ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY **9729/01**
Higher 2

Paper 1 Multiple Choice

24 August 2017
1 hour

Additional Materials: Optical Answer Sheet
                          Data Booklet

READ THESE INSTRUCTIONS FIRST

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

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

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

Read the instructions on the Optical Answer Sheet very carefully.

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

Any rough working should be done in this booklet.

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

This document consists of **14** printed pages, including this cover page.

9729/01/Prelim/17   ANGLO-CHINESE JUNIOR COLLEGE
© ACJC 2017   Department of Chemistry   **[Turn over**

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

1 Carbon disulfide is a colourless volatile liquid with the formula CS_2. The compound is used frequently as a building block in organic chemistry as well as an industrial solvent.

It reacts with nitrogen monoxide, NO, to form a yellow solid and two gases. These two gases are formed in equal amounts.

What are these two gases?

A CO_2, NO_2 **B** CO_2, N_2 **C** CO, N_2 **D** CO_2, N_2O

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

Which of the following ions will be deflected the **most** in an electric field?

A S^{2-} **B** Br^- **C** F^- **D** O^{2-}

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

Nuclear magnetic resonance (NMR) spectroscopy is an analytical technique that uses the magnetic properties of certain atomic nuclei in order to elucidate the structure of an organic molecule.

Atomic nuclei with an even number of protons and an odd number of neutrons (or vice versa) are most suitable for NMR spectroscopy.

Which of the following nuclei is **least** suitable for NMR spectroscopy?

A ^{28}Si **B** ^{31}P **C** ^{103}Rh **D** ^{19}F

4 A 25.00 cm^3 sample of a solution of 0.150 mol dm^{-3} MoO_x^{2-} was passed through a Jones reductor (a column of zinc powder). It was reduced to Mo^{3+}. The filtrate required 22.50 cm^3 of 0.100 mol dm^{-3} acidified $KMnO_4$ (aq) to obtain back the original amount of MoO_x^{2-}.

What is the value of x?

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

5　Neoxanthin is a major xanthophyll found in green leafy vegetables such as spinach.
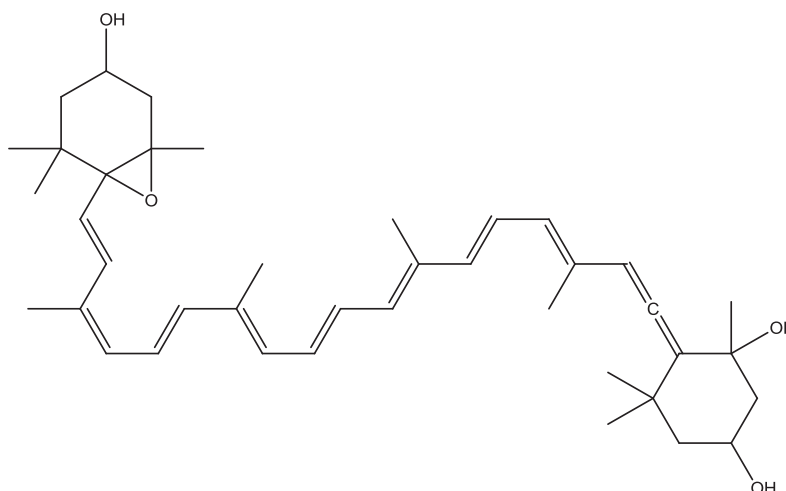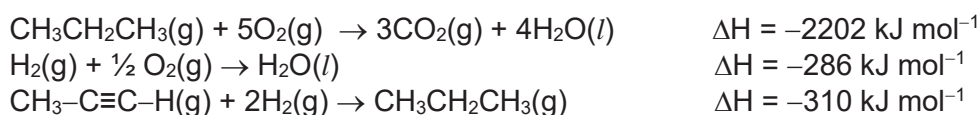

Which of the following σ bonds are present in neoxanthin?

1　A σ bond formed by sp^2–sp^3 overlap.

2　A σ bond formed by s–p overlap.

3　A σ bond formed by sp–sp^2 overlap.

A　1 and 2 only

B　1 and 3 only

C　2 and 3 only

D　1, 2 and 3

6　The enthalpy changes for the following reactions were measured experimentally:

$CH_3CH_2CH_3(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$　　　　$\Delta H = -2202$ kJ mol^{-1}
$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$　　　　$\Delta H = -286$ kJ mol^{-1}
$CH_3-C\equiv C-H(g) + 2H_2(g) \rightarrow CH_3CH_2CH_3(g)$　　　　$\Delta H = -310$ kJ mol^{-1}

What is the enthalpy change of combustion of propyne, $CH_3-C\equiv C-H$, in terms of kJ mol^{-1}?

A　-2226　　　　**B**　-1940　　　　**C**　-1606　　　　**D**　-1320

7　35 cm^3 of 0.001 mol dm^{-3} nitric acid solution was added to 35 cm^3 of sulfuric acid solution of the same concentration. What is the resulting pH of the combined solution?
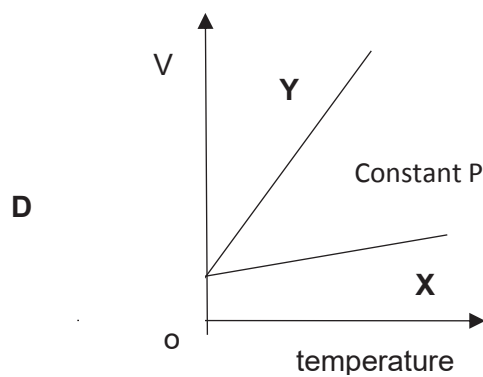
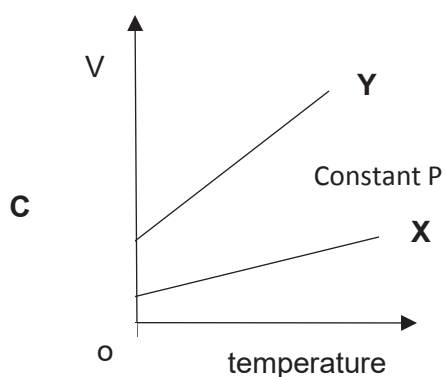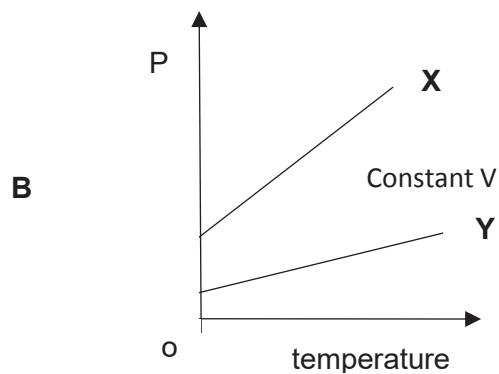**A**　1.5　　　　**B**　2.5　　　　**C**　2.8　　　　**D**　3.0
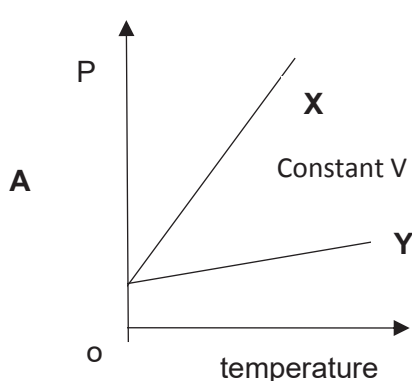
8   In which of the following pairs is the bond angle in the first species smaller than that in the second species?

    1 PBr_3, PBr_4^+

    2 H_2Se, H_2O

    3 SF_2, SCl_2

    A   1 and 2 only

    B   1 and 3 only

    C   2 and 3 only

    D   1, 2 and 3

9   **X** and **Y** are both ideal gases. **X** has the smaller molecular mass.
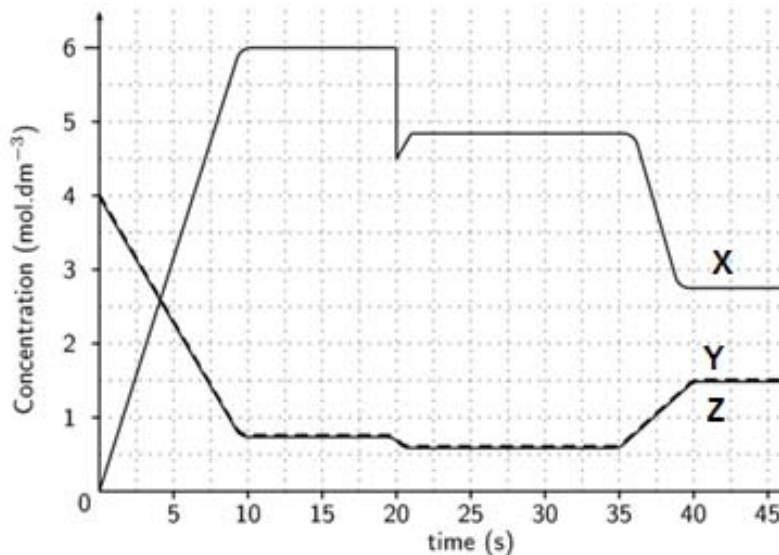
Which of the following diagrams correctly describe the behaviour of equal masses of these gases? All temperatures are measured in ^oC.

