B

12 1) HI is a strong acid. $CH_3CH_2NH_2$ will be protonated. No more weak base present. Not a buffer.

2) 2 mol of HCl and 2 mol of CH_3COOH will be formed from the hydrolysis of CH_3COCl . 2 mole of HCl reacts with 2 moles of NaOH, leaving 1 mole of NaOH. 1 mol of CH_3COONa will be formed from the acid base reaction of 2 moles of CH_3COOH with 1 mole of NaOH, leaving 1 mol of CH_3COOH. Since there is 1 mol of

CH_3COONa and 1 mol of CH_3COOH, a buffer is formed (Think about the species and the possibility of reacting)

3) H_2SO_4 is a stong dibasic acid which will cause $CH_3CH_2NH_2$ to be protonated. Not a buffer

Ans: A

13 $MX_2\ (s) \rightleftharpoons M^{2+}\ (aq) + 2X^-\ (aq)$

$LY\ (s) \rightleftharpoons L^+\ (aq) + Y^-\ (aq)$

A: Ksp increase only when the fwd reaction is endothermic while Ksp decrease when the reaction is exothermic.

B: For solute containing different number of ions, solubility should be calculated to determine which is more soluble. Ksp can only be used for comparison of the no. of ions that made up the two solutes are similar.

C: To calculate for any concentration of ion, it should be IONIC PRODUCT

D: If the solublity of LH is exothermic, a higher temperature will lower the Ksp since the k_b increase a greater extent than k_f.

Ans: D

14 Graph 1: Electronegativity increases across the period.

Graph 2: Si has the highest melting point as it requires the most energy to overcome the strong network of covalent bonding in its giant covalent lattice. P_4 are held by weak id-id interaction, hence low mpt.

Graph 3:

	NaCl	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_5
pH	7	6.5	3	1-2	1-2

Ans: D

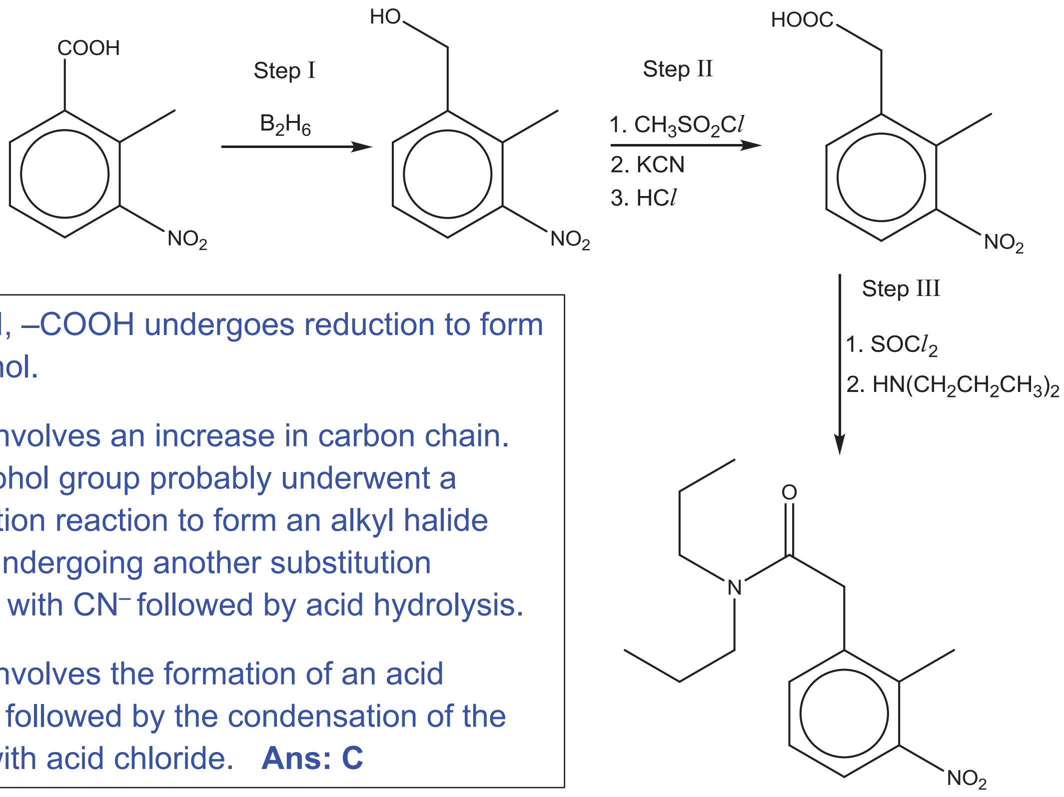
15 1. From the more positive $E^\ominus$, it can be seen the X_2 has the greatest tendency to be reduced. Hence, it has the greatest oxidising power.

2. The $E^{\ominus}$cell will be +1.36 – (+0.54) = +1.90 > 0. Hence, the reaction will occur.

3. From the data booklet, Z_2 is I_2 which is the largest atomic radius, so it has the least tendency to attract electrons to form negatively charge species. Hence, lowest E.A.

Ans: C

16 Which of the following shows the correct type of reaction(s) occurring for each step of the synthesis?



In Step I, –COOH undergoes reduction to form an alcohol.

Step 2 involves an increase in carbon chain. The alcohol group probably underwent a substitution reaction to form an alkyl halide before undergoing another substitution reaction with CN^- followed by acid hydrolysis.

Step 3 involves the formation of an acid chloride followed by the condensation of the amine with acid chloride. **Ans: C**

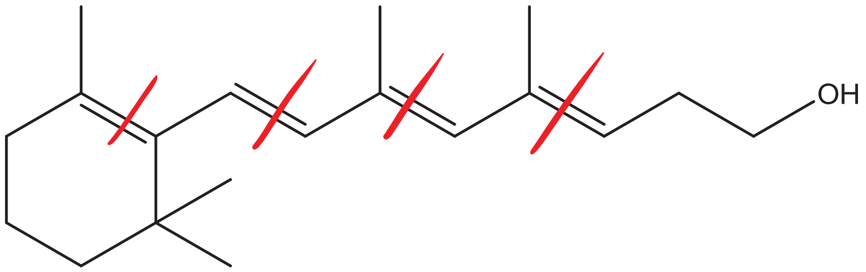
17 The reaction does not have an activation barrier (zero E_A) which means it must be a very energetically favourable reaction which does not involve any bond breaking.

Ans: D

18 **A:** HCl (white fumes) is formed when the alcohol reacts with ethanoyl chloride.

B: is wrong as alkene does not undergo reduction with $LiAlH_4$.

C: is wrong since CO_2 would not be produced when the compound undergoes strong oxidation. No presence of ethanedioic acid that can break down into CO_2.



D: 1 mol of Vitamin A produces 0.5 mol of H_2 and that is 22.7/2 = 11.35 dm^3 at stp.

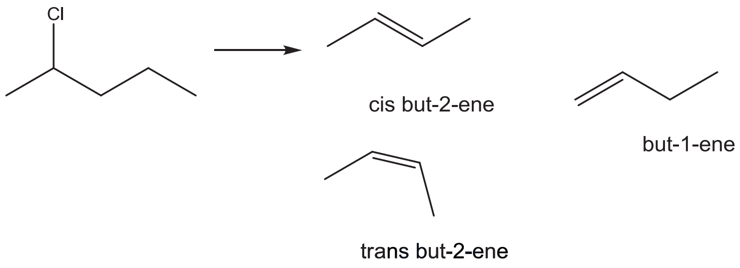
Ans: A

19 Option 1 is wrong since $CH_3CH_2CHClCH_3$ undergoes S_N2 nucleophilic to give a optically active product, $CH_3CH_2CH(OH)CH_3$. The product would be a racemic mixture if it underwent S_N1 mechanism.

Option 2 is correct as $CH_3CH_2CH(OH)CH_3$ and $CH_3CH_2CH_2OCH_3$ are functional group isomers.

Option 3 is correct as C–Br bond is weaker than C–Cl bond and so rate of substitution will increase when the sample is 2–bromobutane.

Option 4 is correct as $CH_3CH_2CH(OH)CH_3$ undergoes elimination with conc, H_2SO_4 to give but–1–ene, cis–but–2–ene and trans–but–2–ene.

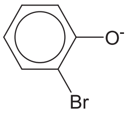


Ans: **D**

20 Conjugate base with smallest pK_b (largest K_b) is the strongest conjugate base; it must come from the weakest acid (smaller K_a).

Strength of acidity is dependent on stability of conjugate anion. The greater the **extent of charge dispersal, the more stable the conjugate anion**.

Order of **decreasing stability of conjugate anion**:



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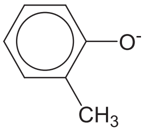
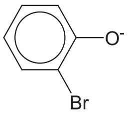


, $CHF_2CH_2O^-$,$(CH_3)_2CHO^-$

Correct order in increasing K_b:



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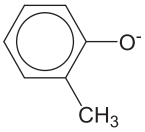


, $CHF_2CH_2O^-$,$(CH_3)_2CHO^-$

Ans: **B**

21 Option A is wrong since the intermediate $CH_3CH_2CH(CN)O^-$ has a tetrahedral shape.

Option B is wrong since a racemic mixture of $CH_3CH_2CH(OH)CN$ would be obtained.

Option C is wrong since there are more –R groups surrounding the carbonyl C in propanone, making the C less electron deficient and also hindering the attack of the nucleophile. Hence the rate should be slower.

Option D is correct due to nucleophilic substitution where the Cl is substituted by CN to give the same product. $CH_3CH_2CH(OH)CN$

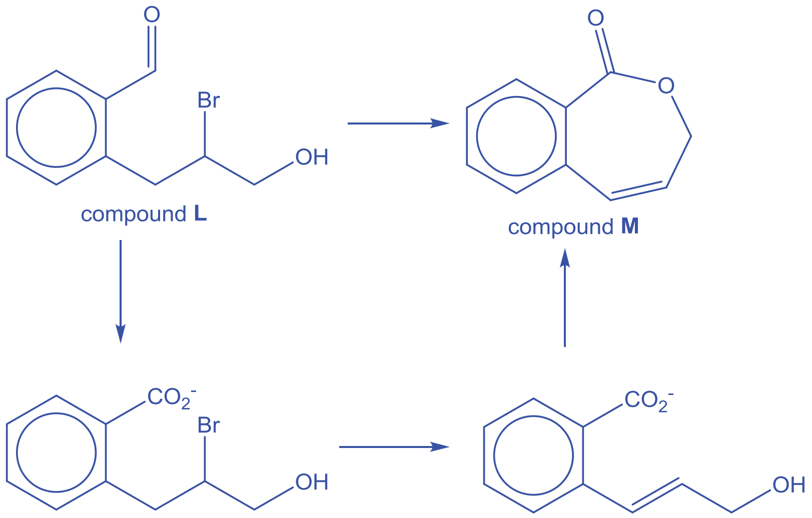
Ans: D

22 Butyl ethanoate is formed from butanol and ethanoic acid

$CH_3CH_2CH_2CH_2O\mathbf{OCCH_3}$ + $\mathbf{H^{18}O}$-H → $CH_3CH_2CH_2CH_2OH$ and $\mathbf{CH_3CO^{18}OH}$

Ans: A

23

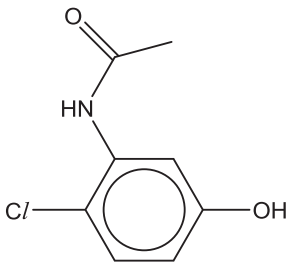


Ans: C

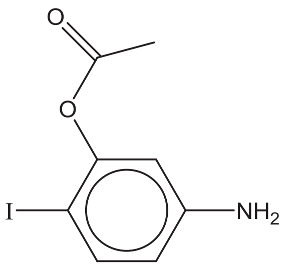
24 α–amino acid has a H_2N-CH(R)- COOH structure. Hence, after oxidative cleavage Option 1 and 4 are probable with the correct empirical formulae.

Ans: B

25 Which of the following reagents would give different observations when added to both compounds in separate test–tubes?



Compound **Y**

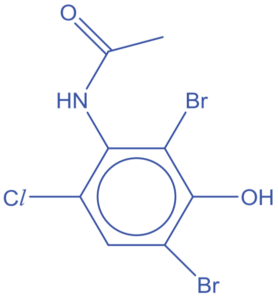


Compound **Z**

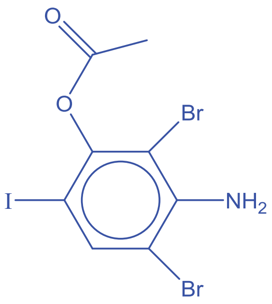
A aqueous bromine

Both compounds would decolourise orange aqueous bromine and form white precipitates.

product of compound **Y**



product of compound **Z**



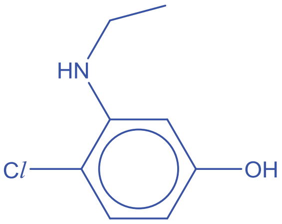
B 2,4–dinitrophenylhydrazine

Neither compounds have carbonyl functional groups and hence not form orange precipitate.

C LiA*l*H$_4$ in dry ether, followed by hot acidified KMnO$_4$

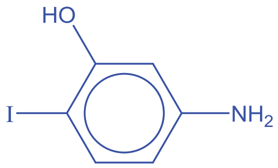
Both compounds would undergo reduction with LiA*l*H$_4$ and form the following :

product of compound **Y**



products of compound **Z**

CH_3CH_2OH



The ethanol would undergo oxidation and decolourise KMnO$_4$.

D ethanolic silver nitrate

Aryl halides would not form precipitate with ethanolic silver nitrate.

Ans: C

26

1. Acid chloride reacts with phenol and alcohol to form ester and amine to form amide. Note that the lone pair of e on N (next to the C=C) is delocalised into the double bond hence nucleophilic subst to form amide is not possible.
2. Alkenes and ketones can be reduced by hydrogen gas to form alkane and secondary alcohol respectively.

3. HBr(g) can react with the alkene via electrophilic addition, the aliphatic alcohol to form RBr via nucleophilic substitution, and both amine functional groups in an acid base reaction.

Ans: B

27 Lone pair of electron on O in alcohol is donated into the empty orbital of H^+.

Ans: B

28 Sucrose is oxidised to carbon dioxide gas while oxygen is reduced to water. Hence electrons will flow from left (anode) to right (cathode).

$E^{\theta}(O_2/H_2O) = +1.23$ V

$+1.25 = +1.23 - E^{\theta}_{(anode)}$

$E^{\theta}_{(anode)} = -0.02$ V **Ans: A**

29 Since 1 mol of complex forms 2 mol of AgI (s), only one iodide ion is present in the complex. Therefore, there should be 5 ammonia ligands in the complex (since complex has co-ordination number 6). Y is $[Cr(NH_3)_5I]\ I_2$.

Ans: C

30 1) Q can use its 3 unpaired 3d and 4s electrons to form ions or bonds hence can exhibit oxidation states from +1 to +5. Therefore $\mathbf{Q_2O_3}$ (oxidation number of Q is +3) is likely to exist.

2) R has a higher nuclear charge than P. Although R has additional electrons (i.e. the 10 3d electrons) in an inner sub–shell, they provide relatively poor shielding (when compared to the 3s and 3p electrons) to the outermost 4s electrons because they are occupying highly diffuse d orbitals. (strength of shielding effect: s > p > d). Hence, the valence 4s electrons of R experience greater effective nuclear charge and are attracted more strongly to the nucleus, resulting in R having a larger 1st IE than P.

3) R^+ has a fully filled d orbital hence d–d transition is not able to take place. Hence the compound is a white solid.

Ans: D

NAME		**Class**	

ST ANDREW’S JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION

Chemistry (9729) **11 September 2017**

Paper 2 Structured Questions **2 hours**

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS:

Write in dark blue or black pen.

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

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

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

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

A Data Booklet is provided.

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

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

For Examiner’s use:

Question	**1**	**2**	**3**	**4**	**5**	**6**	**Total**
Marks	17	5	10	16	6	21	75

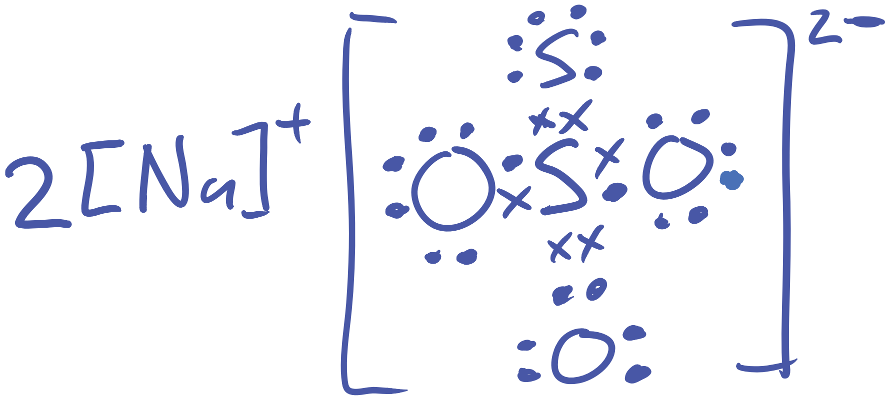
This document consists of XX printed pages (including this page).