10 **X** exists in equilibrium with **Y** and **Z**.

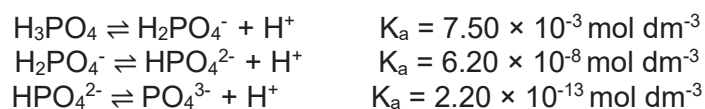$$2\mathbf{X}\,(g) \rightleftharpoons \mathbf{Y}\,(g) + \mathbf{Z}\,(g)$$

The concentrations of **X**, **Y** and **Z** varies across time as shown below. Note that the dotted line refers to both concentrations of **Y** and **Z**.

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

A   The equilibrium constant is dimensionless.

B   **X**(g) was taken out of the system at 20 s.

C   Given that the temperature was decreased at 35 s, it can be concluded that the forward reaction is endothermic.

D   Temperature has no effect on the spontaneity of this reaction.

11   The stepwise dissociation equations of phosphoric acid and the corresponding equilibrium constants are shown below.

$$H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+ \qquad K_a = 7.50 \times 10^{-3}\ mol\ dm^{-3}$$
$$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+ \qquad K_a = 6.20 \times 10^{-8}\ mol\ dm^{-3}$$
$$HPO_4^{2-} \rightleftharpoons PO_4^{3-} + H^+ \qquad K_a = 2.20 \times 10^{-13}\ mol\ dm^{-3}$$
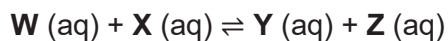
A phosphate buffer with pH 7 needs to be prepared.

Which is the best way to prepare such a solution?

A   Dissolving Na_3PO_4 alone in water.

B   Dissolving H_3PO_4 and NaH_2PO_4 in water.

C   Dissolving Na_2HPO_4 and Na_3PO_4 in water.

D   Dissolving Na_2HPO_4 and NaH_2PO_4 in water.

12 An equilibrium can be represented by the equation below.

$$W (aq) + X (aq) \rightleftharpoons Y (aq) + Z (aq)$$

In 0.50 dm³ of a certain mixture, the concentrations of these substances at equilibrium were as shown:

| Species	W	X	Y	Z
Concentration / mol dm⁻³	1.00	2.00	2.00	1.00

A certain amount of **Y** was added to this equilibrium mixture.

What is the number of moles of **Y** added such that the new equilibrium [**W**] is 1.20 mol dm⁻³?

Assume that the temperature remained constant throughout.

A 0.10 **B** 0.20 **C** 0.75 **D** 1.50

13 A sample of washing powder which contains a mixture of Na_2CO_3 and $NaHCO_3$ was titrated with aqueous hydrochloric acid and the following titration curve was obtained.
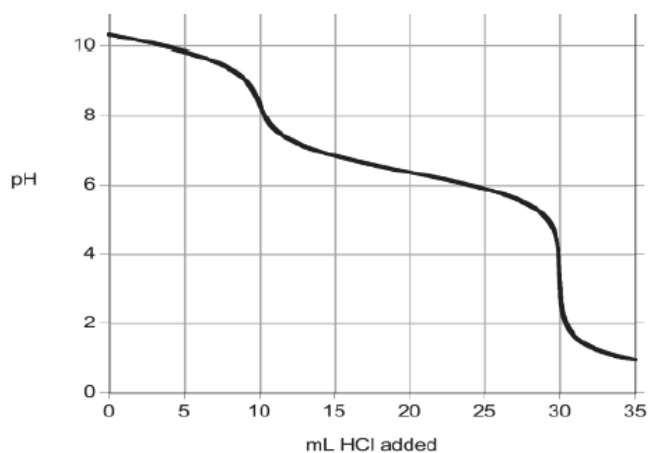
What is the mole ratio of HCO_3^- to CO_3^{2-} in the washing powder?

A 1:1 **B** 1:2 **C** 2:1 **D** 3:1

14 The table below contains the standard reduction potential values for some cobalt and mercury species.

half-equation	E°/ V
Co^{3+} (aq) + e $\rightleftharpoons$ Co^{2+} (aq)	+1.82
Co^{2+} (aq) + 2e $\rightleftharpoons$ Co (s)	-0.28
Hg^{2+}(aq) + e $\rightleftharpoons$ Hg^+(aq)	+0.91
Hg^+(aq) + e $\rightleftharpoons$ Hg(l)	+0.80

Which one of the following predictions is correct?

A   Both Co^{2+} and Hg^+ will disproportionate.

B   Neither Co^{2+} nor Hg^+ will disproportionate.

C   Only Co^{2+} will disproportionate.

D   Only Hg^+ will disproportionate.

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

The reaction between iodide and peroxydisulfate ($S_2O_8^{2-}$) is slow due to its high activation energy.

Which of the following cannot function as a catalyst for the above mentioned reaction?

A V^{2+} B Mn^{2+} C Mn^{3+} D Co^{3+}

16 The decomposition of hydrogen peroxide is a first order reaction.

It takes 20 minutes for a 0.140 mol dm^{-3} solution of hydrogen peroxide to halve its concentration.

How much time (in minutes) does it take for a 0.280 mol dm^{-3} solution of hydrogen peroxide to halve its concentration?

A   80   B   40   C   20   D   10

17 The reaction mechanism between O_2 and HBr is as proposed:
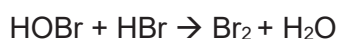
$HBr + O_2 \rightarrow HO_2Br$ (slow)

$HO_2Br + HBr \rightarrow 2HOBr$

$HOBr + HBr \rightarrow Br_2 + H_2O$

Which of the following statements is true?

    A   The bromine in HO_2Br is oxidised in the second step.

    B   The overall equation is $O_2 + 4HBr \rightarrow 2Br_2 + 2H_2O$.

    C   The half-life of this reaction is constant.

    D HO_2Br is the only intermediate.

18 The numerical values of the solubility products at 25 °C for $PbCl_2$ and PbI_2 are 1.70×10^{-5} and 9.80×10^{-9} respectively.

What is the value of the equilibrium constant for the reaction below?

$$PbI_2\ (s)\ +\ 2Cl^-\ (aq) \rightleftharpoons PbCl_2\ (s)\ +\ 2I^-\ (aq)$$

    A 3.01×10^6

    B 1.73×10^3

    C 5.76×10^{-4}

    D 3.32×10^{-7}

19 Mohr's salt is named after the German chemist Karl Friedrich Mohr, who made many important advances in the methodology of titration in the nineteenth century.

It is a double salt because it contains two cations and an anion.

Heating solid Mohr's salt with sodium hydroxide liberated a colourless gas. A green precipitate is also formed. It was insoluble in excess sodium hydroxide. On standing in air the solid turned brown.

What is the formula of Mohr's salt?

    A $AgCr(CO_3)_2$

    B $Ag_2Fe(CO_3)_2$

    C $Fe(NH_4)(SO_4)_2$

    D $Fe(NH_4)_2(SO_4)_2$

20 Photographic film contains silver halides, which absorb light to form silver metal and halogens are formed. Different silver halides have different sensitivity to light and will undergo this process to a different extent.

During the development of the film, a solution of aqueous ammonia or sodium thiosulfate is used to dissolve the unreacted silver halides. However, sodium thiosulfate is preferred, as some silver halides are not soluble in aqueous ammonia.

Which statements concerning the above processes are correct?

1 Metallic silver forms a very stable complex with thiosulfate, hence silver halides are soluble.

2 The decomposition of the silver halide to metallic silver and the respective halogen is easier for AgBr than for AgC*l* because bromide is more reducing than chloride.

3 AgBr is less soluble than AgC*l* in aqueous ammonia, as solubility product of AgC*l* is of a higher value.

A 1 and 2 only

B 1 and 3 only

C 2 and 3 only

D 1, 2 and 3

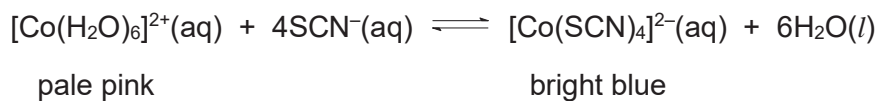**21** *Use of the Data Booklet is relevant to this question.*
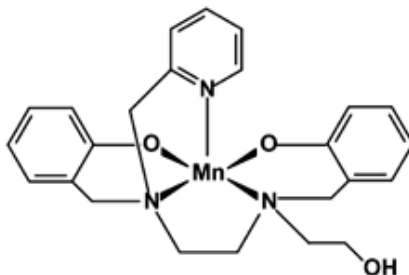
Which of the following statements about the above complex is **false**?

A There are no 4s electrons in manganese in this complex.

B This complex contains five ligands.

C The coordination number of this complex is 5.

D The oxidation number of manganese in this complex is +2.

22 Cobalt forms many coloured complexes with ligands such as H_2O and SCN^-.

A 100 cm³ solution of $Co^{2+}(aq)$ turns from pink to bright blue when 10 cm³ of NaSCN(aq) is added to the solution.
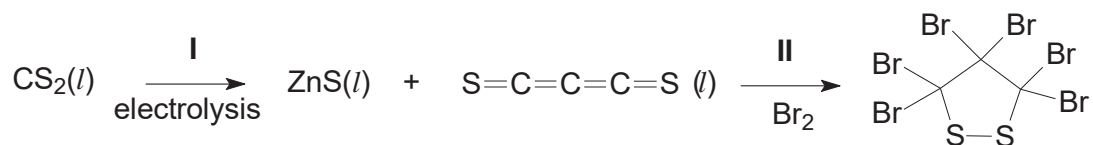
$$[Co(H_2O)_6]^{2+}(aq) + 4SCN^-(aq) \rightleftharpoons [Co(SCN)_4]^{2-}(aq) + 6H_2O(l)$$

      pale pink   bright blue

At equilibrium, $[Co(H_2O)_6]^{2+}$ and $[Co(SCN)_4]^{2-}$ are found to be present in a mole ratio of 1:10.

Given that lg K_c for the equilibrium is 3.00, which of the following statements is **false**?

A   At equilibrium, $[SCN^-] = 3.16 \times 10^{-1}$ mol dm⁻³.

B $[Co(SCN)_4]^{2-}$ is more stable than $[Co(H_2O)_6]^{2+}$.

C   The units of K_c is mol⁻⁴ dm¹².

D   Dilution of the reaction mixture decreases the ratio of $[Co(H_2O)_6]^{2+}$ to $[Co(SCN)_4]^{2-}$ at equilibrium.

23 Carbon disulfide, CS_2, can be electrolysed into carbon subsulfide, C_3S_2, an unusual compound.

The boiling points of these two compounds are 46.2 °C and 90.0 °C respectively.

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

1   Bromine is acting as a reducing agent in **II**.

2 C_3S_2 has the higher boiling point because there are more covalent bonds to be broken than in CS_2.

3   The carbon atoms in C_3S_2 do not share a common oxidation state.

A   2 and 3 only

B   1 and 3 only

C   1 and 2 only

D   1, 2 and 3

24 L-lyxose and D-xylose are monosaccharides.
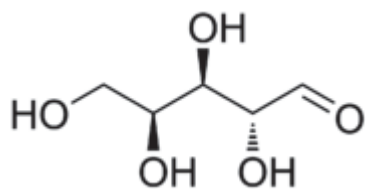
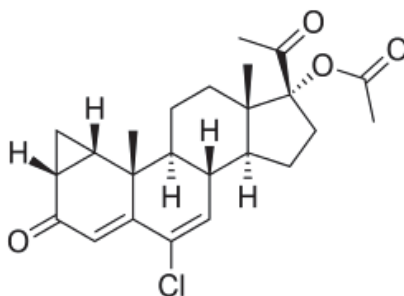L-lyxose   D-xylose
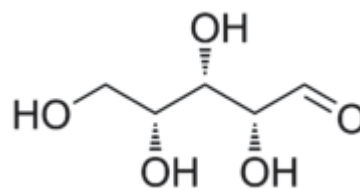
Which of the following statements are true?

1 They have the same melting point.

2 The same volume of hydrogen gas is produced when excess sodium is added to equal amounts of each of them under the same conditions.

3 Both compounds undergo intramolecular nucleophilic substitution to form cyclic esters.

A 1 and 2 only

B 1 and 3 only

C 2 and 3 only

D 2 only

25 Cyproterone acetate (abbreviated as CPA) is a drug that is used in the treatment of androgen-related conditions like acne and prostate cancer.
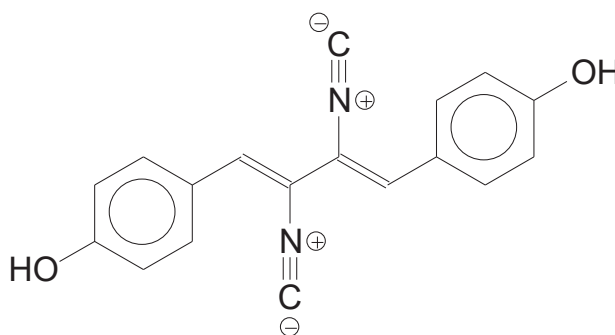

Which of the following statements about CPA are correct?

1 One mole of CPA undergoes condensation with three moles of 2,4-dinitrophenylhydrazine.

2 Two moles of yellow precipitate is formed when one mole of CPA is warmed with alkaline iodine solution.

3 CPA does not cause a colour change in hot acidified potassium dichromate(VI).

A 1 and 3 only

B 1 and 2 only
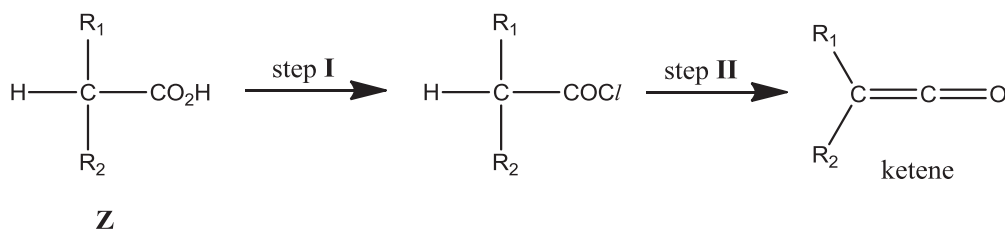
C 2 and 3 only

D 3 only

26 Xantocillin was first isolated from *Penicillium notatum* in the 1950s. It is used as an antibiotic.

xantocillin

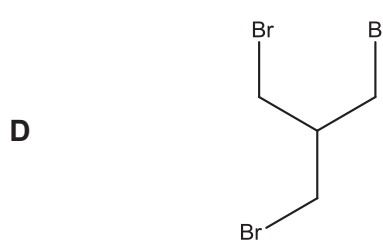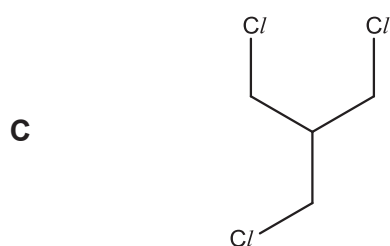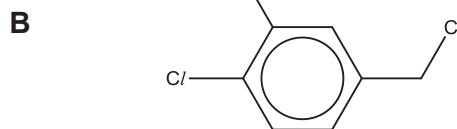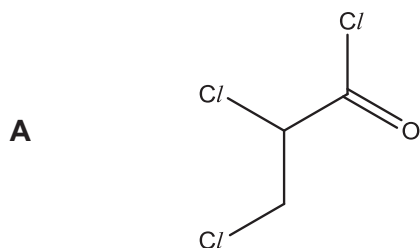Which of the following statements about xantocillin is **false**?

A It is a nitrile.

B It exists as three cis-trans isomers.

C There are four sp hybridised atoms.

D It gives a violet colouration on adding neutral iron(III) chloride.

27 Ketenes are important reagents in organic synthesis. They can be formed from carboxylic acids via the synthetic route below.

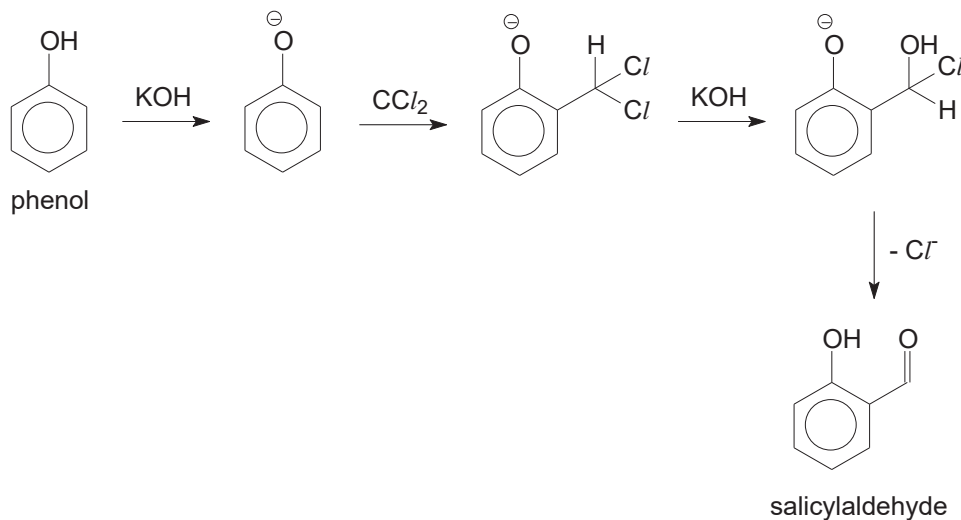Which of the following statements about the above reaction are correct?

1 The ketene will always be non-chiral, no matter which **Z** is used as the starting reactant.

2 Hydrochloric acid can be used as the reagent in step **I**.

3 The ketene can be converted back into **Z** by using water under suitable conditions.

A 1 and 2 only

B 1 and 3 only

C 2 and 3 only

D 1, 2 and 3

28 Aqueous silver nitrate can be used to test for the presence of halogens in organic compounds. Which of the following compounds produces a precipitate most readily when aqueous silver nitrate is added?

**29** The Reimer–Tiemann reaction is a chemical reaction used for the ortho-formylation of phenols, with the simplest example being the conversion of phenol to salicylaldehyde.

Which of the following types of reaction are involved in the above reaction scheme?