Turn Over

Answer **all** the questions

1 Sulfur is a common element on Earth that forms many important chemical compounds. One of these compounds is sodium thiosulfate, $Na_2S_2O_3$, an ionic compound used to treat several medical conditions, such as cyanide poisoning and fungal growths.

(a) **(i)** Draw a dot-and-cross diagram for sodium thiosulfate, $Na_2S_2O_3$. State the shape and bond angle in the thiosulfate ion. [2]



shape around sulfur – tetrahedral

bond angle - 109°

1 mark for correct dot-cross diagram

1 mark for both shape and bond angle

Double bond between S-S atoms is accepted

Additional electrons can be shown as either dot or cross. Triangle/square/circle/any other shape cannot accept.

(ii) Below are the melting points of sodium thiosulfate and sulfur.

Compound	**Melting point / °C**
Sodium thiosulfate	49
Sulfur, S_8	115

Explain why sulfur has a higher melting point than sodium thiosulfate. [3]

Sodium thiosulfate has a giant ionic lattice structure with electrostatic forces of attraction between Na^+ and $S_2O_3^{2-}$ ions. [1]

Sulfur/S_8 is a simple non-polar covalent molecules with instantaneous-dipole-induced-dipole (id-id) interactions between its molecules.[1]

The large number of electrons in each sulfur molecule leads to strong id-id interactions, which require more energy to overcome compared to the ionic bonds in sodium thiosulfate, hence it has a higher melting point than sodium thiosulfate[1]

(b) Another important sulfur compound is sulfuric acid, H_2SO_4. Before the Contact Process was discovered, concentrated sulfuric acid for industrial purposes was produced by the following method.

The mineral pyrite, FeS_2, was first heated in air and oxidised to solid $Fe_2(SO_4)_3$ and sulfur dioxide gas.

$Fe_2(SO_4)_3$ decomposes at 480 °C to form iron(III) oxide and sulfur trioxide gas. The sulfur trioxide gas could be mixed with any volume of water to produce sulfuric acid of the desired concentration. However, this process was expensive and not efficient.

(i) Write a balanced equation, with state symbols for the reaction between pyrite, FeS_2, and oxygen to form $Fe_2(SO_4)_3$. [1]

$2FeS_2(s) + 7O_2(g) \rightarrow Fe_2(SO_4)_3(s) + SO_2(g)$ [1]

(ii) With the aid of an equation, define the term standard enthalpy change of formation of gaseous sulfur trioxide, SO_3. [2]

Standard enthalpy of formation of gaseous SO_3 is the energy released or required when 1 mole of gaseous SO_3 is formed from its constituent elements under standard conditions of 298 K and 1 bar. [1]

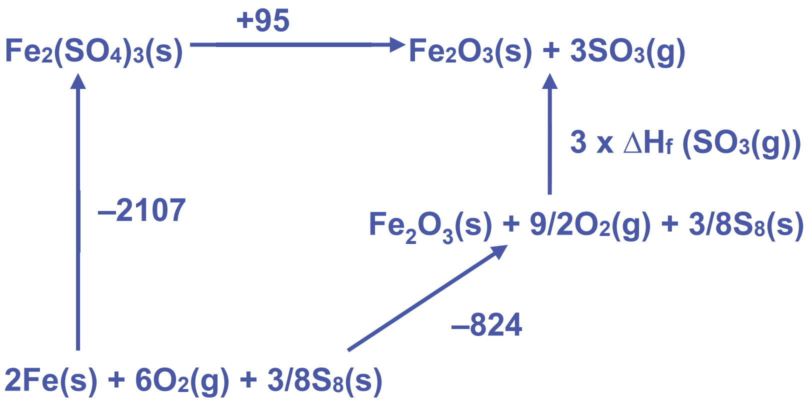
$1/8\ S_8(s) + 3/2\ O_2(g) \rightarrow SO_3(g)$ [1]

(iii) Given the following information, determine the enthalpy change of formation of gaseous sulfur trioxide SO_3.

$Fe_2(SO_4)_3(s) \rightarrow Fe_2O_3(s) + 3SO_3(g) \qquad \Delta H_{rxn} = +95\ kJ\ mol^{-1}$

Substance	**ΔH_f / kJ mol^{-1}**
$Fe_2(SO_4)_3(s)$	–2107
$Fe_2O_3(s)$	–824

[3]



2 marks for energy cycle

$3 \times \Delta H_f (SO_3(g)) + (–824) = –2107 + 95$

$3 \times \Delta H_f (SO_3(g)) = –1188$

$\Delta H_f (SO_3(g)) = –396$ kJ mol^{-1} [1]

OR

$\Delta H_{rxn} = \Delta H_f(\text{products}) – \Delta H_f(\text{reactants}) = +95$ [1]

$–824 – (–2107 + 3\Delta H_f(SO_3(g)) = +95$

[1 mark for correct substitution of values]

$3\Delta H_f(SO_3(g)) = –1188$

$\Delta H_f (SO_3(g)) = –396$ kJ mol^{-1} [1]

(iv) Use the appropriate bond energies given in the *Data Booklet* and the data below to calculate another value for the standard enthalpy change of formation of gaseous sulfur trioxide SO_3.

$\frac{1}{8}S_8(s) + O_2(g) \rightarrow SO_2(g)$ $\Delta H_f = -297 \text{ kJ mol}^{-1}$ [3]

$$\begin{tikzcd}
\frac{1}{8}S_8(s) + \frac{3}{2} O_2(g) \arrow[r, "-297"] \arrow[d, "\Delta H_f (SO_3(g))"] & SO_2(g) + \frac{1}{2}O_2(g) \arrow[d, "\begin{array}{l} \frac{1}{2} \text{ x BE } (O_2) \\ = \frac{1}{2} \text{ x } 496 \\ = +248 \end{array}"] \\
SO_3(g) & SO_2(g) + O(g) \arrow[l, "-BE\ (S{=}O) = -500"']
\end{tikzcd}$$

$\Delta H_f (SO_3(g)) = -549 \text{ kJ mol}^{-1}$

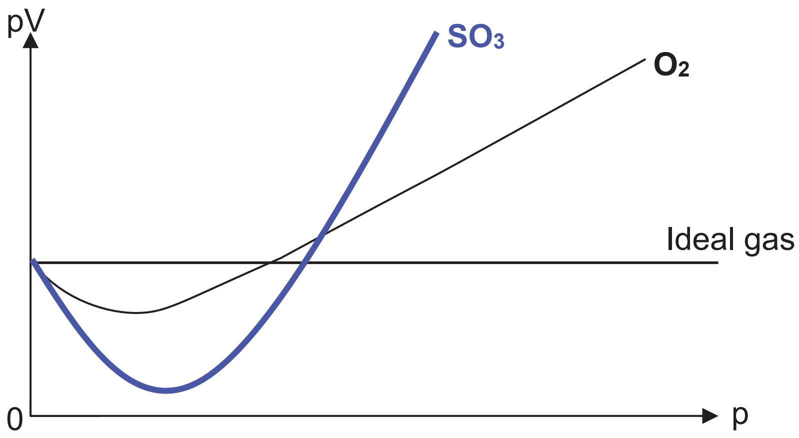
2 marks for energy cycle, ½ mark for each correct arrow with reactants and products

1 mark for calculation

(v) Suggest a reason for the discrepancy between the values in **(b)(iii)** and **(b)(iv)**. [1]

The bond energy data from the data booklet are only average values and would not apply exactly to particular compounds.[1]

(c) The value of pV is plotted against p for 1 mol of oxygen O_2, where p is the pressure and V is the volume of the gas at 300 K.



(i) On the diagram above, draw and label the graph of pV against p for SO_3 at 300 K. [1]

Can cut the ideal gas line at any point, but negative and positive deviation must be more than O_2.

(ii) Explain the difference between the graph of SO_3 and the graph of O_2. [1]

SO_3 has more electrons than O_2, hence it has stronger instantaneous-dipole-induced-dipole interactions and has greater deviation from ideality. [1]

OR

SO_3 has a larger size, hence the volume of SO_3 compared to the total volume occupied by the gas is more significant. [1]

[Total: 17]

2 Transition elements show typical properties that distinguish them from s-block elements, such as calcium. These include variable oxidation states in their compounds, and the formation of coloured complex ions.

(a) An ion of manganese has 3 electrons in its 3d subshell. Suggest the oxidation state of this manganese ion. [1]

+4 [1]

(b) The following table gives data about some physical properties of the elements calcium, chromium, and manganese.

Property	**Ca**	**Cr**	**Mn**
Atomic radius (metallic) / nm	0.197	0.129	0.132
Ionic radius (2+) / nm	0.099	0.073	0.083
Melting point / K	1112	1907	1246
Density / g cm^{-3}	1.54	7.19	7.43
Electrical conductivity / x 10^6 S cm^{-1}	0.298	0.0774	0.00695

(i) Explain why the atomic radii of chromium and manganese are similar to each other. [2]

Mn has more proton and hence greater nuclear charge. However, the two paired electrons in the 4s subshell of Mn also experience interelectronic repulsion.[1] The effect on the radius due to nuclear charge is counteracted by the interelectronic repulsion between the two paired electrons in the 4s subshell.[1]

Accept

Proton number increases and hence nuclear charge increases from Cr to Mn. Shielding effect increases because the electrons are added to the inner 3d subshell. [1] The effect on the radius due to nuclear charge is counteracted by the effect on the radius due to the shielding effect / effective nuclear charge is approximately constant/similar. [1]

(ii) Explain why the density of manganese is significantly greater than that of calcium, using relevant data from the table and the Data Booklet. (No calculations are required.) [2]

Density = mass / volume

Manganese has atomic mass of 54.9, which is greater than the atomic mass of calcium, 40.1. [1]

Manganese has atomic radius of 0.132 nm, which is less than the atomic radius of calcium, 0.197 nm. [1] Or

Manganese has ionic radius of 0.083 nm or 0.058 nm, which is less than the ionic radius of calcium, 0.099 nm. [1]

[Total: 5]

3 A student investigated the thermal decomposition of two carbonates, calcium carbonate and barium carbonate in the following way to determine its exact composition. He used the same amount, in moles, of each carbonate.

$\boldsymbol{M}CO_3$ (s) → $\boldsymbol{M}O$(s) + CO_2 (g) ***M*** is Ca or Ba

He heated the carbonates separately for 5 minutes. The solid obtained after heating was then shaken with distilled water to form an alkaline solution. A portion of the solid remained insoluble and was filtered. A sample of the alkaline filtrate was titrated with hydrochloric acid. No effervescence was observed during the titration.

(a) **(i)** Suggest which carbonate is less likely to decompose completely. Explain your answer. [2]

$BaCO_3$ is more thermally stable and not decomposed completely.

Ionic radius of Ba^{2+} > Ca^{2+} Hence charge density(charge/volume ≈ charge/ionic radius)of Ba^{2+} smaller than Ca^{2+}. [1] Polarising power of Ba^{2+} weaken, less able to polarise the electron cloud of carbonate, less weakening of the C-O bond in the carbonate. Hence the carbonate is less likely to decompose.[1]

(ii) It was observed that the volume of acid used in the titration was smaller for the carbonate which did not decompose completely.

Explain how the incomplete decomposition can result in a lower volume of acid used in the titration. [2]

Incomplete decomposition of $BaCO_3$ will result in smaller amount of BaO being formed [1] BaO is a basic oxide and will dissolve in water to give an alkaline solution and hence less $Ba(OH)_2$ being produced hence requiring lower volume of HC*l* for titration.[1]

$BaO + H_2O \rightarrow Ba(OH)_2$

$Ba(OH)_2 + 2HCl \rightarrow BaCl_2 + 2H_2O$

(b) Explain the difference between the magnitude of the lattice energies of calcium carbonate and calcium oxide. [2]

LE α $\left|\frac{q_+ \times q_-}{r_+ + r_-}\right|$

r^+, q^+ and q^- same for both compound. CO_3^{2-} has a larger ionic radius than O^{2-}.[1]

Thus magnitude of LE of $CaCO_3$ is smaller than that of CaO.[1]

(c) Given that the decomposition of calcium carbonate is an endothermic reaction.

$$\Delta H = +178 \text{ kJ mol}^{-1} \text{ and } \Delta S = +159 \text{ J K}^{-1} \text{ mol}^{-1}$$

Calculate the minimum temperature at which this reaction becomes spontaneous. [2]

$\Delta G = \Delta H - T\Delta S < 0$

$T > 178000/159$ [1]

$T > 1120K$

Minimum temperature is 1120 K. [1]

(d) Beryllium oxide can react with sodium hydroxide.

$$BeO + 2NaOH \rightarrow Na_2BeO_2 + H_2O$$

Explain this behaviour despite Be being a Group 2 element. [2]

Due to the high charge density of Be^{2+}[1], BeO shows a degree of covalent character / amphoteric [1] and thus able to react with a base.

[Total: 10]

Turn Over

4 Gaseous phosphorus(V) chloride dissociates according to the following equation.

$$PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$$

Different amounts of the three gases were placed in a closed container and allowed to come to equilibrium at 200 °C. The experiment was repeated at 425 °C.

The equilibrium partial pressure of the three gases at each temperature are given in the table below.

	Partial pressure / 10^{-3} N m^{-2}		
temperature/°C	PCl_5	PCl_3	Cl_2
200	1.46	11.8	2.77
425	7.61	0.211	0.368

(a) **(i)** Write the expression for the equilibrium constant, K_p, for this reaction. Give the units. [2]

$K_p = \frac{P_{PCl3}P_{Cl2}}{P_{PCl5}}$ [1]

Units: N m^{-2} [1]

(ii) Calculate the value of K_p at each of the temperatures given. [2]

At 200°C

$K_p = (11.8 \times 10^{-3})\,(2.77 \times 10^{-3}) / (1.46 \times 10^{-3})$

= *0.*0224 N m^{-2} [1]

At 425°C

$K_p = (0.211 \times 10^{-3})\,(0.368 \times 10^{-3}) / (7.61 \times 10^{-3})$

= 1.02×10^{-5} N m^{-2} [1]

(iii) Is the forward reaction exothermic or endothermic? Explain your answer. [2]

According to Le Chatelier's Principle, when temperature is increased, endothermic reaction is favoured to "absorb" the additional heat. Since the positon of equilibrium shifts to the left (as evident from the higher partial pressure of PCl_5) at higher temperature, this suggests that the backward reaction is endothermic and hence the forward reaction is exothermic.[1]

Or

Since $K_p = \frac{k_f}{k_b}$, a drop in K_p as temperature increases implies that the rate of backward reaction increases to a greater extent [1]than rate of the forward reaction. This suggests that the backward reaction is endothermic and hence the forward reaction is exothermic.[1]

(b) What will be the effect on the equilibrium partial pressure of PCl_5 when the following changes are carried out on this new equilibrium? Explain your answers clearly.

(i) The pressure of the system is halved at constant temperature. [2]

When pressure is halved, position of equilibrium will shift right [1] as there are more moles of gaseous products to increase the number of moles of gases [1] to increase the pressure. Less PCl_5.

(ii) Helium gas is added at constant volume and temperature. [2]

Individual partial pressures for each gas did not change.[1]

No change in position of equilibrium. [1]

Chloroethane can be made by reacting PCl_3 with ethanol, via nucleophilic substitution mechanism.

$$PCl_3 + CH_3CH_2OH \rightarrow CH_3CH_2Cl + HOPCl_2$$

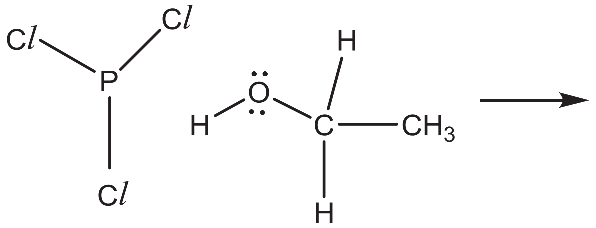
(c) Outline a simple chemical test that can be carried out to see if chloroethane is produced in the mixture after reacting with PCl_3. [2]

Heat chloroethane with aq NaOH. Cool, acidify with nitric acid, then add dilute $AgNO_3$ to sample. [1] A white precipitate should be obtained. [1]

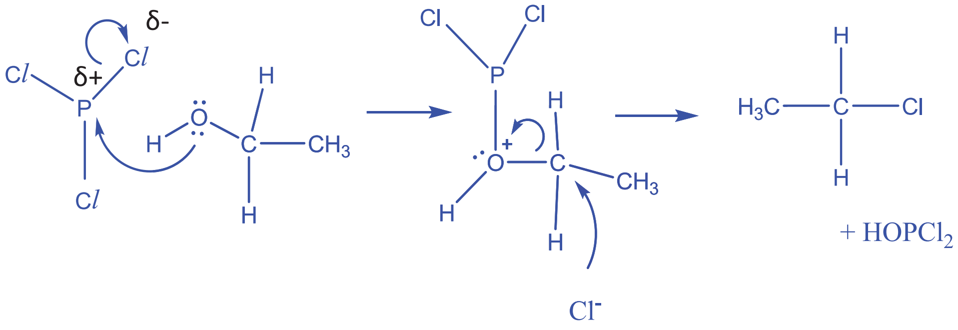
(d) The mechanism is thought to involve these steps.