1 Nucleophilic substitution

2 Electrophilic substitution

3 Elimination

A 1 and 2 only

B 1 and 3 only

C 2 and 3 only

D 1, 2 and 3

30 Hydroboration is one of the many methods to hydrate alkenes to alcohols. An example is shown below.
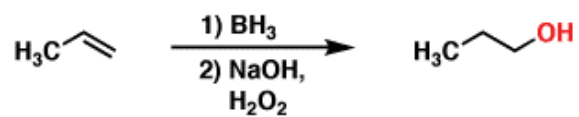
Which of the following alcohols cannot be formed via hydroboration?

A   Butan-2-ol from but-1-ene

B   2-methylpropan-1-ol from 2-methylpropene

C   3-methylpentan-2-ol from 3-methylpent-2-ene

D   4-methylhexan-3-ol from 3-methylhex-3-ene

END OF PAPER

Index No.	Name		Form Class	Tutorial Class	Subject Tutor

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY   **9729/02**
Higher 2

Paper 2   Structured Questions   **15 August 2017**
                                                                    2 hours

Candidates answer on the Question Paper
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, index number, form class, tutorial class and subject tutor's name on all the work you hand in.
Write in dark blue or black pen.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions.
A Data Booklet is provided.

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

For Examiner's Use	
Question no.	**Marks**
1	/ 7
2	/ 13
3	/ 9
4	/ 11
5	/ 5
6	/ 9
7	/ 14
8	/ 7
TOTAL	**/ 75**

This document consists of **21** printed pages, including this cover page.

For more than two millenia human ingenuity has turned natural and synthetic poisons into weapons of war. World War I was especially hailed by historians as the "Chemists' War" because it was the first war in which chemical weapons were used on such an enormous scale, even on civilians. Chemicals were used to bring widespread destruction and death. It set the precedence for World War II. On the bright side, chemicals were used to save millions of soldiers' lives in World War II.

Question 1 examines how chemical weapons were used to kill in World War I, while Question 2 examines the use of chemicals as medicine in the battlefields of World War II.
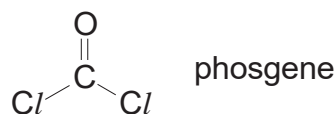
1 A range of different chemicals - chlorine, phosgene and mustard "gas" - were used as weapons throughout World War I.

Their melting and boiling points are tabulated below.

Gas	Melting point / ^{0}C	Boiling point / ^{0}C
chlorine	-101.5	-34.0
phosgene	-118	8.3
mustard "gas"	14.4	217.0

Chlorine was first used on a large scale by the German forces at Ypres in April 1915. It reacts with water in the lungs to form hydrochloric acid, which can quickly lead to death. At lower concentrations, it can cause coughing, vomiting, and irritation to the eyes.

(a) Phosgene is a colourless gas, with an odour likened to that of 'musty hay'.

$$\underset{Cl}{}\overset{\displaystyle \overset{O}{\|}}{\underset{\quad Cl}{C}} \qquad \text{phosgene}$$

Phosgene is known to react violently with water to give hydrochloric acid and carbonic acid. Give the equation of the reaction between phosgene and water.

[1]

**(b)** The Germans introduced another chemical weapon – mustard "gas". It was fired into enemy positions by cannons.

(i) How is the name mustard "gas" misleading?

[1]

1 (b) The structural formula of mustard "gas" is $ClCH_2CH_2SCH_2CH_2Cl$.

Unlike alkyl halides, mustard "gas" reacts instantly with water to form hemi-mustard, $ClCH_2CH_2SCH_2CH_2OH$.

(ii) The following intermediate is thought to be formed by mustard "gas" itself via an intramolecular nucleophilic substitution before the attack of water.
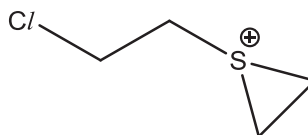
How does this intermediate make the hydrolysis of mustard "gas" easier than that of alkyl halides?

[1]

(iii) The conversion of the intermediate in **b(ii)** to hemi-mustard involves two steps, the first involving the attack by water and the second involving deprotonation.

Use curly arrows to show how the intermediate in **b(ii)** is converted into hemi-mustard.

[2]

1 (b) (iv) Hemi-mustard can be further attacked by water to form **J**, $C_4H_{10}SO_2$.
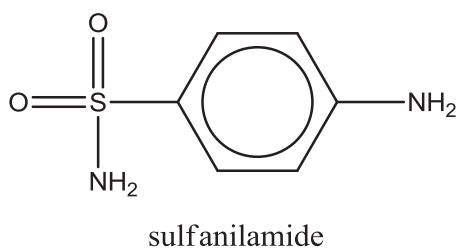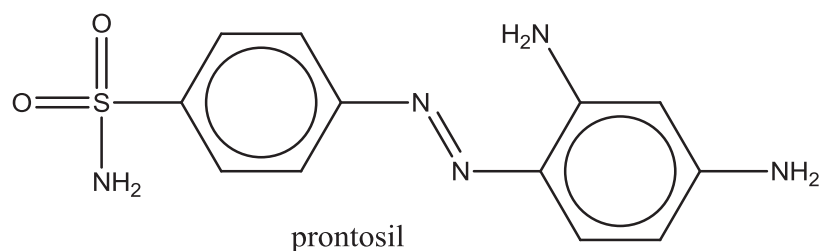
Draw the structure of **J**.

[1]

(v) On reaction with concentrated sulfuric acid at 140 ^{0}C, hemi-mustard can be converted into **K**, C_4H_8SO, which does not decolourise bromine.

Draw the structure of **K**.

[1]

[Total: 7 marks]
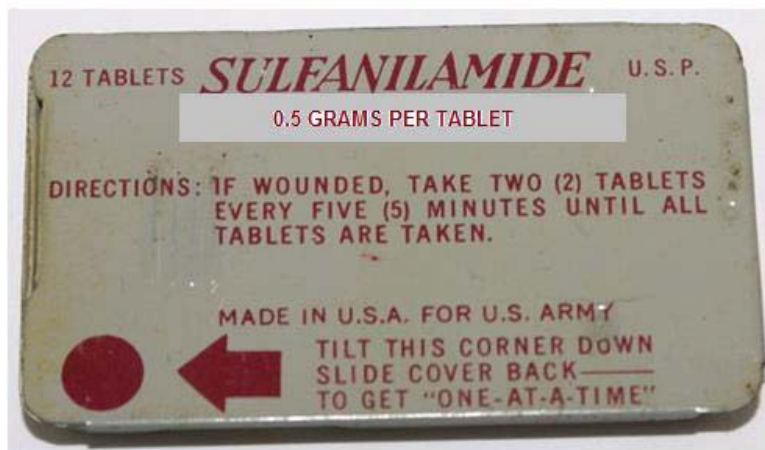
2 (a) Prontosil and sulfanilamide are anti-bacterial drugs.

prontosil

sulfanilamide

These two drugs saved many soldiers in World War II.

The photo below is that of a **sulfanilamide kit** issued by the United States Army to its soldiers during World War II.

One source states that the maximum daily dosage of sulfanilamide is 6.5 g per kg of patient. An average US army soldier may be assumed to weigh about 70 kg.

Sulfanilamide has many side-effects – itching, headache, diarrhoea, pale skin, vomiting, dizziness, fatigue.

Is it safe for a wounded US army soldier to consume as many as 30 **kits** worth of tablets in a single day? Justify with calculations.

[1]

2 (b) Prontosil was found to be active in *vivo* (in human bodies) while sulfanilamide was found to be active both in *vivo* and in *vitro* (in bacterial cultures grown in petri dishes).

It was later proven that intestinal enzymes break down prontosil to sulfanilamide in the human intestine – in this reaction, the oxidation states of certain nitrogen atoms are altered.

There are a few classes of enzymes as listed below.

Transferases catalyse group transfer reactions.

Hydrolases catalyse reactions that involve hydrolysis.

Ligases are used in catalysis where two substrates are litigated and the formation of carbon-carbon, carbon-sulfide, carbon-nitrogen, and carbon-oxygen bonds due to condensation reactions.

Reductases catalyse reduction reactions.

Oxidases catalyse oxidation reactions.

(i) Suggest the type of intestinal enzyme which catalyses the conversion of prontosil to sulfanilamide.

[1]

(ii) Name the side-product in the conversion of prontosil to sulfanilamide.

[1]

To analyse the sulfanilamide content in a pill, it was dissolved in HCl (aq).

(c) Sulfanilamide is not very soluble in water. Explain why sulfanilamide is not soluble in water but is soluble in HCl (aq).

[2]

2 A 0.350 g sample of an antibiotic powder containing sulfanilamide was dissolved to form an aqueous solution.

The solution was diluted and made up to the mark in a 100 cm³ graduated flask. A 25.0 cm³ aliquot was transferred into a conical flask, in which 25.0 cm³ of 0.0200 mol dm⁻³ $KBrO_3$ was added. About 10 g of solid KBr was then added.

BrO_3^- reacts with bromide according to the equation:

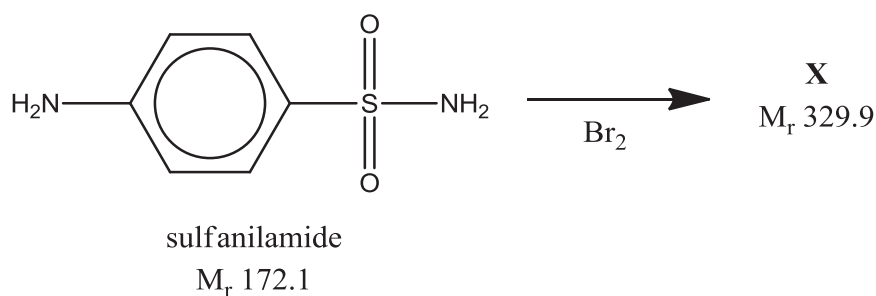$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

(d) **(i)** Calculate the amount of Br_2 formed.

[1]

The bromine formed then reacts with the sulfanilamide to form **X**.

Note that the following equation is not balanced.
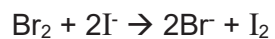

sulfanilamide
M_r 172.1

X
M_r 329.9

(ii) By comparing the M_r of sulfanilamide and **X**, show that **X** is a dibrominated compound.
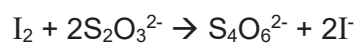
[1]

(iii) Draw the structure of **X**, ignoring the directing effects of the $-SO_2NH_2$ group.

[1]

2 (e) After ten minutes, an excess of KI was added.

$$Br_2 + 2I^- \rightarrow 2Br^- + I_2$$

The liberated iodine was then titrated with 18.00 cm^3 of 0.0900 mol dm^{-3} Na$_2$S$_2$O$_3$.

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

Calculate the amount of bromine which reacted with the KI.

[1]

(f) Using your answers to **(d)** and **(e)**, calculate the amount of sulfanilamide which reacted with the bromine.

[2]

(g) Hence, calculate the percentage mass of sulfanilamide in the sample.

[2]

[Total: 13 marks]

3 Hydrazine (N_2H_4) was first used as rocket fuel in World War II, and has since been used as a propellent for maneuvering spacecraft, as it decomposes rapidly and exothermically into hydrogen gas and nitrogen gas.

Hydrazine may be produced industrially by the Olin-Rashig process from NH_2Cl and ammonia.

$$NH_2Cl \text{ (g)} + NH_3 \text{ (g)} \rightleftharpoons HCl \text{ (g)} + N_2H_4 \text{ (g)}$$

The values of K_c are tabulated below with the corresponding temperatures.

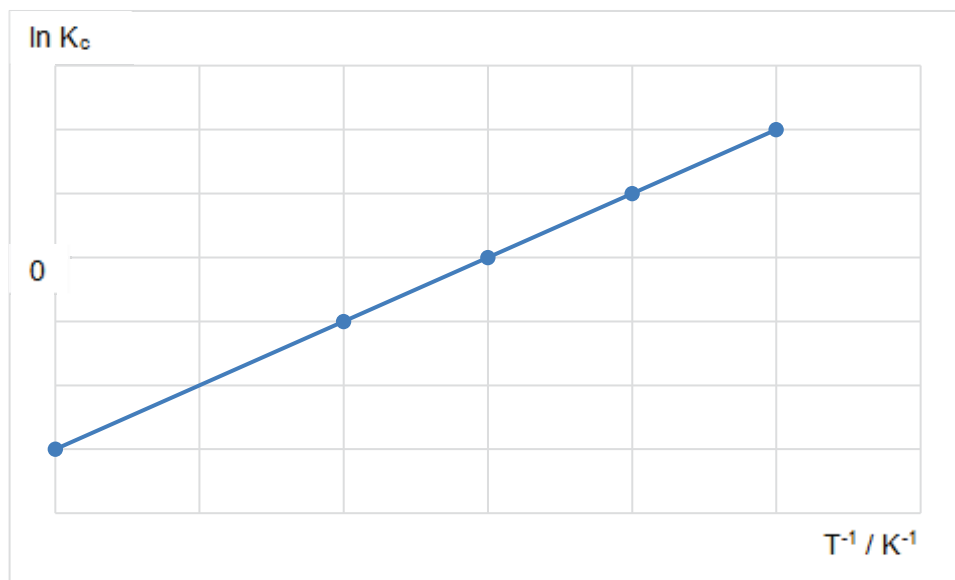| T / K	298	304	503
K_c	1.525×10^6	1.230×10^5	2.201×10^4

(a) State the value of K_p at 304 K. Justify your answer.

[2]

(b) By manipulating the relationship of $K_c = e^{\frac{-\Delta G}{RT}}$, we obtain

$$R \ln K_c = \frac{1}{T}(-\Delta H) + \Delta S.$$

The graph below was plotted with $\ln K_c$ as the y-axis and $\frac{1}{T}$ as the x-axis.

(i) Describe how you would obtain the value of ΔS from the above graph.

[1]

3 (b) (ii) Another way to find the standard entropy change of a reaction is to consider the standard molar entropies of the species involved.

Species	HCl (g)	N$_2$H$_4$ (g)	NH$_2$Cl (g)	NH$_3$ (g)
Standard molar entropy / J mol^{-1} K^{-1}	187	239	201	193

Calculate the standard entropy change of the Olin-Rashig process.

[1]

(iii) Hence, using your answer to **b(ii)** and the equation in **(b)**, calculate the standard enthalpy change of the Olin-Rashig reaction, including its units.

[1]

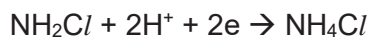**(c)** The pK$_a$ and pK$_b$ values of the two reactants – monochloramine (NH$_2$Cl) and ammonia - are tabulated below.

Product	NH$_2$Cl	NH$_3$
pK$_a$	14	32.5
pK$_b$	15	4.75

Explain these differences as much as you can.

[2]

3 (d) Monochloramine is an oxidising agent.

$$NH_2Cl + 2H^+ + 2e \rightarrow NH_4Cl$$

The reduction potentials of the above half-reaction is +1.45 V.

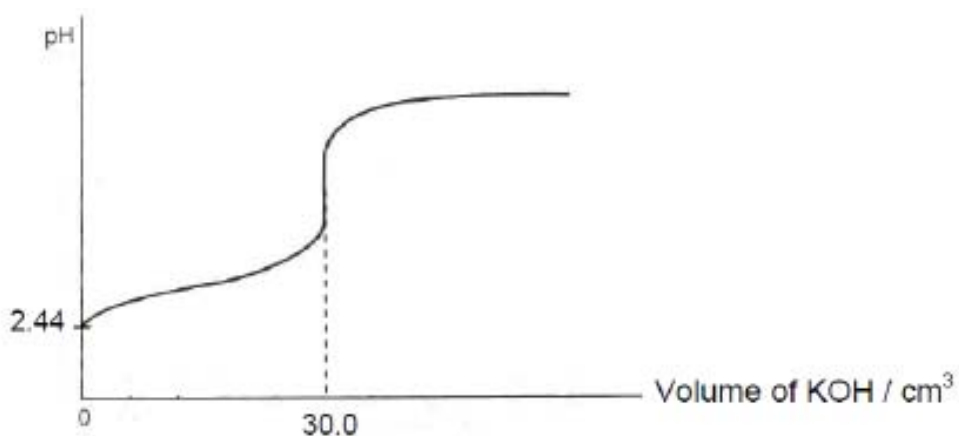However, in alkaline medium, the reduction potential is + 0.74 V.

Explain the difference between these two reduction potentials.

[2]

[Total: 9 marks]

4 (a) Ethanoic acid, a weak monobasic acid, is the main component in vinegar.

When a 20.0 cm^3 sample of vinegar was titrated against 0.05 mol dm^{-3} aqueous potassium hydroxide using a pH meter, the following graph was obtained.

(i) Show that the concentration of the ethanoic acid solution is 0.0750 mol dm^{-3}.

[1]

(ii) Hence use your answer and the initial pH to show that ethanoic acid is a weak acid.

[2]

4 (a) (iii) Show that the acid dissociation constant of ethanoic acid has a numerical value of 1.85×10^{-4}.

[2]

(iv) Calculate the value of the pH after 15.00 cm³ of aqueous potassium hydroxide has been added.

[1]

(v) Write a suitable chemical equation, with state symbols, to explain why the equivalence pH is above 7.