- The first step is where P-C*l* bond breaks. P is electron deficient and reacts with alcoholic O to form a protonated oxygen intermediate.
- The C-O bond is broken. C*l*⁻ act as a nucleophile.

Complete the diagram to suggest a mechanism to show how chloroethane is formed. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows.



[3]



Nucleophilic Substitution

2marks for both sets of arrows

1 mark for intermediate

dipoles

Lone pair on Cl during intermediate step

No penalty for slow/fast

(e) Explain why chlorobenzene cannot be made in the same way using phenol and PCl_3. [1]

The **lone pair of electrons on O can delocalise into the benzene ring** and resulting in **strengthening of the C-O bond**. [1] Hence the bond does not break easily for NS to take place.

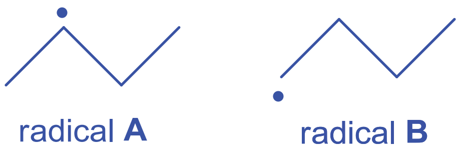
[Total: 16]

5 Bromine reacts with organic compounds in different ways.

(a) When butane reacts with gaseous bromine in the presence of ultraviolet light, the major product was 2-bromobutane instead of 1-bromobutane. Using the stability of the intermediates, explain the observation. [3]

The reaction of gaseous bromine and butane is **free radical substitution**, where the **ultraviolet light splits the bromine-bromine sigma bond in the bromine molecule homolytically** to form 2 bromine radicals / atoms. **[1 mark for either stating FRS or the formation of bromine radical]**

The bromine radical formed reacts with the butane molecule to form the following 2 different radicals.



[1]

can describe in words – 2 alkyl groups vs 1 alkyl group / lone electron on 1st vs 2nd carbon / primary vs secondary radical

Radical **A** is formed in a larger proportion than radical **B** because the carbon with the radical in radical **A** has **1 additional electron donating alkyl group** than in radical **B**. This **stabilises the radical to a greater extent** and hence lead to the higher proportion of 2-bromobutane formed despite having a smaller number of hydrogen atoms to be substituted.**[1]**

(b) A solution of 2-bromobut-2-ene, upon heating with ethanolic silver nitrate solution, does not form a cream precipitate.

Upon addition of concentrated sulfuric acid in the cold and followed by heating with ethanolic silver nitrate, 2-bromobut-2-ene formed a cream precipitate.

Explain the above observations. [3]

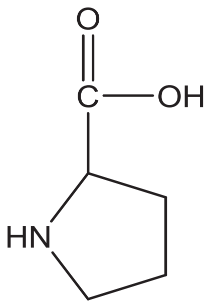
The bromine atom's lone pair of electrons would **delocalise into the alkene functional group, forming a partial double bond**. This partial double bond is **very strong** and hence would not break upon heating and thus no cream-white precipitate was formed. **[1]**

Upon addition of sulfuric acid, the pi-bond in the alkene would **undergo electrophilic addition and hence break**. **[1]** Therefore the bromine atom no longer delocalises its electrons and the carbon-bromine single bond remains. Upon heating with silver nitrate solution, **nucleophilic substitution occurs / the carbon-bromine single bond would break heterolytically, forming the bromide ion**. **[1]** Upon addition of aqueous silver nitrate, would result in the formation of silver bromide, the cream precipitate.

[Total: 6]

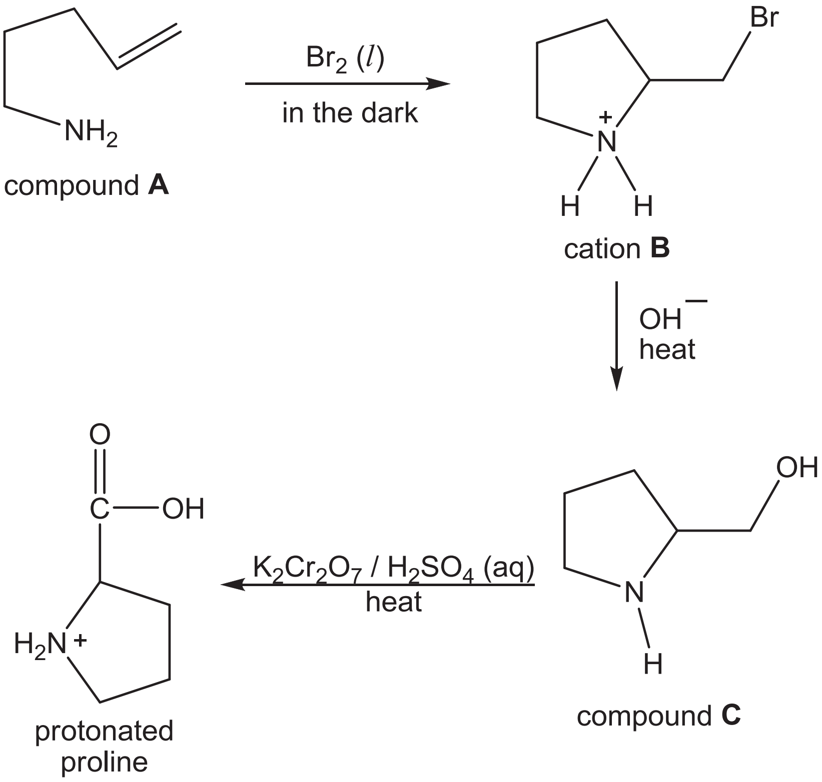
6 Proteins, found within the human body, are formed by amino acids. These amino acids are classified as either essential (cannot be synthesised by the human body) or non-essential (can be synthesised by the human body) amino acids.

(a)



Proline

Proline, one of the non-essential amino acids, is associated with the production of collagen which promotes healthy skin and heart muscle. Protonated proline can potentially be synthesised in the following manner.

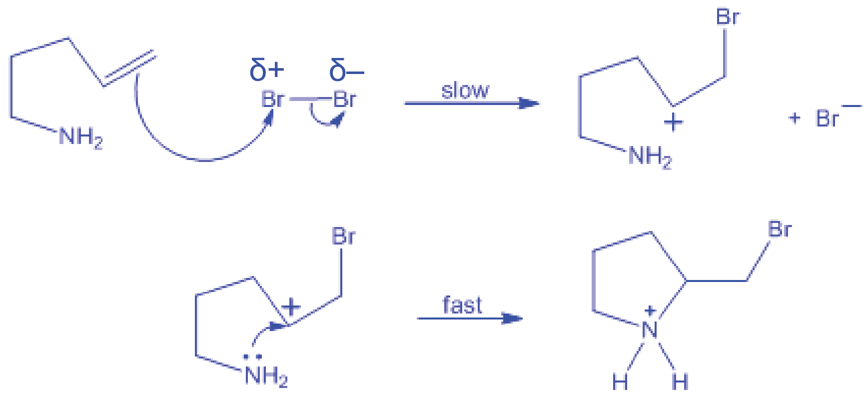


The reaction of compound **A** with liquid bromine occurs via a two-step mechanism.

- compound **A** reacts with bromine to form a carbocation intermediate in the first step.
- the ammonium ion is formed in the second step.

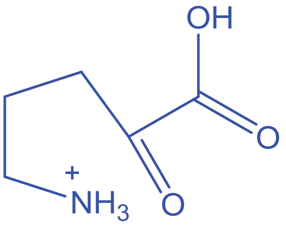
(i) Name and suggest the mechanism for this reaction. Show any relevant lone pairs, dipoles and charges, and indicate the movement of electron pairs with curly arrows. [3]

Electrophilic addition **[1]**



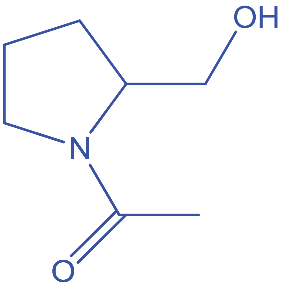
[1] – for each equation (inclusive of dipoles, lone pairs, slow/fast, etc.)

(ii) This synthesis also produces another organic compound (molecular formula $C_5H_{10}NO_3Br$). Suggest the skeletal formula of the cation. [1]



[1]

(iii) Compound **C** was extracted and reacted with 1 mole of ethanoyl chloride to form a neutral compound **D** with molecular formula $C_7H_{13}NO_2$. Draw the structure of compound **D**. Explain why this product is formed. [2]



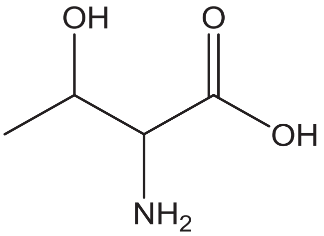
[1]

The amine functional group reacts with ethanoyl chloride as it is a stronger nucleophile as the lone pair of electrons on the nitrogen atom are **more available / likely to attack** the electron-deficient carbon on ethanoyl chloride than the oxygen atom in the alcohol functional group. [1 – availability of lone pair of electrons]

OR

N is less electronegative than O, hence l.p more available to attack. [to be confirmed as answer]

(b)



Threonine

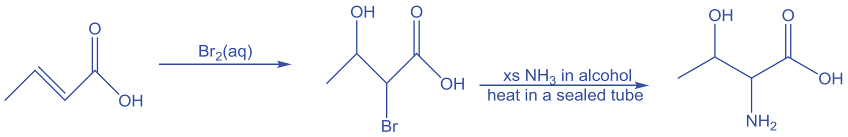
Threonine, one of the essential amino acids, maintains protein balance within the human body and supports the cardiovascular, liver, central nervous and immune system functions.

In the laboratory, threonine could be synthesised from but-2-enoic acid.

(i) State the type of isomerism exhibited by but-2-enoic acid. [1]

cis-trans isomerism

(ii) Suggest a 2-step synthesis for the formation of threonine from but-2-enoic acid, showing the intermediate clearly in your answer. [3]



reagents and conditions **[1]** for each step

intermediate **[1]**

(iii) By considering the stereoisomers of threonine, suggest why only 25% of the synthesised threonine could be used in the human body. [2]

Threonine exhibits **enantiomerism** due to the **presence of 2 chiral carbons**. **[1]** There is a total of **4 possible enantiomers** and **only one of which** matches the threonine within the human body. **[1]**

Accept optical isomers / isomerism

(c) **(i)** Suggest whether threonine or proline has the more basic amine group. Explain your answer. [2]

Proline's amine functional group is **more basic** than that of threonine's.**[1]** Proline's amine functional group is a secondary amine whereas threonine's amine functional group is a primary amine. The **lone pars are more available for protonation due to two/more electron-donating groups** in the secondary amine, hence proline is more basic. **[1]**

OR

On top of which threonine has **an additional secondary alcohol functional group**, which **causes the availability of the lone pair of electrons on the nitrogen atom in the amine to be less available to be donated to a proton**.[1]

(ii) Explain, in terms of their structures, the higher solubility of threonine in water as compared to benzoic acid in water. [2]

Threonine exist as **a zwitterion [1]** in water whereas benzoic acid exist as a simple covalent molecule in water.

Threonine would form **ion-dipole interactions with water molecules** and **releases significantly more energy** as compared to the **hydrogen bonds** formed between benzoic acid molecules with water molecules. Thus threonine is more soluble in water as compared to benzoic acid.**[1]**

(d) According to dieticians, a teenager requires approximately 1.00 g of calcium each day. This particular mineral is found predominantly in milk, cheeses and yogurts, which most individuals consume in the morning.

(i) Procedure to extract calcium ions is stated as follows :

1. A cup of milk (300 ml) was first filtered to remove impurities before excess amounts of sodium carbonate was added to form $CaCO_3$.

2. The mixture was then refiltered and the white residue (assumed to be solely calcium carbonate) was washed once again with deionised water and filtered again.
3. The white residue was then dissolved in 0.500 dm^3 of 0.160 mol dm^{-3} hydrochloric acid. 25.0 cm^3 of this resulting solution was then titrated against 0.125 mol dm^{-3} sodium hydroxide. The titre volume was found to be 26.45 cm^3.

What is the recommended number of cups of milk each day a teenager should consume to meet the daily requirements? [3]

amount of sodium hydroxide used = 0.00330 mol

amount of excess hydrochloric acid present in 0.500 dm^3 of resulting solution = 0.0661 mol **[1]**

amount of hydrochloric acid used to dissolve the white precipitate ($CaCO_3$) = 0.0138 mol

amount of calcium carbonate = 0.00693 mol **[1]**

mass of calcium ions in 1 cup of milk = 0.278 g

no. of cups needed = 1 / 0.278 = 3.60

hence the teenager should drink about 4 cups of milk a day. **[1]**

3.6 cups also accepted as answer

(ii)

Compound	Amount per serving
Vitamin A	5000 IU
Vitamin C	300 mg
Vitamin D	600 IU
Vitamin E	30 IU
Vitamin K	80 mcg
Thiamin (Vitamin B-1)	50 mcg
Riboflavin (Vitamin B-2)	50 mg
Folic Acid	600 mcg
Vitamin B-12 (as Cyanocobalamin)	50 mcg
Calcium (as in calcium carbonate)	200 mg

Iodine (as Potassium iodide)	150 mcg
Magnesium (as magnesium oxide)	50 mg
Zinc (as zinc oxide)	25 mg
Selenium (as L-Selenomethionate)	200 mcg
Molybdenum (as sodium molybdate)	75 mcg

A typical multivitamin dietary supplement tablet would have the above composition. Given that the teenager does not consume any form of dairy products, how many tablets would a teenager need to take to achieve the daily requirement of calcium? [1]

No. of tablets = 1.0 g / 0.2 g = 5 **[1]**

(iii) A student wants to test the validity of the composition of calcium in this tablet and decided to follow the steps mentioned in **(d)(i)**.

State 1 possible problem that the student would face. [1]

1. The calcium carbonate precipitate would be formed along with copper carbonate, magnesium carbonate, etc.
   OR
2. The tablet would have to be treated initially to dissolve it completely.

[1 mark for any point]

[Total: 21]

~ END OF PAPER ~

NAME		**Class**	

ST ANDREW'S JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION

Chemistry (9729) **15 September 2017**

Paper 3 Free Response **2 hours**

Additional Materials: Data Booklet, Writing Paper

READ THESE INSTRUCTIONS:

Write in dark blue or black pen.

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

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

Section A

Answer **all** questions. Marks [60]

Section B

Answer **one** question. Marks [20]

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 XX printed pages (including this page).

Section A

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

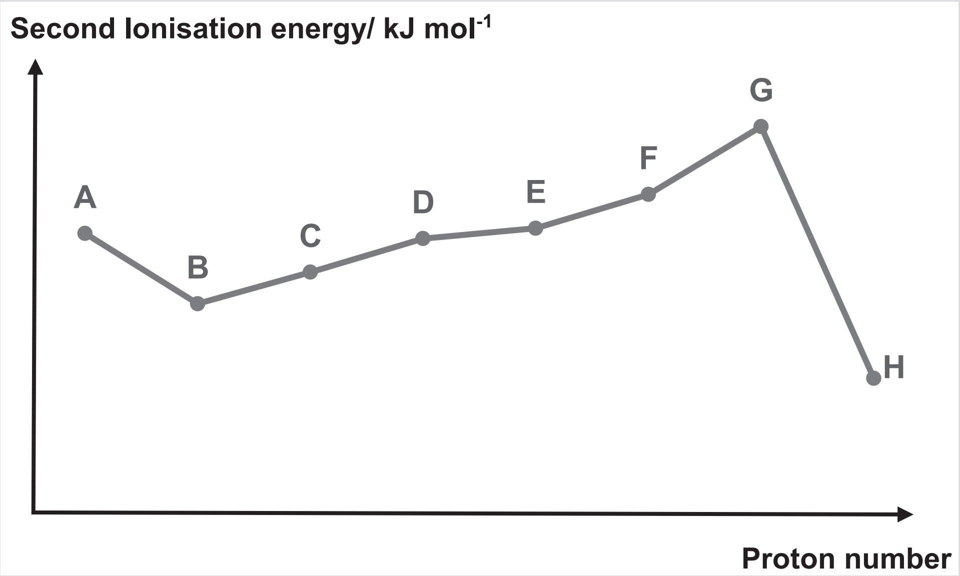
1 **(a)** Iodine is a lustrous purple-black solid at standard conditions that sublimes readily to form a violet gas.

(i) Give the equation that represents the *second ionisation energy* of *iodine*. [1]

$I^+(g) \rightarrow I^{2+}(g) + e^-$ [1]

$\Delta H>0$ is not required since this is not a definition question.

(ii) The graph below shows the second ionisation energies of eight elements with consecutive atomic number. [2]



Which of the above elements, **A** to **H**, is iodine? Explain your answer.

Element **E**. [1] The sharp drop from **G** to **H** indicates that **G** is from Group 1 where the second ionisation energy involves the removal of an electron from the **inner** principal **quantum shell**, which is nearer to the nucleus, requiring more energy. [1] Hence Element **E** is in Group 17 and is iodine.

(iii) Explain the trend in second ionisation energies from elements **A** to **G**, including the irregularity for element **B**. [4]

The second IE generally increases from **A** to **G** because from **A** to **G**, there is an increase in proton number and hence nuclear charge while shielding effect is almost constant as electrons are added to the same quantum shell. [1] Hence effective nuclear charge increases and the attraction for the outermost electron becomes increasingly stronger. [1] More and more energy is required to remove the strongly attracted valence electron as we move across the period.