[1]

(b) (i) Solution **A** was prepared by adding 10.00 cm³ of the potassium hydroxide solution to 25.0 cm³ of the ethanoic acid solution.
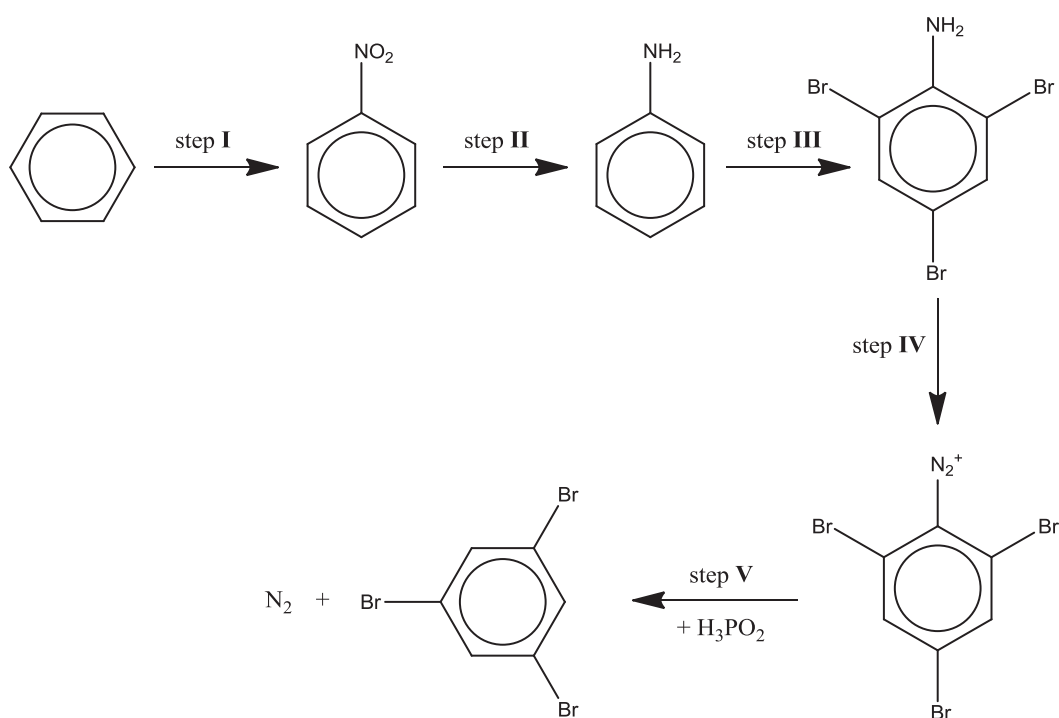
Calculate the pH of solution **A**.

[2]

(ii) When a small amount of acid or base is added to solution **A**, its pH remained relatively constant. Explain, with the aid of equations, why this is so.

[2]

[Total: 11 marks]

5 Study the synthetic route from benzene to 1,3,5-tribromobenzene, shown below.

(a) State the reagents and conditions used in steps **I** and **II**.

[2]

(b) By examining the positions of the bromine atoms, suggest why 1,3,5-tribromobenzene cannot be made directly from benzene with bromine.

[1]

(c) Phosphinic acid, H_3PO_2, is used in step **V**. Only one out of its three hydrogen atoms is acidic. A non-acidic hydrogen substituted on the benzene to liberate nitrogen gas.
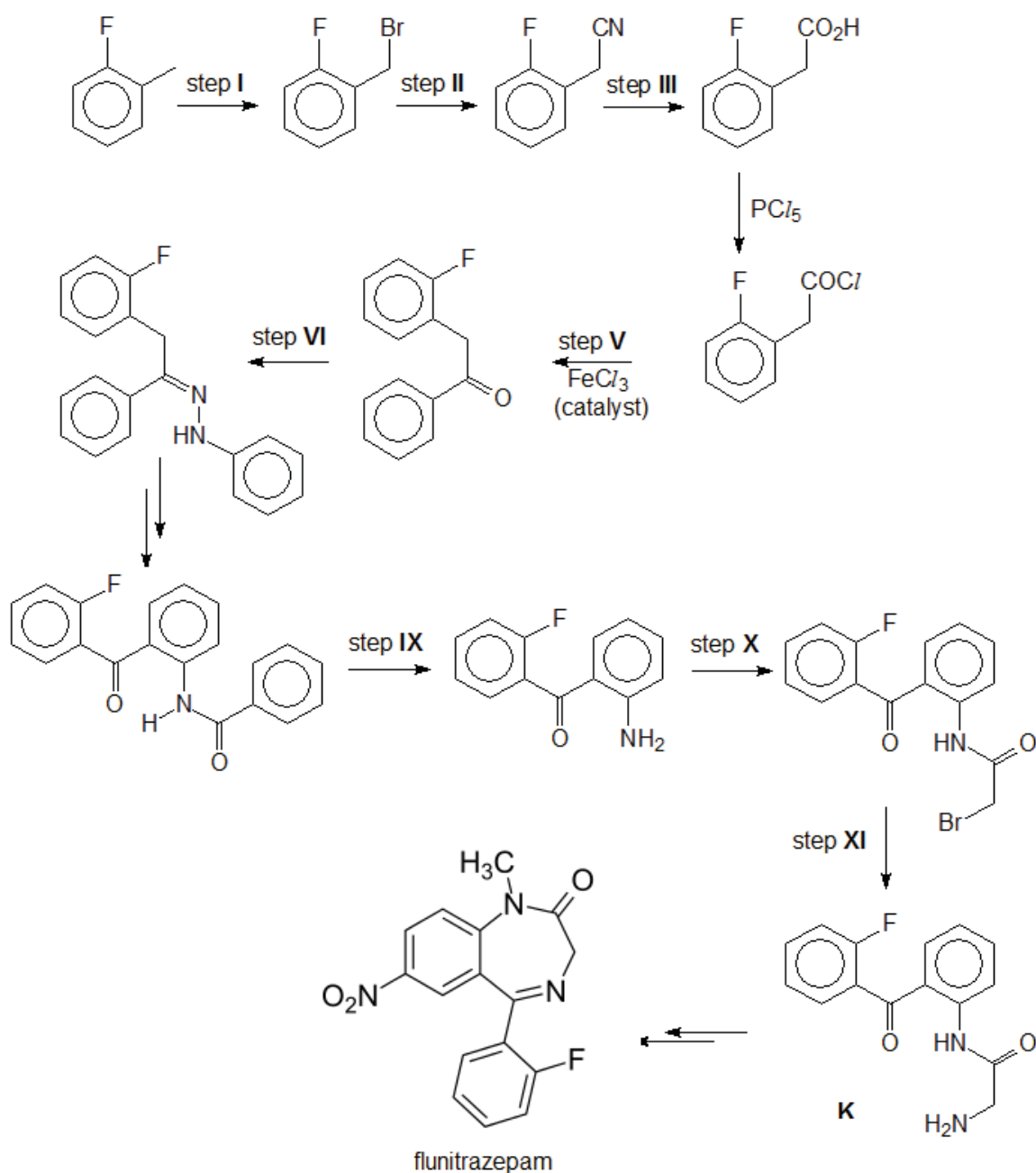
Draw the structure of phosphinic acid and circle the hydrogen atom which substitutes on the benzene.

[2]

[Total: 5 marks]

6 (a) Flunitrazepam is a drug used in the short-term treatment of insomnia and as a pre-medication in surgical procedures and for inducing anaesthesia.

Study the synthetic route to flunitrazepam shown below.
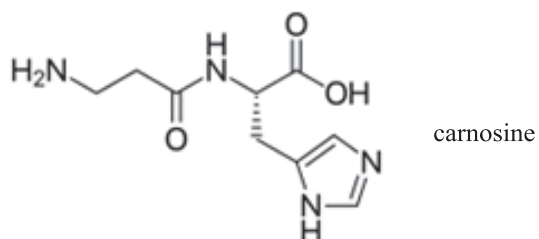

flunitrazepam

**6 (a)** Fill in the table below with the appropriate reagents and conditions.

Step	Reagents and conditions
I	
II	
III	
V	
VI	
XI	

[6]

6 (b) Carnosine is a dipeptide health supplement. It first appeared in the mainstream health community around a decade ago in the form of supplements, eye-drops and skin creams.

carnosine

(i) One of the products is β–alanine (structure shown below) when carnosine is hydrolysed with hot KOH (aq).
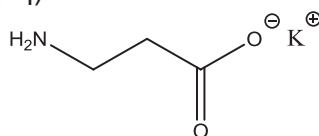
Draw the structural formula of the other product.

(ii) α-alanine is one of the twenty essential amino acids. It is a constitutional isomer of β–alanine. Unlike β–alanine, it is chiral. Draw the skeletal formula of α-alanine.

(iii) Sarcosine is another constitutional isomer of β–alanine. It is an α-amino acid, just like α-alanine. Draw the structural formula of sarcosine.

[3]

[Total: 9 marks]

7 Sulfur forms many cyclic allotropes with different ring sizes. In the solid state, the most stable allotrope of sulfur is the form of S_8. In the gas phase, all ring sizes from S_3 to S_{12} have been detected.

(a) In the gas phase, the different ring sizes are in equilibrium. The equation for the equilibrium between $S_7(g)$ and $S_8(g)$ is given below:

$$7S_8\,(g) \rightleftharpoons 8S_7\,(g)$$
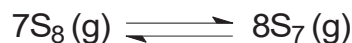
(i) Give the expression for the equilibrium constant, K_c, for the reaction between S_7 and S_8 as written above.

[1]

When dissolved in an organic solvent, S_6, S_7 and S_8 were all detected in equilibrium in the following proportions by mass:

| Allotrope	S_6	S_7	S_8
% by mass	1.5	0.5	98.0

(ii) Calculate the amount of S_7 and S_8 at equilibrium when 1.00 g of sulfur is dissolved in 1.00 dm³ of solvent.

[2]

(iii) Calculate the value of the equilibrium constant in **(i)**.