Second IE of **B** is lower than that of **A** because the electron is removed from the valence 5p subshell which is further away from the nucleus compared to the 5s subshell in **A**. [1] It also experiences additional screening effect by the two 5s. These factors outweigh the effect of increase in nuclear charge from A to B, resulting in a weaker attraction by the nucleus.[1]
Less energy is required to remove the outermost electron in **B** than that in **A**.

(iv) Suggest, with reason, which of the above elements, **A** to **H**, can form an amphoteric oxide. [2]
Hence, write an equation to show the reaction of this amphoteric oxide with hydrochloric acid. (You are not required to provide the identity of the element in the equation.)
Element **A** has amphoteric oxide since it is in Group **13** [1] and its oxide would have both ionic and covalent character.
$\mathbf{A}_2O_3 + 6HCl \rightarrow 2\mathbf{A}Cl_3 + 3H_2O$ [1]
or
$In_2O_3 + 6HCl \rightarrow 2InCl_3 + 3H_2O$ [1]
No ecf from part (ii)

(b) Hydrogen peroxide reacts with acidified iodide ions to liberate iodine, according to the following equation:

$$H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \rightarrow 2H_2O(l) + I_2(aq)$$

The rate of reaction can be measured by the increase in the concentration of iodine formed over time. The reaction was determined to be zero order with respect to $[H^+]$.

The following results were obtained by varying the concentrations of hydrogen peroxide and iodide ions.

Expt	Initial $[H_2O_2(aq)]$ / mol dm^{-3}	Initial $[I^-(aq)]$ / mol dm^{-3}	Initial rate / mol dm^{-3} min^{-1}
1	0.020	0.040	1.2×10^{-4}
2	0.020	0.050	1.5×10^{-4}
3	0.050	0.040	3.0×10^{-4}
4	0.020	0.500	1.5×10^{-3}
5	0.050	1.000	7.5×10^{-3}

(i) What is understood by the terms *order of reaction* and *half-life*. [2]

The order of reaction with respect to a reactant is the power to which the concentration of that reactant is raised in the experimentally determined rate equation. [1]

Or Let the Rate = $k[A]^m[B]^n$, where m and n are the order of reaction wrt [A] and [B] respectively. [1]

Half-life, $t_{½}$, is the time taken for the reactant concentration to decrease to half of its original value.[1]

(ii) Determine the order of the reaction with respect to $[H_2O_2]$ and $[I^-]$ and hence suggest the units of the rate constant of this reaction. [3]

Let rate= $k[H_2O_2(aq)]^m[I^-(aq)]^n$

Compare experiments 1 & 2, keeping $[H_2O_2(aq)]$ constant

$$\frac{1.2\text{x}10^{-4}}{1.5\text{x}10^{-4}} = \frac{k(0.020)^m(0.040)^n}{k(0.020)^m(0.050)^n}$$ (or use inspection method)

n = 1

Rate of reaction is <u>1st order</u> with respect to [I^-(aq)] [1]

Compare experiments 1 & 3, keeping [I^-(aq)] constant

$$\frac{1.2\text{x}10^{-4}}{3.0\text{x}10^{-4}} = \frac{k(0.020)^m(0.040)^n}{k(0.050)^m(0.040)^n}$$ (or use comparing method)

m = 1

Rate of reaction is <u>1st order</u> with respect to [H_2O_2(aq)] [1]

Hence,

rate= k[H_2O_2(aq)][I^-(aq)]

units of k = $\text{mol}^{-1}\ \text{dm}^3\ \text{min}^{-1}$ [1]

(iii) The half-life of hydrogen peroxide in experiment 4 was 9.24 min. Predict the half-life of hydrogen peroxide in experiment 5. [1]

For Expt 4 and 5, since [I^-(aq)] >> [H_2O_2(aq)], [I^-(aq)] is approximately constant.

Thus, rate = k'[H_2O_2(aq)] (a pseudo first order reaction) where

k' = k[I^-(aq)]

$$t_{1/2} = = \frac{\ln 2}{k'} = \frac{\ln 2}{k[I^-]}$$

$t_{1/2}$ of H_2O_2 in experiment 4 = 9.24 min (for [I^-(aq)] = 0.500 mol dm^{-3})

$t_{1/2}$ of H_2O_2 in experiment 5 = **4.62 min** (for [I^-(aq)] = 1.00 mol dm^{-3}) [1]

To investigate the rate of the above reaction, a teacher suggested titrating the iodine formed with sodium thiosulfate solution at specified time intervals.

(iv) Write an equation for the reaction between iodine and thiosulfate. [1]

$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$ [1]

State symbols not required but penalized when wrong ones are provided.

(v) Suggest how the reaction can be quenched at specified time intervals. [1]

The reaction can be quenched by:

- adding $NaOH/NaHCO_3/Na_2CO_3$ to remove the $H^+(aq)$
- sudden cooling of the reaction mixture
- sudden dilution through the addition of large volume of water

any of the above method [1]

(vi) With reference to the *Data Booklet*, explain why hydrochloric acid is not a suitable acid used for the reaction between hydrogen peroxide and iodide. [2]

$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ $E^\ominus = +1.36$ V

$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$ $E^\ominus = +1.77$ V

$E^\ominus_{cell} = +1.77 - 1.36 = +0.41$ V [1 for quoting and calculating]

H_2O_2 can oxidise chloride to chlorine[1] while it itself is reduced to H_2O. Hence, the oxidation of iodide may not be complete.

[Total:19]

2 Metals have been used widely since ancient times.

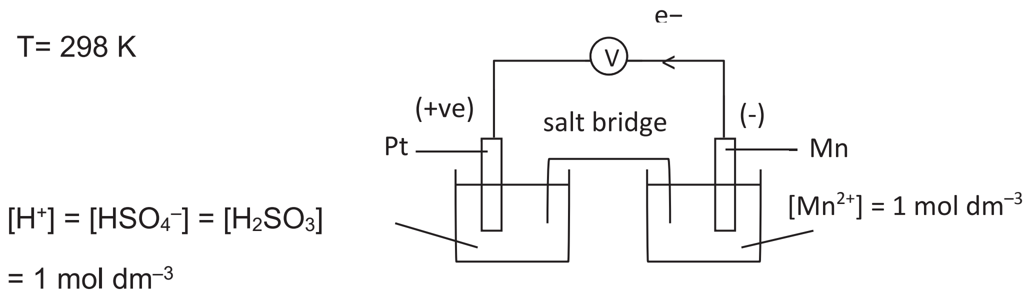
(a) An electrochemical cell is constructed using solutions of $NaHSO_4$, H_2SO_3, and $MnSO_4$ with suitable electrodes.

The relevant half reactions are:

$HSO_4^-(aq) + 3H^+(aq) + 2e^- \rightleftharpoons H_2SO_3(aq) + H_2O \quad E^\ominus = +0.17\ V$

$Mn^{2+}(aq) + 2e^- \rightleftharpoons Mn(s) \qquad E^\ominus = -1.18\ V$

(i) Draw a fully labelled diagram of the above electrochemical cell to measure the cell potential under standard conditions, indicating clearly the direction of the electron flow in the external circuit. [3]



[1] – e^- flow

[1] – voltmeter, salt bridge (can BOD from diagram) + Mn and Pt electrodes

[1] – label all the solutions (HSO_4^- , H_2SO_3, H^+) & 1 mol dm^{-3} and temperature

(ii) Write a balanced equation for the reaction that would take place if the electrodes of the cell were connected together by an external circuit. [1]

$Mn + HSO_4^- + 3H^+ \rightarrow Mn^{2+} + H_2SO_3 + H_2O$ [1]

(iii) Calculate the standard cell potential for this cell [1]

$E^\ominus_{cell} = +0.17 - (-1.18) = +1.35\ V$ [1]

(iv) Calculate the standard Gibbs free energy change, $\Delta G^{\ominus}$, for the cell above. [1]

$\Delta G^{\ominus} = -nFE^{\ominus}$, where n = 2 electrons transferred

$= -2 \times 96500 \times (+1.35) = -260550\ \text{J mol}^{-1} = -261\ \text{kJ mol}^{-1}$ [1]

(v) Suggest, with reasons, what happens to the $E^{\ominus}_{cell}$ when the following are done to the electrochemical cell above. [4]

1) The pH of the HSO_4^- /H_2SO_3 half−cell is increased.

2) A solution of sodium hydroxide to the Mn^{2+} /Mn half−cell.

$HSO_4^-\,(aq) + 3H^+\,(aq) + 2e^- \rightleftharpoons H_2SO_3\,(aq) + H_2O$

1. When <u>$[H^+]$ is reduced /pH increases</u> , equilibrium position shifts to the <u>left</u> to replenish the $[H^+]$, hence <u>$E^{\theta}_{cathode}$ becomes less positive</u> [1]. As E_{cell} = E (cathode) - E (anode), and E (cathode) become less positive, hence, the E_{cell} of the cell <u>becomes less positive. [1]</u>

$Mn^{2+}(aq) + 2e^- \rightleftharpoons Mn(s)$ <u>E_{anode}</u>

2. When NaOH is added, $Mn(OH)_2$ (s) will be formed and <u>$[Mn^{2+}]$ will decrease</u>. Position of equilibrium will <u>shift left</u> to increase $[Mn^{2+}]$, hence <u>E_{anode} becomes more negative.[1]</u> <u>E_{cell} becomes more positive</u>. [1]

(b) In an electrolytic cell, a current of 0.250 A is passed through a concentrated solution of a chloride of iron, producing iron metal and gas, **Y**.

(i) Write the equation for the half-reaction take occurs at the anode. [1]

$2\,Cl^- \rightarrow Cl_2 + 2e^-$ [1]

(ii) When the cell operates for 2 hours, 0.521 g of iron is deposited at one of the electrodes. Determine the formula of the chloride of iron in the original solution. [2]

Charge = 0.25 x 2 x 60 x 60 = 1800 C

Amt of electrons = 1800/96500 = 0.0187 mol

Amt of iron formed= 0.521/55.8 = 0.009336 mol

Mole ratio of electrons taken in: iron deposited = 0.0187: 0.009336 ≈2:1 [1]

Formula of iron chloride = $FeCl_2$ [1]

(iii) Write a balanced equation for the overall reaction that occurs in the cell. [1]

$Fe^{2+} + 2Cl^{-} \rightarrow Cl_2 + Fe$ [1]

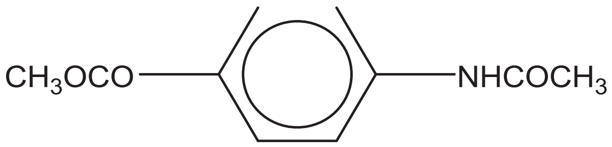
(iv) Calculate the current that would produce the gas **Y** from the solution at a rate of 2.50 g per hour. [2]

Amt of chlorine gas liberated per hour = 2.5/ 71 = 0.03521 mol

Charge required per hour= 2 x 96500 x 0.03521 = 6795 C[1]

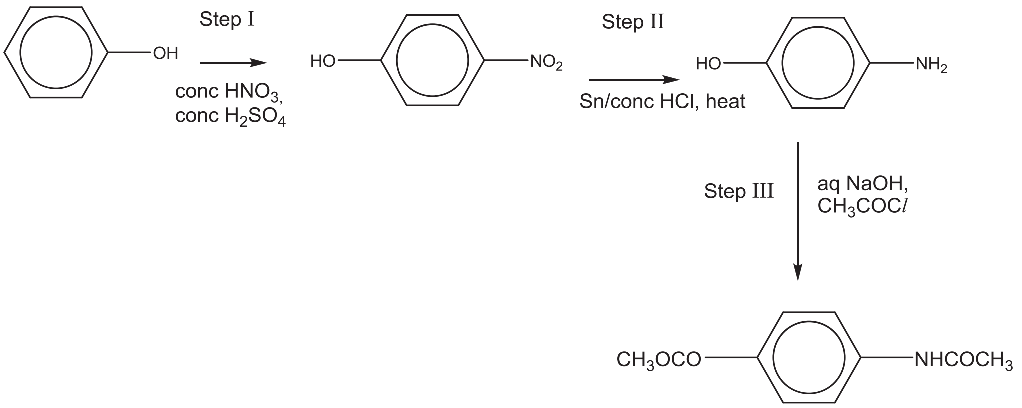
Current = Charge / time = 6795 /(60 x 60) = 1.89 A [1]

(c) Metals are also used as catalysts in organic synthesis. The derivative of acetaminophene is investigated for the treatment of headaches.



Derivative of acetaminophene

(i) A student suggested a flawed synthesis of the derivative of acetaminophene starting from phenol. Identify and explain the error in each step. [3]



Step I: Only dilute HNO_3 instead of conc H_2SO_4 and conc HNO_3 need to be used as phenol is more reactive than benzene/ or –OH group is an activating substituent.

OR conc H_2SO_4 and conc HNO_3 will produce a tri-substituted product.

OR the reagents will result in multiple substituted products.

[1]

Step II: HCl will neutralise phenylamine and form a salt instead

OR There is need to perform careful neutralisation of NaOH to remove the proton from phenylammonium ion.

[1]

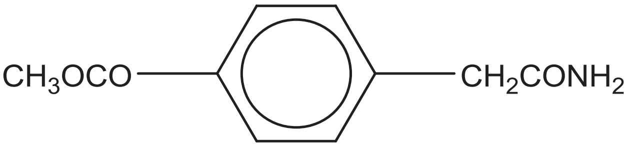
Step III: Acid chloride will hydrolyse to give CH_3CO_2H and HCl which will be neutralised by aq NaOH, hence not able to react with the phenol and phenylamine.

OR Acid chloride will react with aq NaOH, hence not able to react with the phenol and phenylamine.

OR Neutralisation takes place between acid chloride and NaOH and hence condensation will not take place.

[1]

(ii) Compound **Z** is an isomer of the derivative of acetaminophene. Suggest a simple chemical test to distinguish between the derivative of acetaminophene and compound **Z**. [2]



compound **Z**

Test: aq NaOH, heat. [1]

Observations: Compound **Z** produces pungent NH_3 gas that turns **moist** red litmus paper blue but derivative of acetaminophene does not produce pungent NH_3 that turns moist red litmus paper blue.

OR

Compound **Z** gives pungent NH_3 that forms white fumes with concentrated HCl but derivative of acetaminophene does not give pungent NH_3 that forms white fumes with concentrated HCl [1]

[Total:21]

3 **(a)** Blood obtains its colour from its respiratory proteins which occur as octahedral metal complexes. It is different in different organisms.

Protein	Source	Metal per subunit	De-oxygenated colour	Oxygenated colour
Haemoglobin	Mammals, birds, fish, reptiles, insects	1 Fe	red-purple	red

Haemocyanin	mollusks, crustaceans, spiders	2 Cu	colourless	blue

(i) Explain why oxygenated haemoglobin and haemocyanin are coloured. [3]

The oxygenated haemoglobin and haemocyanin contains transition metals ion in the centre of the complexes.

In the isolated gas phase, all partially filled 3d orbitals of the transition metal ions are degenerate. In the presence of ligand such as oxygen, the 3d orbitals split into 2 groups with a small energy gap between them. [1]

An electron from the lower energy d orbital absorbs energy from the visible region (or visible spectrum) of the electromagnetic spectrum with wavelength corresponding to the energy gap is absorbed and get promoted to a higher energy d orbital.[1]

The light energy not absorbed is reflected and observed as colour of its the oxygenated blood. (Or the colour observed is complementary to the colour absorbed.) [1]

(ii) Using the Cartesian axes, like those shown in Figure 3.1, draw **fully labelled** diagrams of the following. [2]

- One of the d-orbitals at the lower energy level in an octahedral complex. Label the diagram “lower”.
- One of the d-orbtials at the upper energy level in an octahdral complex. Label this diagram “upper”.