[1]

(b) In the solid phase, S_8 crystallises in two well-known allotropic forms: orthorhombic and monoclinic. Both combust in excess oxygen to form liquid SO_3. The standard enthalpy changes of combustion of these two forms are as follows:

$$\Delta H_c\,(S_8,\ \text{orthorhombic}) = -296.8 \text{ kJ mol}^{-1}$$
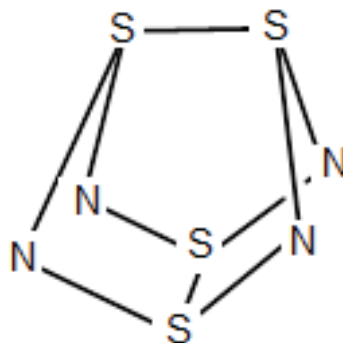$$\Delta H_c\,(S_8,\ \text{monoclinic}) = -297.1 \text{ kJ mol}^{-1}$$
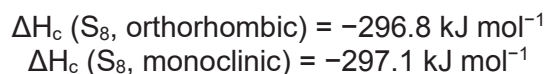
Draw an energy level diagram to conclude which is the more stable form.

[2]

7 (c) Sulfur also forms an interesting cage-like compound with nitrogen, S_4N_4.

(i) There are π bonds in S_4N_4 which are alternating.

The π bonds are omitted in the structural formula shown above.

Fill in the missing π bonds onto the structural formula above.
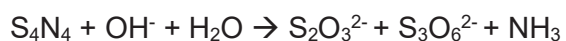
[1]

S_4N_4 reacts with hot NaOH(aq) to give thiosulfate ($S_2O_3^{2-}$) and trithionate ($S_3O_6^{2-}$) in 1:2 ratio. Ammonia is the gaseous side-product.

(ii) Suggest what makes this reaction spontaneous.

[1]

(iii) The skeletal equation is as such:

$$S_4N_4 + OH^- + H_2O \rightarrow S_2O_3^{2-} + S_3O_6^{2-} + NH_3$$

Balance the ionic equation.

[1]

7 (d) There are two possible structures of the metabisulfite ion ($S_2O_5^{2-}$), as shown below.
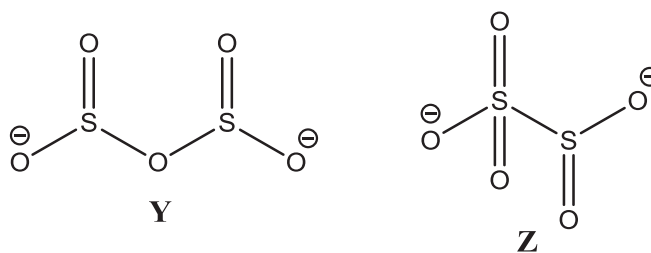
(i) Using appropriate values from the Data Booklet, calculate the enthalpy changes of atomisation of **Y** and **Z**. Hence deduce which is more stable.

[2]

(ii) Metabisulfite (structure **Z**) decomposes to SO_2 and sulfite (SO_3^{2-}) in a single step. Draw curly arrows to show the electron movement in this decomposition.

[1]

7 **(d)** **(iii)** Potassium metabisulfite, $K_2S_2O_5$, is a white crystalline powder.

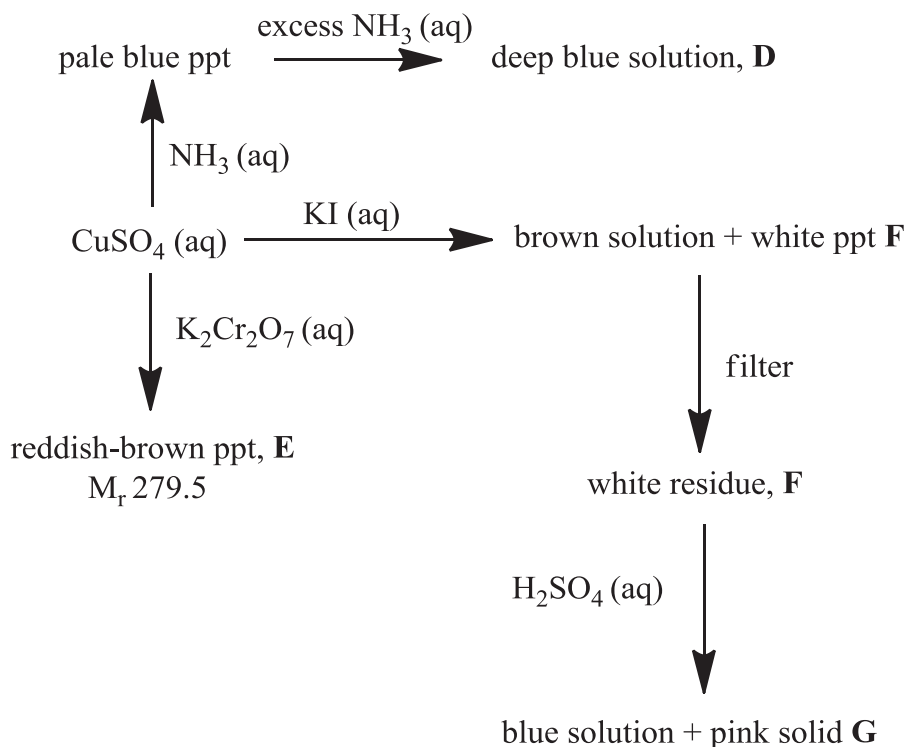It is chemically very similar to sodium metabisulfite, $Na_2S_2O_5$, with which it is sometimes used interchangeably. Potassium metabisulfite is generally preferred out of the two as a food preservative as it does not contribute sodium to the diet.

Explain why potassium metabisulfite decomposes at a higher temperature on heating than sodium metabisulfite.

[2]

[Total: 14 marks]

8 (a) Copper(II) sulfate can undergo a series of reactions as shown in the reaction scheme below.

$$\text{CuSO}_4\,(aq) \xrightarrow{\text{NH}_3\,(aq)} \text{pale blue ppt} \xrightarrow{\text{excess NH}_3\,(aq)} \text{deep blue solution, } \mathbf{D}$$

$$\text{CuSO}_4\,(aq) \xrightarrow{\text{KI (aq)}} \text{brown solution + white ppt } \mathbf{F}$$

$$\text{CuSO}_4\,(aq) \xrightarrow{\text{K}_2\text{Cr}_2\text{O}_7\,(aq)} \text{reddish-brown ppt, } \mathbf{E}\quad M_r\,279.5$$

brown solution + white ppt **F** $\xrightarrow{\text{filter}}$ white residue, **F** $\xrightarrow{\text{H}_2\text{SO}_4\,(aq)}$ blue solution + pink solid **G**

Identify **D**, **E**, **F** and **G**.

D: **F**:

E: **G**:

[4]

(b) Ionisation isomerism is a special type of constitutional isomerism in which the isomers form different ions in solution.

There is a pair of cobalt(III) ionisation isomers, **K** and **L**. They have molecular formula $CoBrSO_4(NH_3)_4$. **K** is red while **L** is dark violet.

On addition of aqueous barium nitrate, only **K** gave a white precipitate.
On addition of aqueous silver nitrate, only **L** gave an off-white precipitate.

(i) Give the structural formulae of the cations in **K** and **L**.

K:

L:

[2]

(ii) Explain briefly why **K** and **L** exhibit different colours.

[1]

[Total: 7 marks]

END OF PAPER

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY **9729/03**
Higher 2

Paper 3
18 August 2017
2 hours

Additional Materials: Writing Paper
Data Booklet
Cover Page

READ THESE INSTRUCTIONS FIRST

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

Answer **all** questions in Section **A**.
Answer **either** question 4 or 5 in Section **B**.
Start each question on a new sheet of writing paper.

A Data Booklet is provided.
The use of an approved calculator is expected, where appropriate.
You are reminded of the need for good English and clear presentation in your answers.

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

This document consists of **17** printed pages, including this cover page.

9729/03/Prelim/17 ANGLO-CHINESE JUNIOR COLLEGE

Section A – Answer **ALL** questions. Begin each question on a fresh piece of writing paper.

1 This question is about Period 3 and Group 2 elements.

(a) Phosphorus sulfide, P_4S_3, is used in small amounts in the tip of a matchstick. On striking a matchstick, this compound burns to form sulfur dioxide and phosphorus pentoxide.

  (i) Write the equation for this reaction. [1]

  (ii) The melting points of the two oxides formed in **(a)(i)** differ significantly from that of silicon(IV) oxide (SiO_2). Account for this difference in terms of structure and bonding of each oxide. [2]

  (iii) The solid oxide formed in **(a)(i)** dissolves in water to give an acidic solution.

  Write the equation for this reaction and give an approximate pH of the solution formed. [2]

(b) A Group 2 nitrate exists as a hydrate $M(NO_3)_2.xH_2O$. On heating, 1.80 g of this hydrate lost 0.55 g in the form of steam, as it was converted into the anhydrous nitrate, $M(NO_3)_2$. Subsequent heating to constant mass produced a white residue and mixture of two gases. The gases produced were passed through aqueous sodium hydroxide. The remaining gas occupied 95 cm^3 at 101 kPa and 30 °C.

  (i) Write an equation, with state symbols, representing the thermal decomposition of Group 2 nitrates, $M(NO_3)_2$. [1]

  (ii) Assuming that the gas behaves ideally, calculate the amount of remaining gas formed. [1]

  (iii) Hence, calculate the value of x and deduce the identity of metal **M**. [3]

(c) Calcium oxide is the key ingredient for the process of making cement.

  When 1.50 g calcium is burned in air, calcium oxide is formed together with a red brown solid.