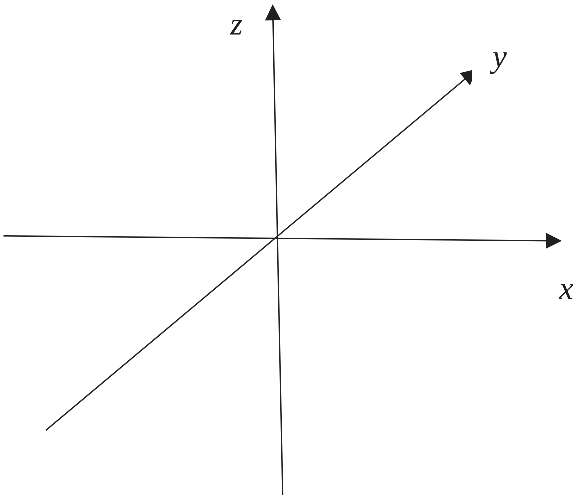
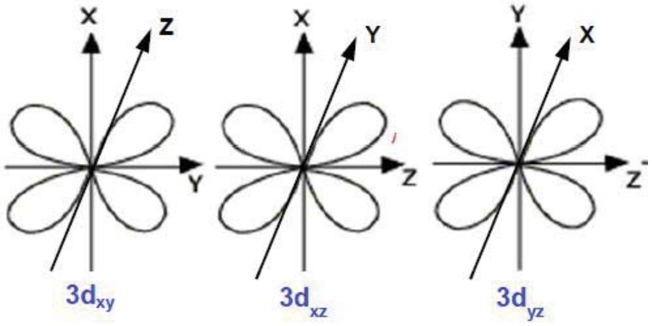
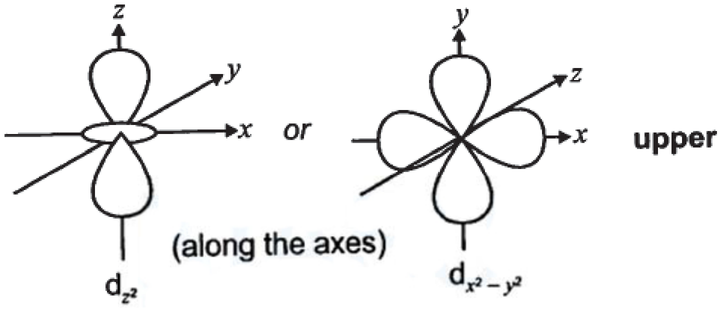


Figure 3.1

Lower: any



Upper: either



Students can change the position of x, y and z axes in their respective diagrams. Orbitals must be labelled.

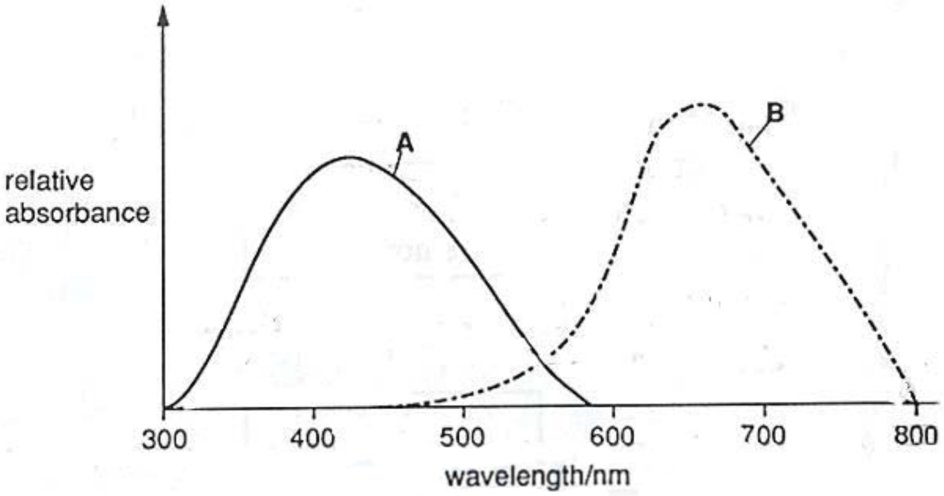
(iii) Explain why the splitting of the d subshell occurs in an octahedral complex using your answer in **(a)(ii)**. [2]

The electrons in the upper d orbitals are pointing towards the lone pairs of electrons on the ligands,[1] hence will be repelled by them and resulting in higher energy. [1]

OR

In octahedral complexes, the lone pairs of electrons on the 6 ligands approach the central ion along the axes. Thus, the energy of an electron in either the upper d orbitals ($3d_{x^2-y^2}$ or $3d_{z^2}$) experience greater electronic repulsion, resulting in higher energy. [1]

(b) Oxygenated haemoglobin and haemocyanin were analysed and the absorption spectrum was observed.



Colour	Wavelength (nm)	Colour	Wavelength (nm)
Violet	380 – 400	**Yellow**	560 – 580
Blue	400 – 490	**Orange**	580 – 620
Green	490 – 560	**Red**	620 – 800

(i) Which graph represents the absorption spectrum of oxygenated haemocyanin? Explain your answer. [2]

Graph B. [1] The wavelength not absorbed is ~380 – 470 nm. This means that the light reflected is blue/violet (accept indigo). [1]

(ii) Which oxygenated blood (haemoglobin or haemocyanin) has a larger energy gap between the d subshells after splitting? Explain your answer. [2]

Haemoglobin has a larger energy gap [1] as $\Delta E = hc/\lambda$, haemoglobin absorbs as a lower wavelength, hence it has a larger energy gap. [1]

(iii) The deoxygenated haemocyanin has a Cu^+ central ion. State the electronic configuration of Cu^+. Hence, suggest why the deoxygenated haemocyanin is colourless? [2]

Cu^+ $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ [1]

Cu^+ has a fully filled 3d-subshell or fully filled 3d-orbitals. Hence, d-d transition of electrons from the lower d-orbitals to the higher orbital is not possible. [1] Hence, no energy from the visible region of the electromagnetic spectrum with wavelength corresponding to the energy gap is absorbed or reflected.

(c) Carbon monoxide, chlorine and phosgene are the best known toxic gases. Many of these gases are assigned an NFPA 704 health rating of 4 (may be lethal) or 3 (may cause serious or permanent injury).

Toxic Gas	Chemical formula	Colour	Odour	NFPA 704 Health Rating
carbon monoxide	CO	colourless	No	3

chlorine	Cl_2	green	Yes	4
phosgene	CCl_2O	colourless	No	4

(i) Describe, in terms of bonding, what happens when carbon monoxide is absorbed in the human blood and hence, explain why it is given a NFPA 704 health rating of 3. [2]

Carbon monoxide (CO) forms dative bond with Fe^{2+} in haemoglobin more readily than O_2 molecule (since Fe-CO bond is stronger than Fe-O_2 bond); or

CO displaces the oxygen in oxyhaemoglobin (HbO_2) to form carboxyhaemoglobin (HbCO).

Or

Being a stronger ligand, carbon monoxide, CO can be bonded less reversibly to the metal centre. [1]

$$HbO_2 + CO \rightarrow HbCO + O_2$$

This consequently cuts down the supply of oxygen to the body and so, accounts for the toxic nature of carbon monoxide, resulting in suffocation. This could lead to serious or permanent injury or death. [1]

Hence, it is given a NFPA 704 health rating of 3.

(ii) Chlorine was widely used as a chemical warfare in World War I. However, it was replaced by phosgene as a more effective chemical warfare. Suggest one possible reason why chlorine was replaced by phosgene. [1]

Chlorine has a distinct odour and is green in colour while phosgene is colourless and have a more subtle smell. Hence, it is more difficult for troops to detect and take counter measure. [1]

Other reasons:

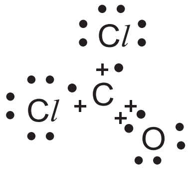
Chlorine is water-soluble and so the effect would be minimised by placing a water-soaked rag over mouth and nose.[1]

Do not accept “Phosgene is much more toxic and deadly than chlorine”; same NFPA value.

(d) Phosgene reacts with water to release hydrogen chloride and carbon dioxide gas.

$CCl_2O + H_2O \rightarrow CO_2 + 2HCl$ ------------Reaction **1**

(i) Draw the dot-and-cross diagram of phosgene and suggest its bond angle. [2]



[1]

Bond angle= 120° [1]

(ii) Suggest the type of reaction involved in Reaction **1**. [1]

Nucleophilic substitution or Hydrolysis [1]

(The water acts as a nucleophile; the lone pair on O of water attacks the δ+ C of phosgene)

(ii) Gaseous spills of phosgene can be removed using ammonia. The reaction is similar to Reaction **1**. Suggest how phosgene reacts with ammonia, using a chemical equation . [1]

[Turn over

$CCl_2O + 4NH_3 \rightarrow CO(NH_2)_2 + 2NH_4Cl$

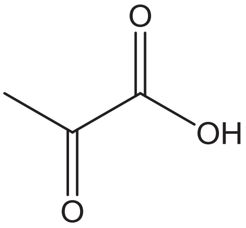
Or $CCl_2O + 2NH_3 \rightarrow CO(NH_2)_2 + 2HCl$ [1]

[Total:20]

Section B

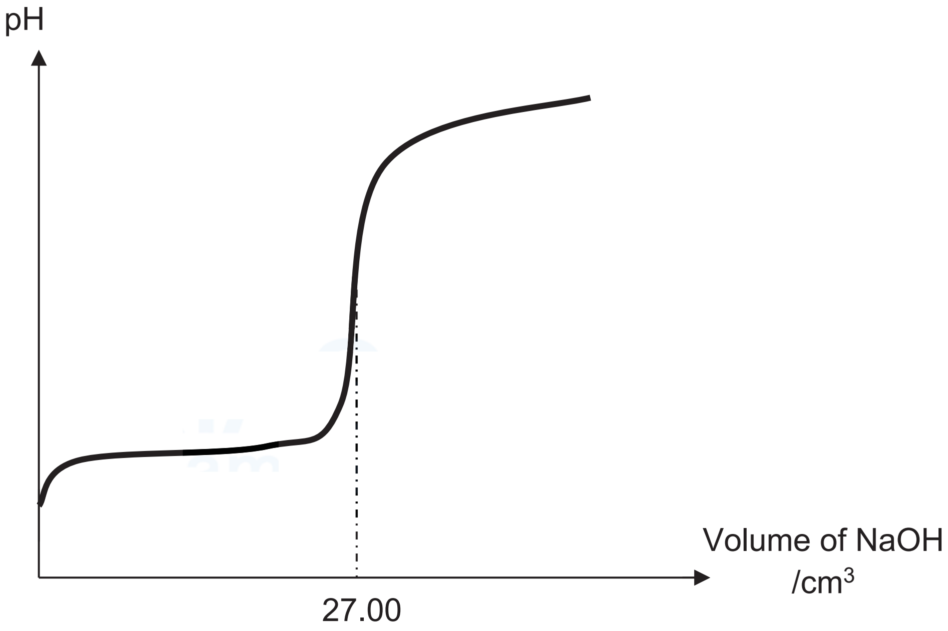
Answer **one** question from this section.

4. Pyruvic acid is an important component in the human body. It is involved in various processes such as the Krebs Cycle.



Pyruvic acid

(a) 30.0 cm^3 of pyruvic acid was titrated against 0.15 mol dm^{-3} of NaOH. The following titration curve was obtained.



(i) Given that the solution of pyruvic acid is only 15.3 % dissociated, calculate the value of K_a for pyruvic acid, stating clearly its units. [2]

[Pyruvic acid] = $\frac{0.15 \times 0.027}{0.03}$ = 0.135 mol dm^{-3}

[H^{+}] = 0.135 x 0.153 = 0.02065 mol dm^{-3} [1]

K_a = $\frac{0.02065^2}{0.135}$ = 3.16 x 10^{-3} mol dm^{-3} [1 with units]

Or

K_a = (0.135)(0.153)^2 = 3.16 x 10^{-3} mol dm^{-3} [2 with units]

(ii) Calculate the volume of NaOH added to obtain a solution of pH 12. [2]

pOH = 2

[OH^{-}] = 0.01 mol dm^{-3} [1]

Let the volume of NaOH added be x dm^3.

[OH^{-}] = $\frac{0.15(x-0.027)}{x+0.03}$ = 0.01

x = 0.0311 dm^3

31.1cm^3 of NaOH was added. [1]

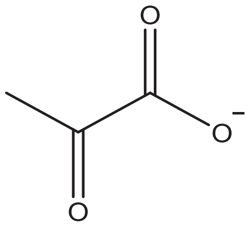
(iii) Suggest a suitable indicator for this titration. [1]

Phenolphthalein [1]

Penalise for wrong spelling

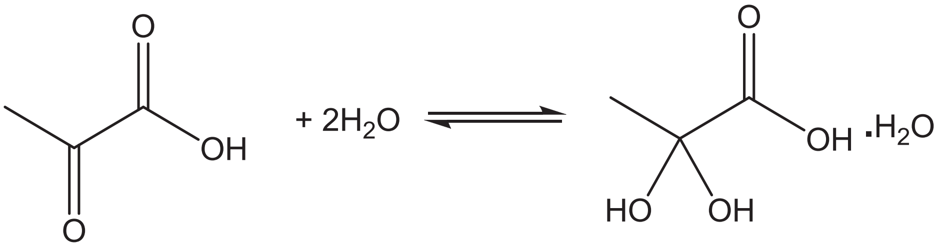
(iv) Blood has a working pH of 7.35 to 7.45. Suggest why pyruvic acid is found in trace amounts in blood. Hence, draw the major species of pyruvic acid in blood. [2]

Pyruvic acid is a weak acid. Since its pK_a value (as calculated based on (a)(i) calculation is 2.50) is less than 7 ,[1] its tendency to remain as pyruvic acid molecule in blood (which has working pH of 7.35 to 7.45) is low, hence it is only found in trace amounts in blood. [1] Hence, in blood, pyruvic acid will exist in the pyruvate(salt/conjugate base) form.



[1]

(b) An experiment to study the equilibrium between pyruvic acid and its hydrated form was done by Y. Pocker in 1969. The following data was obtained.



pyruvate hydrate

Temperature/ K	$\frac{[\text{pyruvate hydrate}]}{[\text{pyruvic acid}]}$
278	3.47
294	1.75
304	1.06
324	0.47

(i) Deduce whether the hydration of pyruvic acid is an endothermic or exothermic reaction. [2]

Temperature increases, more pyruvic acid is present. Backward and forward reaction both increases. However, rate (constant) of backward reaction increases more that of forward reaction. [1] Backward reaction is the endothermic reaction. Thus hydration of pyruvic acid is exothermic. [1]

Or

Temperature increases, more pyruvic acid is present. This implies that position of equilibrium shifts left.[1] Since increase in temperature always favours the endothermic reaction, the backward reaction is endothermic.

Thus hydration of pyruvic acid is exothermic. [1]

Conclusion must be supported by correct reason. 0 if say exothermic but reason contradicts.

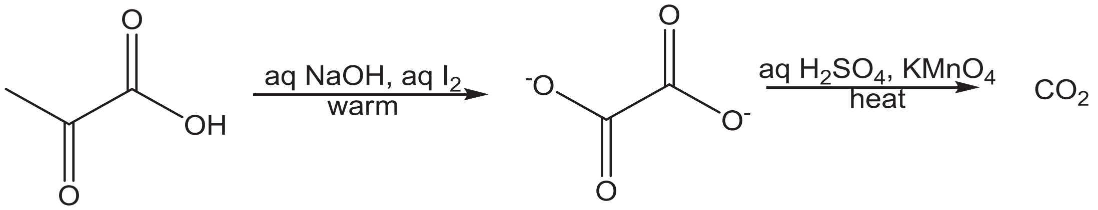
BOD and give 1 mark if only state exothermic but no reason provided.

(ii) The pyruvate hydrate has a higher pK_a value than pyruvic acid. Explain. [2]

Higher pK_a indicates that pyruvate hydrate is less acidic than pyruvic acid.[1] The -C=O group is more electron-withdrawing than the 2-OH groups, hence stabilising the conjugate base of the pyruvic acid more.[1] Hence, pyruvic acid is more acidic.

Alternate answer: Conjugate base of pyruvic acid is more resonance-stabilised due to the C=O and COO$^-$.

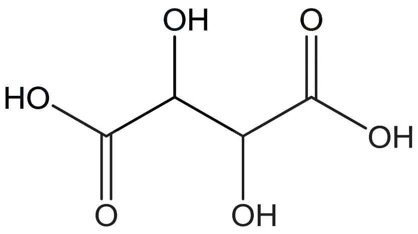
(c) Suggest a 2-step synthesis for the formation of carbon dioxide from pyruvic acid. [3]



Each reagent and condition –[1]

Intermediate – [1]

(d) Pyruvic acid was first synthesised in the laboratory through the distillation of tartaric acid with potassium hydrogen sulfate. The structure of tartaric acid is shown below.



Tartaric acid

(i) Suggest why tartaric acid has a much higher melting point than pyruvic acid. [2]

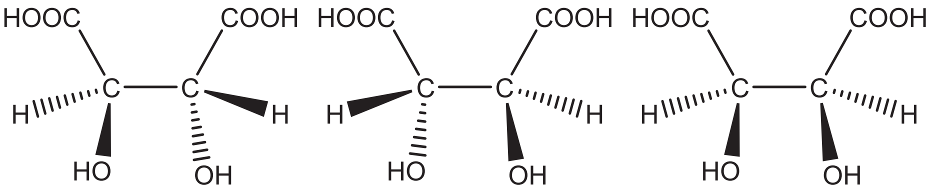
Tartaric acid and pyruvic acid are both polar simple covalent molecules with intermolecular hydrogen bonding.[1] However, tartaric acid can form more extensive intermolecular hydrogen bonding (since it has more –COOH and –OH groups). More energy required to break the more extensive intermolecular hydrogen bonding.[1]

OR

Pyruvic acid would dimerise while tartaric acid would polymerise [1] and hence id-id between the tartaric acid polymers is stronger than the id-id between pyruvic acid dimers. [1]

(ii) There are three stereoisomers present in tartaric acid. Two of them rotate plane of polarised light in opposite direction, whereas one has no effect on plane of polarised light. [4]

Draw **all** the stereoisomers of tartaric acid and explain why one of the stereoisomers does not rotate the plane of polarised light.



[1m each]

There is a plane/line of symmetry present in that stereoisomer

Or it is a meso compound. [1]

[Total: 20]

5 **(a)** Thallium(I) chromate, Tl_2CrO_4, has a solubility product of 8.67 x 10^{-13} mol^3 dm^{-9} at 25 °C.

(i) Calculate the solubility of Tl_2CrO_4 in 0.05 mol dm^{-3} K_2CrO_4. [2]

$K_{sp} = [Tl^+]^2[CrO_4^{2-}]$ units mol^3 dm^{-9}

Let the solubility be x mol dm^{-3}

$8.67 \times 10^{-13} = [2x]^2[0.05]$ [1]

$x = 2.08 \times 10^{-6}$ mol dm^{-3} [1]

(ii) Given that the numerical K_{sp} value of $BaCrO_4$ is 1.17×10^{-10}, deduce which precipitate will be formed first if K_2CrO_4 was added slowly into a solution containing 0.015 mol dm^{-3} of Ba^{2+} and 0.015 mol dm^{-3} Tl^+. [2]

For $BaCrO_4$ ppt to form, $[CrO_4^{2-}] = \frac{1.17x10^{-10}}{0.015} = 7.8 \times 10^{-9}$ mol dm^{-3}

For Tl_2CrO_4 ppt to form, $[CrO_4^{2-}] = \frac{8.67\times10^{-13}}{0.015^2} = 3.85 \times 10^{-9}$ mol dm^{-3}

[1 for both calculations]

Since less $[CrO_4^{2-}]$ is required to form Tl_2CrO_4, it will precipitate first. [1]

(b) Transition elements are known to form coloured complexes. Chromium is one of the common transition element used today.

(i) An equilibrium exists between chromate(VI) ion and dichromate(VI) ions. [2]

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

Explain why changes in pH will cause changes in the colour of the solution.

When pH increases, the equilibrium position will shift left as OH^- will react with H^+. More yellow CrO_4^{2-} formed. [1] When pH decreases, the equilibrium position will shift right to remove the excess H^+. More orange $Cr_2O_7^{2-}$ formed. [1]

(ii) When gallium, Ga, is added to an acidified $Na_2Cr_2O_7$ solution, a series of colour changes takes place until a blue solution is obtained. [3]

Using relevant data from the *Data Booklet* and the data given below, explain the observation of the colour changes.

$$Ga^{3+} + 3e^- \rightleftharpoons Ga \qquad E^\ominus = -0.53V$$

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

$Cr^{3+} + e \rightleftharpoons Cr^{2+} \qquad E^\ominus = -0.41V$ $\Big\}$ [1 for quote]

$Cr_2O_7^{2-} + 2Ga + 14H^+ \rightarrow 2Cr^{3+} + 2Ga^{3+} + 7H_2O$ $E^{\ominus} = +1.86V$ [1]

Orange   *green [1]*

$3Cr^{3+} + Ga \rightarrow 3Cr^{2+} + Ga^{3+}$ $E^{\ominus} = +0.12V$ [1]

Green   *blue*

$3Cr^{2+} + 2Ga \rightarrow 3Cr + 2Ga^{3+}$ $E^{\ominus} = -0.382V$

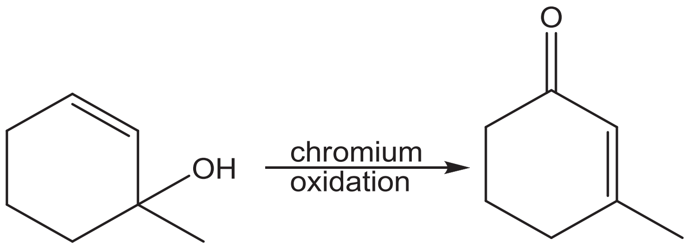
Cr^{2+} cannot be further reduced to Cr by Ga.

(iii) Suggest why the blue solution slowly changes to a green solution when it is left standing in air. [1]

Cr^{2+} is oxidised to Cr^{3+}.

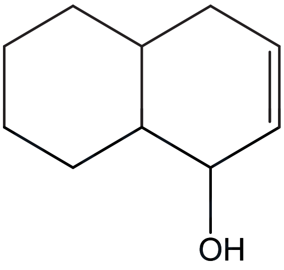
$4Cr^{2+} + O_2 + 2H_2O \rightarrow 4Cr^{3+} + 4OH^-$ $E^{\ominus}_{cell} = +0.81V$ [1]

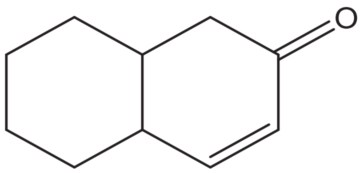
(c) Chromium oxidation is a special type of reaction in which oxidation and a rearrangement takes place. An example of a chromium oxidation is as shown.



1-methylcyclohex-2-enol   3-methylcyclohex-2-enone

(i) Draw the structure of the product when the following compound undergoes chromium oxidation. [1]





[1]

(ii) Suggest a simple chemical test to distinguish between [2]

1-methylcyclohex-2-enol and 3-methylcyclohex-2-enone.

2,4-DNPH, warm [1] No penalty for missing ‘warm’

Orange ppt for 3-methylcyclohex-2-enone and no orange ppt for 1-methylcyclohex-2-enol [1]

(d) Compound **F**, $C_4H_9O_3N$, is a neutral and chiral compound which is soluble in water. When compound **F** is heated with dilute sulfuric acid and potassium dichromate(VI), compound **G**, $C_4H_6O_5$, is formed. 1 mol of compound **G** reacts with aqueous sodium carbonate to produce 1 mol of CO_2. If compound **F** is heated with concentrated sulfuric acid and potassium dichromate(VI), compound **H**, $C_4H_4O_4$, is formed instead. When compound **F** reacts with LiA*l*H_4 in dry ether, a compound **J** which is no longer neutral is formed. [7]

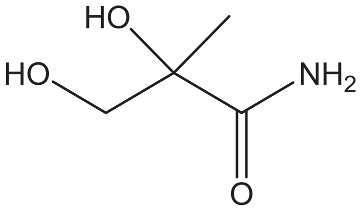
Deduce the structures of compounds **F**, **G** **H** and **J**, and explain the reactions involved.

	Deduction [cap at 3 marks]
Compound **F**, $C_4H_9O_3N$, is a neutral compound which is soluble in water.	F is not a carboxylic acid or amine since it is neutral. [1] OR F can be an amide, ester or contains alcohol groups since it can form H bonding with water, making it soluble. [1]
When Compound **F** is heated with acidified potassium dichromate(VI), Compound **G**, $C_4H_6O_5$, is formed	-oxidation of primary alcohol and hydrolysis - $-CONH_2$ in **F**/ Amide is present in **F** [1]
1 mol of compound **G** reacts with aqueous sodium carbonate to produce 1 mol of CO_2.	-acid-carbonate reaction (accept acid-base reaction) **G** contains two –COOH groups [1]

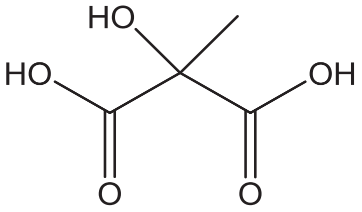
Compound **F** is heated with concentrated sulfuric acid and potassium dichromate(VI), Compound **H**, $C_4H_4O_4$, is formed instead	-elimination of water -alkene in **H** [1]
Compound **F** reacts with $LiAlH_4$ in dry ether, Compound **J** is formed	-reduction - -$CONH_2$ in F becomes –CH_2NH_2 in J[1]

Max 2 marks

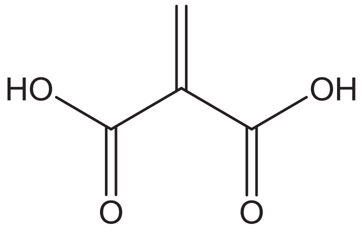
F:



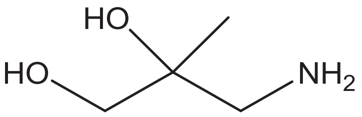
G:



H:



J:



1 mark each structure

[Total: 20]

d~END OF PAPER~

H2 Chemistry Preliminary Exam Practical Suggested Solution

1 Determination of the M_r of a hydrated ethandioate salt

Calcium ethanedioate is the major component of the most common type of human kidney stones. It is one of a series of salts formed from ethanedioic acid, $H_2C_2O_4$. Another of these salts can be represented by the formula $\mathbf{X}_2C_2O_4.H_2O$, where **X** is a Group 1 metal.

Solution **Q** contains 64.5 g dm^{-3} of $\mathbf{X}_2C_2O_4.H_2O$ in deionised water. You are not provided with **Q.**

FA 1 is a diluted solution of **Q**, in which 35.70 cm^3 of **Q** was made up to 250 cm^3 with deionised water in a graduated flask.

FA 2 is 0.0200 mol dm^{-3} potassium manganate(VII), $KMnO_4$.

FA 3 is 1.00 mol dm^{-3} sulfuric acid, H_2SO_4.

In this question, you will perform a titration. The data from this titration will be used to determine:

- the concentration of $C_2O_4^{2-}$ in **Q**,
- the M_r of $\mathbf{X}_2C_2O_4.H_2O$, and hence the identity of **X**.

(a) Titration of FA 1 against FA 2

In this titration, **FA 2** is run from the burette into the conical flask containing **FA 1** and **FA 3**. Initially, the colour of the **FA 2** will take some time to disappear.

After some **FA 2** has been added, sufficient $Mn^{2+}(aq)$ ions will be present to allow the reaction to occur faster.

The end-point is reached when a permanent pale pink colour is obtained.

(i)
1. Fill the burette with **FA 2**.
2. Using a pipette, transfer 25.0 cm^3 of **FA 1** into the conical flask.
3. Using an appropriate measuring cylinder, transfer 50.0 cm^3 of **FA 3** to the same conical flask.
4. Heat this solution to about 65 °C.
5. Run **FA 2** from the burette into this flask until a **permanent** pale pink colour is obtained.
6. Record your titration results in the space provided on page 3. Make certain that your recorded results show the precision of your working.
7. Repeat points **1** to **6** as necessary until consistent results are obtained.
8. **Turn off your Bunsen burner**.

Results

Final burette reading/ cm^3	**25.10**	**25.10**
Initial burette reading/ cm^3	**0.00**	**0.00**
Volume of FA 2/$KMnO_4$/Titrant / cm^3	**25.10**	**25.10**
Values used (Tick consistent readings ±0.10 cm^3)	✓	✓

[5]

(ii) From your titrations, obtain a suitable volume of **FA 2** to be used in your calculations.

Show clearly how you obtained this volume.

Average volume of FA 2 = (25.10 + 25.10)/2 = 25.10 cm^3

Volume of **FA 2** =…25.10 cm^3….

[1]

(b) **(i)** The equation for the reaction between ethanedioate ions and manganate(VII) ions is shown below.

$5C_2O_4^{2-}(aq) + 2MnO_4^{-}(aq) + 16H^{+}(aq) \rightarrow 10CO_2(g) + 2Mn^{2+}(aq) + 8H_2O(l)$

Calculate the amount, in moles of ethanedioate ions, $C_2O_4^{2-}$ in 25.0 cm^3 of **FA 1**.

amount of MnO_4^{-} in FA 2 = (25.10/1000) X 0.02 = 0.000502 mol

amount of $C_2O_4^{2-}$ in 25 cm^3 of FA 1 = 0.000502/2 X 5 = 0.001255 mol

[1]

Amount of $C_2O_4^{2-}$ in 25 cm^3 of **FA 1** =…0.001255 mol or 0.00126 mol…

1 **(b)** **(ii)** Determine the concentration, in mol dm^{-3}, of $C_2O_4^{2-}$ in **Q**.

amount of $C_2O_4^{2-}$ in 250 cm^3 of FA 1 = 0.001255 X 10 = 0.01255 mol

$[C_2O_4^{2-}]_{in\ \mathbf{Q}}$ = 0.01255 / (35.70/1000) = 0.3516 mol dm^{-3}

[2]

Concentration of $C_2O_4^{2-}$ in **Q** =…0.3516 or 0.352 mol dm^{-3}

(iii) Use your answer to **(b)(ii)** to calculate the M_r of the ethanedioate salt.

M_r of $\mathbf{X}_2C_2O_4.H_2O$ = 64.5 / 0.3516 = 183.4

M_r of the ethanedioate salt = 183.4 ……………

Hence, deduce the identity of **X**.
Show your working.

[A_r: C, 12.0; O, 16.0; H, 1.0; Li, 6.9; Na, 23.0; K, 39.1; Rb, 85.5; Cs, 132.9; Fr. 223.0]

Ar of X = [183.4 – 2(12.0) – 5(16.0) – 2(1.0)]/2 = 38.7

X = Potassium

[3]

X is K……

1 **(c)** A student performed the experiment in **(a)(i)** using a sample of another ethanedioate salt. The student obtained a mean titre value of 22.20 cm^3. The teacher calculated that the volume of **FA 2** required should have been 22.40 cm^3. The teacher told the student that the total percentage error from the apparatus in the experiment was 0.4 %.

Calculate the error in the student's result, based on these data. State **and** explain whether or not the student's result is accurate.

Student's experimental error = $\frac{22.40 - 22.20}{22.40} \times 100\% = 0.8928 = 0.893\%$

Since student's experimental error (0.893%) is more than the apparatus error(0.4%), therefore the student's result is inaccurate.

[2]

[Total: 14]

2 Evaluation of the reliability of a gas collection method in determining a value for the *M*$_r$ of the ethanedioate salt.

In this experiment, you will react the ethanedioate salt with potassium manganate(VII), in the presence of a small amount of manganese(II) ions. You will measure the volume of CO_2 gas produced at timed intervals and determine the maximum volume of CO_2 gas produced.

FA 4 is a solution containing manganese(II) ions, Mn^{2+}.

You will need access to the **FA 1**, **FA 2** and **FA 3** solutions you used earlier.

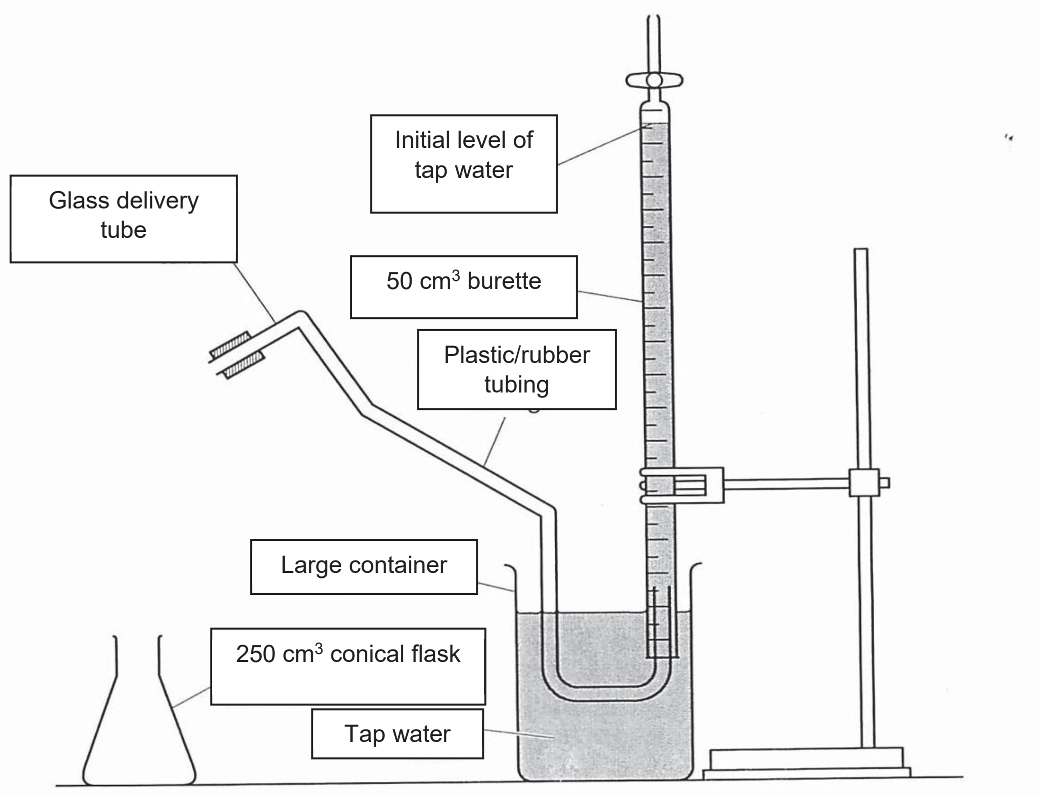


Fig. 2.1

You will measure the level of water in the burette at timed intervals.

In an appropriate format in the space provided on page 7, prepare a table in which you may record each burette reading and the time it was taken.

In addition, your table will need to show the total volume of CO_2 collected up to that time, recorded to one decimal place.

1. Set up the apparatus as shown in Fig. 2.1. You should insert the plastic/rubber tubing to a sufficient depth so that it will not subsequently shake loose.

2. Adjust the water level in the burette until it is between 48.0 cm^3 and 50.0 cm^3. You may find it helpful to use an empty dropping pipette to introduce small amounts of air from the bottom of the burette tube.
3. Use appropriate measuring cylinders to add to the 250 cm^3 conical flask.
   - 20.0 cm^3 of **FA 1**
   - 50.0 cm^3 of **FA 3**
4. Using a dropping pipette, add about 1 cm^3 of **FA 4** to the conical flask.
5. Using an appropriate measuring cylinder, measure out 30.0 cm^3 of **FA 2.**
6. Transfer the **FA 2** into the conical flask and insert the bung into the conical flask.
7. Allow any bubbles created in the burette when the bung was inserted in the conical flask to rise to the top. Start the stopwatch, read and record the initial water level in the burette.
8. Note: Once you have started the stopwatch, allow it to continue running for the duration of the experiment. You must not stop the stopwatch until the reaction is complete.
9. Check that the plastic/rubber tubing is securely positioned in the burette.
10. Hold the flask by its neck and gently swirl it continuously.
11. At *t* = 0.5 min, read and record the water level in the burette, to 1 decimal place, together with the time it was measured, in your table.
12. Continue to gently swirl the flask. Read and record the water level in the burette every half minute, until the reaction is complete.

(a) (i) Experimental Results

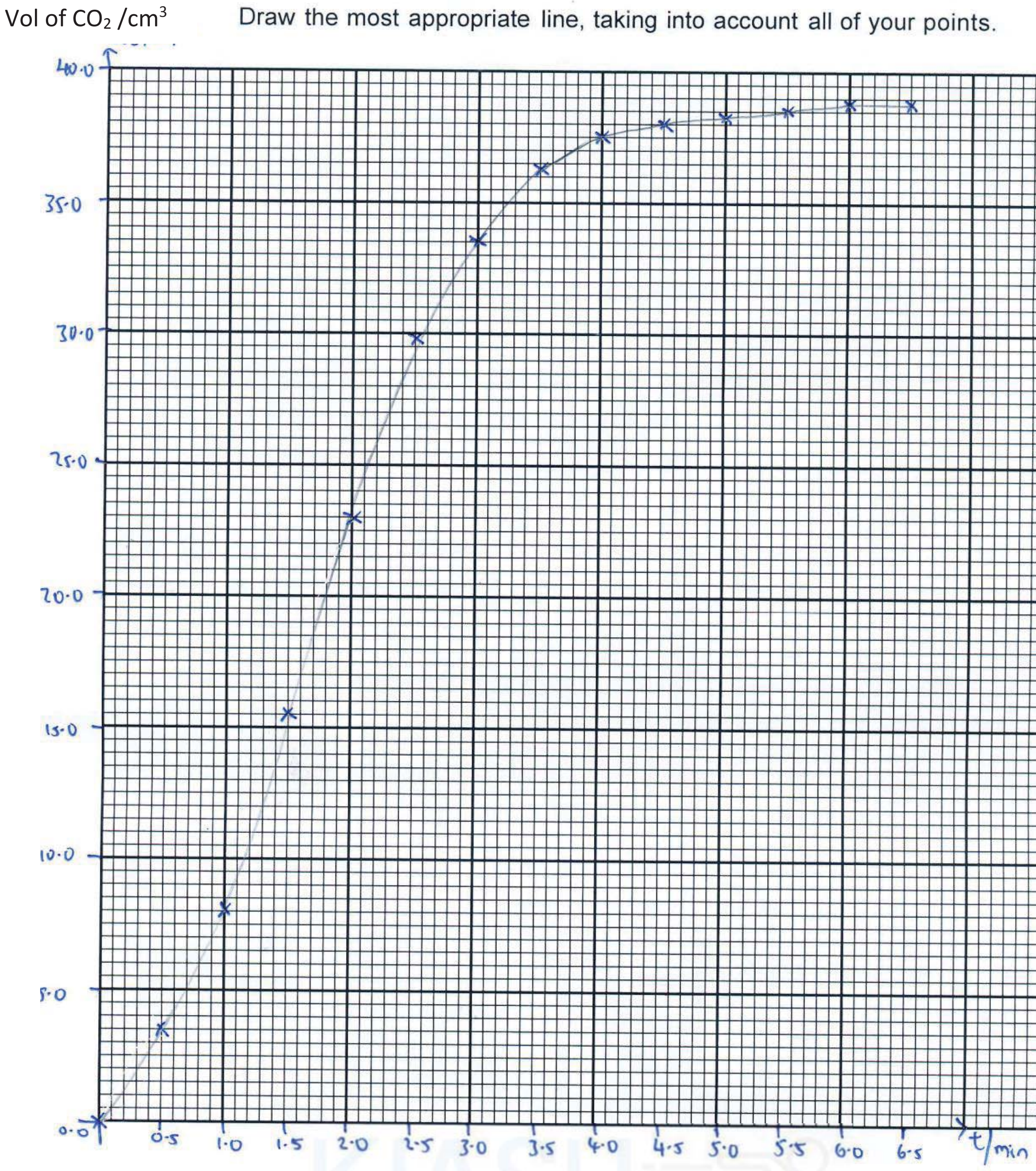
Time / t / min	Burette reading / cm^3	(Volume / vol) of CO_2 / cm^3
0.0	50.0	0.0
0.5	46.5	3.5
1.0	42.0	8.0
1.5	34.5	15.5
2.0	27.0	23.0
2.5	20.2	29.8
3.0	16.5	33.5
3.5	13.8	36.2
4.0	12.5	37.5
4.5	12.0	38.0
5.0	11.6	38.4

5.5	11.5	38.5
6.0	11.4	38.6
6.5	11.4	38.6
7.0	11.4	38.6

[3]

2 **(a)** **(ii)** Plot on the grid below, a graph of the volume of CO_2 on the y-axis, against time, *t,* on the x-axis

Draw the most appropriate line, taking into account all of your points.



[4]

2 **(a)** **(iii)** The equation for the reaction between ethanedioate ions and manganate(VII) ions is shown below.

$5C_2O_4^{2-}(aq) + 2MnO_4^{-}(aq) + 16H^{+}(aq) \rightarrow 10CO_2(g) + 2Mn^{2+}(aq) + 8H_2O(l)$

Use this equation, and appropriate data from your graph, to calculate a value for the amount, in moles of ethanedioate ions, $C_2O_4^{2-}$, present in 20.0 cm^3 of **FA 1**.

[molar volume of gas = 24.0 $dm^3\ mol^{-1}$ at r.t.p.]

From graph, max volume of CO_2 = 38.55 cm^3

amount of CO_2 produced = 38.55 / 24000 = 0.001606 mol

amount of $C_2O_4^{2-}$ in 20.0 cm^3 of FA1 = 0.001606 / 2 = 0.000803 mol

Amount of ethanedioate ions, $C_2O_4^{2-}$, in 20.0 cm^3 of **FA 1** = 0.000803 mol **[1]**

(b) **(i)** Using your answer to question **1(b)(i)**, calculate the amount of ethanedioate ions in 20.0 cm^3 of **FA 1**. Hence, determine the maximum volume of CO_2 at r.t.p. that could have been produced from 20.0 cm^3 of **FA 1**.

amount of $C_2O_4^{2-}$ in 20 cm^3 of FA 1 = 0.001255 / 25 X 20 = 0.0001004 mol

amount of CO_2 produced = 0.0001004 X 2 = 0.002008 mol

maximum volume of CO_2 = 0.002008 X 24000 = 48.19 cm^3

maximum volume of CO_2 produced from 20.0 cm^3 of **FA 1** = 48.2 cm^3 **[4]**

(ii) Suggest a reason for the difference between the total volume of CO_2 you collected and the maximum volume of CO_2 calculated in **2(b)(i)**.

Some of the CO_2 could have stayed dissolved in the water bath/Some CO_2 could have escaped when the conical flask was stoppered. **[1]**

(iii) Suggest an improvement to this experiment that would overcome this problem.

Uses a non-aqueous gas collecting system such as a frictionless gas syringe. **[1]**

Use a dropping funnel to add in **FA2** to start the reaction to minimise the escaping of gas.

2 **(b)** **(iv)** In Question **1** you calculated a value for the M_r of the ethanedioate salt. The total volume of CO_2 collected in **2(a)(i)** could also be used to calculate a value for the M_r of the ethanedioate salt.

Suggest which of these two M_r values would be higher. Explain your answer.

The M_r calculated from the collection of gas method will be higher as the volume measured will be lower than expected, causing the number of moles of salt to be lower and hence the M_r to be higher. **[1]**

(c) The presence of Mn^{2+} ions, which are produced in the reaction between MnO_4^- ions and $C_2O_4^{2-}$ ions, is thought to catalyse this reaction.

(i) A student performed the experiment you performed in **2(a)(i)** but forgot to add **FA 4** to the mixture of **FA 1** and **FA 3** before adding the **FA 2**.

The student performed the experiment at the same temperature as your experiment and obtained the graph shown in **Fig. 2.2**.

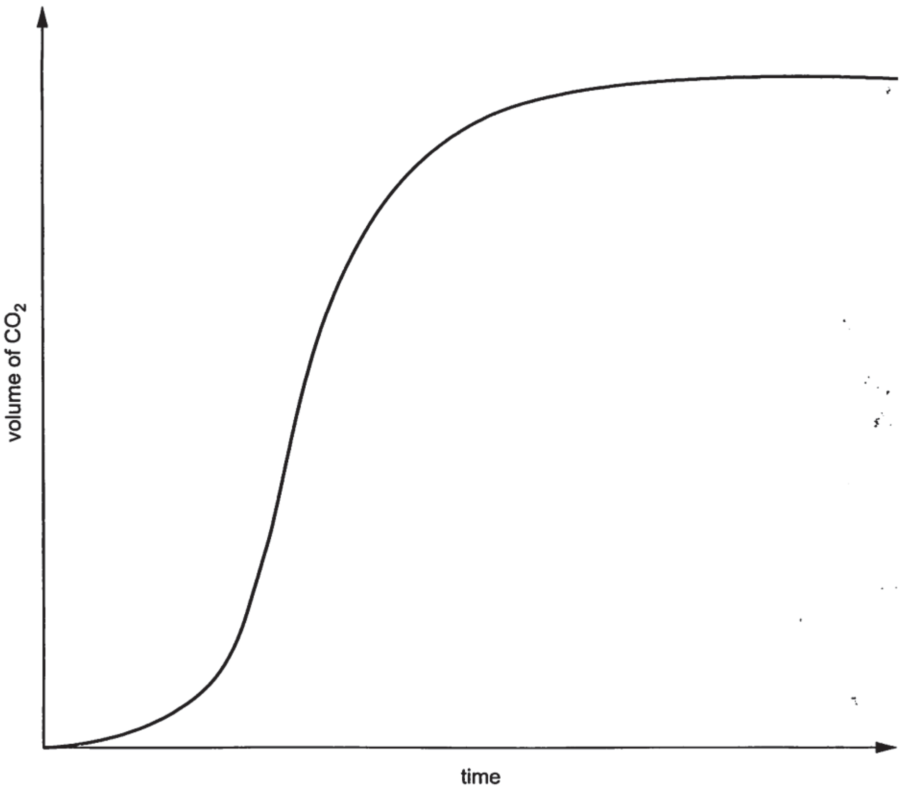


Fig. 2.2

2 **(c)** **(i)** Consider the **shape** of the graph in **Fig 2.2** and your graph in **2(a)(ii)**.

Describe one major difference between the shapes. Suggest an explanation for your answer.

Difference The graph in 2(a)(ii) is steeper at the start of the experiment.

Explanation Mn^{2+} was added right from the start and hence the reaction was catalysed right from the beginning unlike the student's experiment where there were little Mn^{2+} at the beginning to catalyse the reaction, causing the student's initial gradient to be gentler. **[2]**

(ii) For the titration in **1(a)(i)** between ethanedioate ions, $C_2O_4^{2-}$, and manganate(VII) ions, MnO_4^-, the solution needs to be at about 65 °C at the start. As cold **FA 2** is added, the temperature of the mixture decreases. However, this decrease in temperature does not cause the rate of reaction between $C_2O_4^{2-}$ ions and MnO_4^- ions added from the burette to decrease.

Suggest an explanation for this.

The stable rate is due to Mn^{2+} ions being produced. The presence of the Mn^{2+} catalyst cancels out the effect of the drop in temperature. **[1]**

2 (d) Planning

The oxidation of iodide ions, I^-, by peroxodisulfate ions, $S_2O_8^{2-}$, is known to be catalysed by Fe^{2+} or Fe^{3+} ions.

A similar reaction, shown below, in which ethanedioate ions, $C_2O_4^{2-}$, are oxidised by peroxodisulfate ions, $S_2O_8^{2-}$, may be catalysed by Cu^{2+} ions and by Ag^+ ions.

$$S_2O_8^{2-} + C_2O_4^{2-} \rightarrow 2\ SO_4^{2-} + 2\ CO_2$$

(i) Suggest an explanation why both of these reactions are slow when performed in the absence of a catalyst.

The reactants are both negatively charged and experience repulsion and thus resulted in a high activation energy barrier between them. **[1]**

(ii) Plan an investigation to test how well, **if at all**, Cu^{2+} ions and by Ag^+ ions catalyse the reaction between $C_2O_4^{2-}$ ions and $S_2O_8^{2-}$ ions.

In your plan, you should include details of:

- the reactants and conditions that you would use,
- the apparatus you would use and the procedure you would follow,
- the measurements you would take,
- an outline of how you would use your results to compare the effectiveness of each ion as a potential catalyst.

Suggested Planning Procedure

Note: It was assumed that the temperature and pressure conditions for the conduct of the 3 experiments is at rtp conditions

Experiment 1 (uncatalysed reaction)

1. Using a 50 cm^3 measuring cylinder, measure out 15 cm^3 of **$X_2C_2O_4$ of concentration 0.05 moldm^{-3}** into a 250 cm^3 conical flask. Add 5 cm^3 of deionised water using a dropping pipette (or 10 cm^3 measuring cylinder).
2. Use a separate 50 cm^3 measuring cylinder, measure out 20 cm^3 of a solution of $Na_2S_2O_8$ of concentration 0.05 moldm^{-3}.
3. Set up the apparatus as shown in Fig. 2.1
4. Check that the plastic/rubber tubing is securely positioned in the burette.
5. Transfer the 20 cm^3 of a solution of $Na_2S_2O_8$ into the conical flask and insert the bung into the conical flask. (Using dropping funnel to transfer 20 cm^3 of solution will be better to minimise gas escape.)
6. Allow any bubbles created in the burette when the bung was inserted in the conical flask to rise to the top. Start the stopwatch, read and record the initial water level in the burette.
7. Hold the flask by its neck and gently swirl it continuously.
8. At t = 0.5 min, read and record the water level in the burette, to 1 decimal place, together with the time it was measured, in your table.
9. Continue to gently swirl the flask. Read and record the water level in the burette every half minute, until the reaction is complete. i.e. at least 3 burette readings are the same.
   (Estimated volume of CO_2 is 36 cm^3)

Pre-Calculation:

No. of moles of $C_2O_4^{2-}$ (limiting agent) = 0.05x15/1000 = 0.00075 mol

Volume of CO_2 produced

= 0.00075 X 2 X 24000 = 36 cm^3 assuming r.t.p.

Catalysed Experiment 2 and 3

10. Repeat steps 1 to 9 but now with the introduction of the catalysts Ag^+ (Experiment 2) and Cu^{2+} (Experiment 3), once at each time. Do take note that 5 cm^3 of each catalyst (of equal concentration 0.100 mol dm^{-3} is to be added in **step 1**.
11. Compare the time taken for the maximum amount of CO_2 to be produced for Experiment 1 (uncatalysed reaction) with Experiment 2 (Ag^+ as catalyst) and Experiment 3 (Cu^{2+} catalyst). The better catalyst

will be the one that produces the maximum amount of CO_2 in the shortest period of time.

Or Plot the graph of the volume of CO_2 against the time taken. The more effective catalyst is determined by the catalyst that produce a steeper gradient.

Alternatively,

9. Record the time required to produce 20 cm^3 (a stated volume, based on pre-calculation) of CO_2. The more effective catalyst is determined by the catalyst that produce the volume in a shorter time.

[7]

[Total: 26]

3 You are provided with the solid **K12** which contains one cation given in the Qualitative Analysis Notes.

You are to perform the tests below to identify the cation present in **K12** and suggest the nature of **K12.** Record your observations in the spaces provided. Your answers should include

- Details of colour changes and precipitates formed,
- The names of any gases evolved and details of the test used to identify each one.

You should indicate clearly at what stage in a test a change occurs.

Marks are **not** given for chemical equations.

No additional or confirmatory tests for ions present should be attempted.

Tests	**Observations and Deductions**
1 Heat **K12** alone.	K **12** turns to a colourless liquid. Gas evolved turns moist blue litmus red Gas evolved turns acidified $KMnO_4$ paper colourless SO_2 (g) Gas relights glowing splinter O_2(g)
2 Warm **K12** with dilute hydrochloric acid. Keep the solution.	Gas evolved turns moist blue litmus red then bleaches Cl_2 (g) Oxidising agent present

3	To the solution from test **2**, add dilute nitric acid and barium nitrate(V) solution	White ppt forms, insoluble in acid. SO_4^{2-} $BaSO_4$ ppt
4	Warm **K12** with a freshly made solution of iron(II) sulfate solution.	Pale green solution turns brown/ red brown K **12** is an oxidising agent
5	Dissolve **K12** in dilute nitric acid. Add manganese(II) sulfate solution and two drops of silver nitrate(V) solution to act as a catalyst. Boil the mixture.	Pale pink colour turns brown then to black/purple solution (ppt) Mn^{2+} oxidise to MnO_2 then to MnO_4^- K **12** is an oxidising agent
6	Warm **K12** with sodium hydroxide solution.	Colourless solution obtained. Pungent smell gas which turns moist red litmus blue NH_3 gas NH_4^+ present

Nature of **K12:** **Oxidising agent**

Cation it contains: NH_4^+

[9]

[Total: 9]

4 Planning

You are provided with 3 unlabelled bottles and each bottle contains one of the following organic compounds,

- Butanamide
- Lactic acid, $CH_3CH(OH)CO_2H$
- Pyruvic acid, CH_3COCO_2H

(a) Outline a sequence of simple chemical tests to identify each of the above organic substances. You may use any other common laboratory chemical reagents and apparatus, if necessary. You are **not** allowed to identify the substances by elimination. You are reminded that most of the compounds listed are *flammable* liquids. **[3]**

Test	Expected Observations & Deductions
Using a dropper, add 1 cm^3 of compound into 3 separate test-tubes. To 1 cm^3 of compound in a test-tube, add 2 cm^3 of aqueous NaOH. Boil/ Heat in a **water bath** for 5-10 min. Test any gas evolved with moist red litmus paper	**Moist red litmus paper turns blue (NH_3) - butanamide**
To the 2 samples that did not produce a positive observation for test 1, using a dropper to 1 cm^3 of compound in a test-tube, add 1 cm^3 of 2,4 DNPH dropwise until excess. Warm the mixture.	**Orange ppt forms. – pyruvic acid**
To 1 cm^3 of the compound in a test-tube, add 1 cm^3 of dilute sulfuric acid, follow by a few drops of $K_2Cr_2O_7$(aq). Heat the mixture in a hot water-bath for 3 -5 min.	**Orange solution turns green-lactic acid**
Alternatives: pyruvic acid can be tested with 2,4 DNPH, warm ➔ lactic acid with aqueous Na_2CO_3 ➔ butanamide with NaOH(aq), heat.	

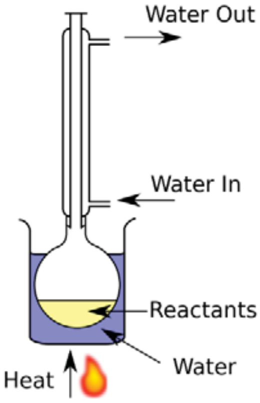
(b) Suggest a safety measure that you would consider in carrying out your plan.

Using a hot water bath for heating instead of using a direct naked flame from the Bunsen burner as most organic compounds are highly flammable.

[1]

(c) State the required reagents and conditions. Draw a set-up of the apparatus for the synthesis of pyruvic acid from lactic acid.

$KMnO_4(aq)/H_2SO_4(aq)$, heat under reflux OR $K_2Cr_2O_7(aq)/ H_2SO_4(aq)$, heat under reflux



[2]

[Total: 6]

The End

Marking Procedure

Hierarchy to be used in calculating mean titres in question 1(a)(i):

- value of 2 identical titres
- average of titres within 0.05 cm^3
- average of titres within 0.1cm^3, etc.

Use the selected titres to determine the mean titre for the end-point.

Note: For calculations, the principle of no double penalty (error carried forward) applies. For connecting parts, marking from point of first enalty onwards will be based on correct method only.

Qn	Skills assessed	Marking Scheme	Mark	Mark Ref (MR)
1(a)(i)	PDO Layout **P1**	Tabulates initial and final burette readings and volume added in the titration table. Table has correct headers and units. Tabulation may be vertical or horizontal; lines are not essential but there should be no absences of headers. Where units have not been included in the header, there should be the appropriate unit for each entry in the table. Do NOT award this mark if any final and initial burette readings are inverted or 50 is used as the initial burette reading.	1	**1**
	PDO Record **P2**	All the final/initial burette readings, for all accurate titres in the titration table, are recorded to the nearest 0.05 cm^3. Treat all titres as "accurate" unless labelled 'rough' or first titre is recorded to a lower precision than subsequent titres.	1	**2**
	MMO Quality **M1**	Has at least two uncorrected titres for end-point within 0.10 cm^3. *Uncorrected titres refers to flawed calculated titres by the candidate.*	1	**3**
A student's 'rough'/'trial' titre value can be considered by the examiner when selecting titre values for the mean titre calculation if the student has 'validated' this value either by ticking it or by using it in an expression in (a)(ii). (By doing either of these, the student has declared it to be no longer a 'rough' / 'trial' value).				

1(a)(i)	MMO Quality Accuracy **M2** **M3**	Calculate the student's **mean titre as described on page 3**. Award **MR4** to **MR6** based on the difference, Δ titre, between Student's and Supervisor's mean titre. Give 2 marks Give 2 marks if this difference is ≤ ±0.20 Give 1 marks if this difference is > ±0.20 but ≤ ±0.40 Give 0 mark if this difference is > ±0.40	2	**4** **5**
(ii)	MMO Decision **M4**	Student obtains appropriate "average", to 2 d.p., from any experiments with uncorrected end-point titre values within 0.20 cm^3. Do not award this mark if the titres used are not identified either in the table (by, for example, a tick) or in a calculation. Do not award this mark if there are arithmetic errors in the table.	1	**6**
(b)(i)	ACE Interpret **A1**	(Let mean titre volume = V_m) $nMnO_4^-$ = V_m X 10^{-3} X 0.0200 = n_1 $nC_2O_4^{2-}$ in 25.0 cm^3 = n_1 X 5/2 = n_2	1	**7**
(ii)	ACE Interpret **A2** **A3**	[$C_2O_4^{2-}$] in **FA1** = n_2 ÷ (25.0/1000) [$C_2O_4^{2-}$] in **Q** = [$C_2O_4^{2-}$] in **FA1** X 250 ÷ (35.70/1000) Alternative method: $nC_2O_4^{2-}$ in 250 cm^3 = 10 n_2 [$C_2O_4^{2-}$] in **Q** = 10 n_2/ 35.7 X 1000	1 1	**8** **9**
(iii)	ACE Interpret **A4** **A5** **A6**	$M_r(X_2C_2O_4.H_2O)$ = 64.5 ÷ [$C_2O_4^{2-}$] in **Q** = M_r(Salt) A_r(**X**) = (M_r(Salt) – 88 – 18) ÷ 2 Calculates A_r (i.e ÷ 2) **and** **X** = group 1 metal closest to A_r(**X**) = (potassium/**K**)	1 1 1	**10** **11** **12**
1(c)	ACE Interpret **A7**	Overall experimental error = $\frac{22.40 - 22.20}{22.40} \times 100\% = 0.890\%$ Candidate states experiment is not accurate	1	**13**

	Conclusion **A8**	**and** justifies this in terms of experimental error being> apparatus error. Allow ecf argument based on incorrectly calculated experimental error. (Note: Do not award MR14 if no calculation of error is done)	1	**14**
Question 2				
2(a)(i)	PDO Layout **P3**	Tabulates burette readings at times t = 0 until the end of the experiment, time/min and volume of CO_2/cm^3. Tables have correct headers and units Tabulations may be vertical or horizontal; lines are not essential but there should be no absences of headers. Where units have not been included in the header, there should be the appropriate unit for each entry in the table.	1	**15**
	PDO Record **P4**	All burette readings and CO_2 volumes to **0.1cm³**, and times to **0.5 min**	1	**16**
	MMO Collecting **M5**	Full set of results with final readings which have 2 to 3 values that are the same.	1	**17**
(ii)	PDO Layout **P5**	Axes correct way round + correct labels + units + scale. Sensible linear scale must be chosen so that plotted points occupy at least half the graph grid in both x and y directions Penalise for	1	**18**
	PDO Layout **P6**	All points correctly plotted to within $\pm\frac{1}{2}$ small square. Check all points and put ticks if correct.	1	**19**
2(a)(ii)	PDO Manipulate **P7**	Graph line must be best fit line.	1	**20**

	MMO Quality **M6**	Award MR22 based on the difference, Δvolume$_{CO2}$, between student's and Supervisor's values for the maximum volume of CO_2 collected. Give 1 mark if this difference is ≤ 5.0 cm^3 Give 0 marks for a difference > 5.0 cm^3	1	**21**
(a)(iii)	ACE Interpret **A9**	$nC_2O_4^{2-}$ = (volume of CO_2 collected ÷ 24000) /2	1	**22**
(b) (i)	ACE Interpret **A10**	$nC_2O_4^{2-}$ in 20 cm^3 of **FA1** = n_2 X (20.0/25.0) = n_3 max volume CO_2 = n_3 X 24000 X 2 (cm^3)	1	**23**
	PDO Display **P8**	Shows working in all calculations in **1(b)**, **1(c)**, **2(a)(iii)** and **2(b)(i)**. All calculations must be relevant although they may not be complete or correct. Any calculation not attempted loses this mark.	1	**24**
	PDO Display **P9**	Shows appropriate significant figures (3 or 4 sf) in **all** final answers in **1(b)**, **1(c)**, **2(a)(iii)** and **2(b)(i)**. Any calculation not attempted loses this mark.	1	**25**
	PDO Display **P10**	Shows appropriate units in all answers in **1(a)(ii),** (cm^3); **1(b)(i)**, (mol); **1(b)(ii)**, (moldm^{-3}); **1(c)**, (%); **2(a)(iii)**, (mol) and **2(b)(i)**, (cm^3). Any calculation not attempted loses this mark.	1	**26**
2(b)(ii)	ACE Conclusion **A11**	Collected volume of CO_2 lower than max volume as **some CO_2 dissolved in water.** OR **Some gas escaped** when/before the conical flask was stoppered. Allow other relevant answers.	1	**27**

(iii)	ACE Improve **A12**	Uses a non-aqueous gas collecting system such as a syringe. Use a dropping funnel to add in **FA2** to start the reaction to minimise the escaping of gas. Allow other relevant	1	**28**
(b)(iv)	ACE Interpret **A13**	Argues clearly that as the **volume of CO_2 measured is too low**, so $nC_2O_4^{2-}$ will be too low, so **M_r (likely to be) too high**.	1	**29**
(c)(i)	ACE Interpret **A14**	Difference: Describes that the shape of the given graph **shows a slow initial rate that increases** after some time whilst the candidate's own graph shows **a fast rate from the start** Explanation: In student's experiment without the addition of FA 4, Mn^{2+} formed by reaction catalyses the reaction and increases rate so the gradient of the graph becomes steeper.	1	**30**
	A15	Or at the beginning, there is very little Mn^{2+} to catalyse the reaction, hence the gradient of the graph is gentler.	1	**31**
(ii)	ACE Interpret **A16**	The stable rate is due to more Mn^{2+} ions being produced. As the concentration of the Mn^{2+} catalyst increases it cancels out the effect of the drop in temperature.	1	**32**
(d)(i)	Plan **PI1**	Repulsion between two negatively charged ions causes the activation energy to be high.	1	**33**
(ii)	Plan **PI2**	1. Describes a **sensible 'end-point'**; either the **time required to produce a stated volume of CO_2** or the **time needed for the reaction to be completed**.	1	**34**
	PI3	2. Proposes to use **the apparatus** specified from **2(a)** – or improved but workable apparatus and adds the catalyst before one of the reactants.	1	**35**
	PI4	3. Stipulates that the **same temperature** must be used. It is not necessary to describe how this is to be done in this case, but simply to state that it must be done. Allow the description of any sensible method of achieving this for this mark, even if 'to ensure that the same temperature is used' is not specifically stated.	1	**36**
		4. Controls concentrations and volumes for all other reactants.	1	**37**
	PI5	5. Proposes the **use of a non-catalysed control** to identify any TM Ions that do not catalyse this reaction.	1	**38**
	PI6		1	**39**

	PI7	6. Uses equal amounts (moles) of each TM ion either weighing out each TM compound or makes up equal concentrations of TM compounds solutions and uses equal volumes. **7.** Compares results on the basis of <u>**fastest / least time**</u> is the best catalyst. **Or compare volume within a specified time.**	1	**40**

3. Carry out the following experiments with K **12**. Enter your observations and deductions in the space provided.

Tests	Observation and Deduction
1 Heat K **12** alone	K **12** turns to a **colourless liquid**. [1] Gas evolved turns moist blue litmus paper red[1] Gas evolved **turns acidified $KMnO_4$ paper colourless** [1] SO_2 (g) [1] Gas relights glowing splinter [1] O_2(g) [1]
2 Warm K **12** with ilute hydrochloric acid. eep the solution.	Yellowish green gas, pungent smell, turns **moist blue litmus red then bleaches** [1] Cl_2 (g) [1] Oxidising agent present [1]
3 To the solution from est **2**, add dilute nitric cid and barium nitrate V) solution	White ppt forms [1] $BaSO_4$ ppt $SO_4{}^{2-}$[1]
4 Warm K **12** with a reshly made solution of ron(II) sulfate solution	Pale green solution turns **brown/ red brown** [1] K **12** is an oxidising agent [1]
5 Dissolve K **12** in nitric nitric acid. Add manganese(II) sulfate solution and two drops of silver nitrate(V) solution to act as a catalyst. Boil the mixture	Pale pink colour turns **brown then to black ppt (or black solution or purple solution)** [1] Mn^{2+} oxidise to MnO_2 then to MnO_4^- K **12** is an oxidising agent [1]
6 Warm K **12** with sodium hydroxide solution	**Colourless** solution obtained. [1] Pungent smell gas which turns **moist red litmus blue** [1] NH_3 gas[1] NH_4^+ present [1]

You are not required to identify K **12** but write any deductions you can about the ions it contains.

Nature of K **12**: ___**Oxidising agent**______________________

Cation it contains: ____NH_4^+__________________ ___

[Total: 9]

3 – 9 bservations	5 marks	**6-9 deductions**	4 marks
6-7 observations	4marks	**4-5 deductions**	3 marks
4-5 observations	3 marks	**2-3 deductions**	2 marks
3 observations	2 marks	**1 deductions**	1 mark
2 observations	1 marks		
1 observation	0 marks		

4.

You are provided with 3 unlabelled bottles and each bottle contains one of the following organic compounds,

- Butanamide
- Lactic acid, $CH_3CH(OH)CO_2H$
- Pyruvic acid, CH_3COCO_2H

(a) Outline a sequence of simple chemical tests to identify each of the above organic substances. You may use any other common laboratory chemical reagents and apparatus, if necessary. You are **not** allowed to identify the substances by elimination. You are reminded that most of the compounds listed are *flammable* liquids.

(a) Test	Expected Observation
Using a dropper, add 1 cm^3 of compound into 3 separate test-tubes. **To 1 cm^3 of compound in a test-tube, add 2 cm^3 of aqueous NaOH.** **Boil in a water bath for 5-10 min.** **Test any gas evolved with moist red litmus paper**	**Moist red litmus paper turns blue (NH_3) - butanamide**
To the 2 samples that did not produce a positive observation for test 1, using a dropper to 1 cm^3 of compound in a test-tube, add 2,4-DNPH dropwise until excess. Warm the mixture.	**Orange ppt forms. – pyruvic acid**
To 1 cm^3 of the compound in a test-tube, add a few drops (or 1-2 drops) of acidified $K_2Cr_2O_7(aq)$. Heat the mixture in a hot water-bath	**Orange solution turns green-lactic acid**

If missing quantities /details, credit 1 mark for right sequence of test with correct observations.

(b) Suggest a safety measure that you would consider in carrying out your plan. [1]

Using a **hot water bath** for heating instead of using a direct naked flame from the Bunsen burner **as most organic compounds are highly flammable**.

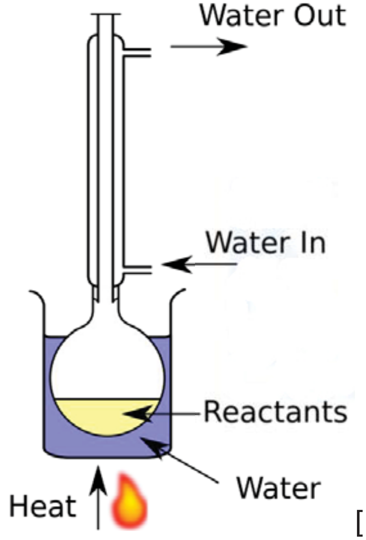
Or Wear gloves because organic acids/sulfuric acid are corrosive.

OR Wear goggles to protect the eyes from contact with chemicals.

) Draw a set-up of the apparatus for the synthesis of pyruvic acid from lactic acid. State the required reagents and conditions. [2]

Reagents and conditions: $KMnO_4$(aq)/H_2SO_4(aq), heat (under reflux) OR [1]

$K_2Cr_2O_7$(aq)/ H_2SO_4(aq), heat (under reflux)



[1]

Details of set-up must have:

- **Condenser with water in and out labelled**
- **Round-bottom flask**
- **Water bath**
- **Must label heat**

[Total: 6]