  The red brown solid has the following composition by mass: Ca, 81.1%; N, 18.9%. Adding water to the red brown solid produces calcium hydroxide and 19.2 cm^3 of ammonia gas at room temperature and pressure.

  (i) Deduce the formula of the red brown solid. [2]

  (ii) Write the chemical equation for the reaction between the red brown solid with water. [1]

  (iii) Write the chemical equation for the reaction of calcium with O_2 and hence calculate the mass of CaO formed when 1.5 g of calcium is burnt in O_2. [2]

1 **(d)** A diagonal relationship is said to exist between certain pairs of diagonally adjacent elements in the second and third Periods of the Periodic Table.

For instance, lithium shows similar chemical properties to magnesium.

(i) Write the equation for the thermal decomposition of lithium carbonate. [1]

(ii) Explain why this is unlike that of the other Group 1 carbonates. [1]

(e) Lithium nitride, Li_3N, is a red solid. It is the only stable Group 1 nitride. The nitrides of all the Group 2 elements are known.

Li_3N is currently investigated as a storage medium for hydrogen gas.

$$Li_3N + 2H_2 \rightleftharpoons 2LiH + LiNH_2$$

State the role of hydrogen. [1]

(f) A diagonal relationship also exists between boron and silicon.

B_2O_3 is acidic, like SiO_2 but unlike the oxides of the other Group 13 elements.

(i) Write a balanced chemical equation, with state symbols, that illustrates the acidic nature of SiO_2. [1]

(ii) Write a balanced chemical equation, with state symbols, that illustrates the acidic nature of B_2O_3, given that it forms a similar anion as in **(i)**. [1]

[Total: 20]

2 **(a)** Divalent metal cations like tin and cadmium form insoluble precipitates with NaOH (aq).

The K_{sp} of $Sn(OH)_2$ is 5.45×10^{-27} mol^3 dm^{-9}.

(i) If the concentration of $Cd(OH)_2$ in a saturated solution is 1.217×10^{-5} mol dm^{-3}, determine the solubility product of $Cd(OH)_2$. [1]

(ii) Calculate the molar solubility of $Sn(OH)_2$ in a solution of pH 8. [2]

(iii) A certain solution has 0.002 mol dm^{-3} each of Cd^{2+} and Sn^{2+}.

Calculate the pH range over which the two cations can be effectively separated. [2]

(b) Propanone, also known as "acetone", is one of the most important solvents in organic chemistry – it can be used to dissolve many things from fats and waxes to airplane glue and nail polish.

It decomposes to **H** and ketene ($H_2C=C=O$). At 600 °C, the decomposition rate constant is 8.7×10^{-3} s^{-1}.

(i) Suggest the identity of **H**. [1]

(ii) Determine the half-life of the reaction at 600 °C. [1]

(iii) How much time is required for 75% of a sample of propanone to decompose at 600 °C? [1]

(iv) The Arrhenius equation links different parameters (its activation energy, the absolute temperature, and its rate constant at that temperature) of a reaction together.

$$k = Ae^{-\frac{E_a}{RT}}$$

Given that the half-life of the reaction at 500 °C is 8700 s and using your answer to **(ii)**, calculate the activation energy (including its units) of this reaction. [2]

2 **(c)** Under appropriate conditions, butane can be made to isomerise reversibly to 2-methylpropane at 298K.

butane   (g)   ⇌   (g)   2-methylpropane
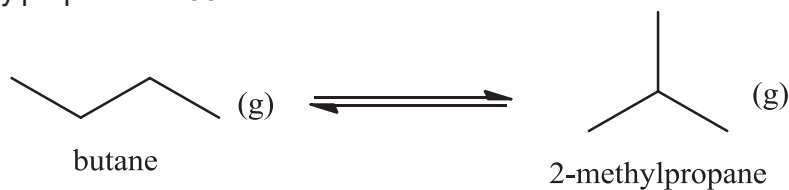
	butane	2-methylpropane
S°/ J K^{-1} mol^{-1}	310	295
ΔH_f°/ kJ mol^{-1}	-127.2	-135.6

(i) Calculate the ΔG° for the forward isomerisation reaction. [2]

(ii) Given that ΔG° = -RT ln K_p, calculate the equilibrium constant, K_p, for the isomerisation reaction. [1]

(iii) Write the K_p expression for the isomerisation equilibrium. [1]

(iv) Determine the mole fractions of the two gases at equilibrium. [3]

(v) In the industry, 2-methylpropane is used to make compound **Y**, C_8H_{18}.

Y has the whole range of carbon atoms; it contains primary, secondary, tertiary and quaternary carbon atoms.

Draw the structural formula of **Y**, assuming that the original carbon skeleton did not rearrange. [1]

2 **(d)** Life in the universe is widely thought to have originated from methanal, HCHO, through the Formose reaction.

In this reaction, methanal is converted into a vast range of sugars like ribose and from there to RNA, an important hereditary material.

2HCHO
M_r 30

M_r 60

HCHO

X

Y
M_r 90

HCHO

A'
M_r 120

B
M_r 150

HCHO

A

HCHO

B'

HCHO

C

C'
M_r 180

HCHO

D
M_r 210

(i) **X** and **Y** are functional group isomers.

Y does not rotate the plane of plane-polarised light. Fehling's and Tollens' tests are the only tests which can differentiate between **X** and **Y**.
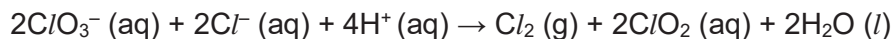
Draw the structural formula of **Y**. [1]

(ii) Suggest a reason why the interconversion of **C** to **C'** cannot be done in a single step. [1]

(iii) Draw the structural formula of **D**. [1]

[Total: 21]

3   This question is on Group 17, the halogens.

Chlorate(V), ClO_3^-, reacts with chloride according to the equation:

$$2ClO_3^- \text{ (aq)} + 2Cl^- \text{ (aq)} + 4H^+ \text{ (aq)} \rightarrow Cl_2 \text{ (g)} + 2ClO_2 \text{ (aq)} + 2H_2O \text{ (}l\text{)}$$
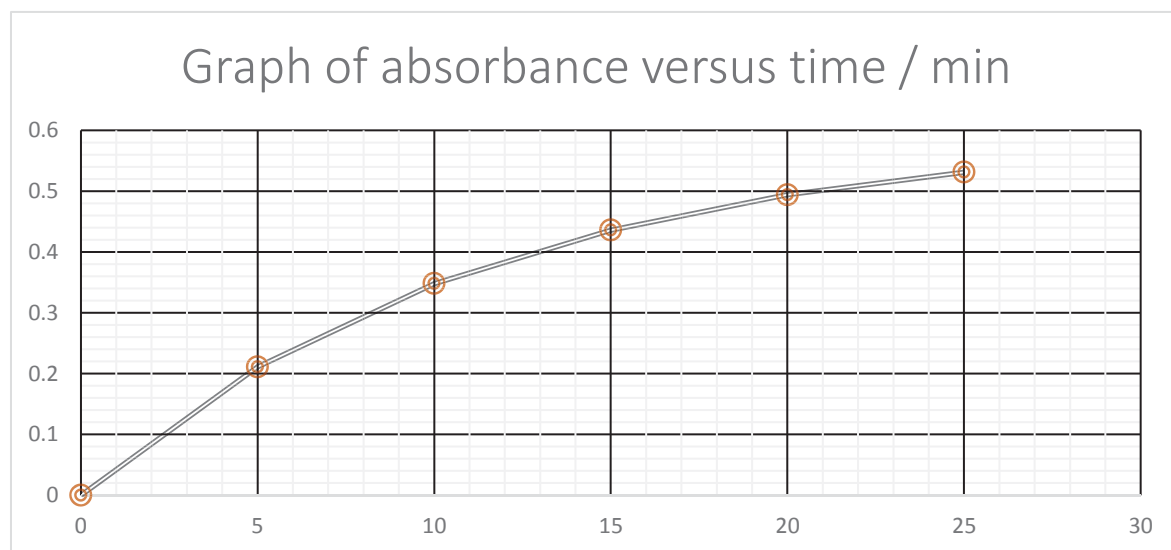
(a)   To study the kinetics of chlorate(V)-chloride reaction, an experiment was conducted using a mixture in which the concentrations of the reactants are as follows: 0.000480 mol dm^{-3} of ClO_3^-, 0.1 mol dm^{-3} of Cl^- and 0.4 mol dm^{-3} of H^+.

At five-minute intervals, small samples of the reaction mixture were withdrawn, quenched and placed into the UV-vis spectrometer to record its absorbance value. The absorbance value corresponds to the concentration of the product ClO_2.

The results of the above experiment are shown below.

Time/min	0	5	10	15	20	25
Absorbance/A	0.000	0.211	0.348	0.436	0.494	0.531

The graph of absorbance/A against time/min is plotted below.

Graph of absorbance versus time / min

3 **(a)** **(i)** Beer-Lambert's Law states that the absorbance values, A, is directly proportional to the concentration of absorbing species, c, as shown below.

$$A = \varepsilon c l$$

where ε is the molar extinction coefficient and l is the path length, which is usually 1.0 cm.

This equation can be used to calculate the absorbance value when maximum amount of ClO_2 was formed.

Show that the maximum absorbance value in the above experiment is 0.600, given that ε of ClO_2 is 1250 $mol^{-1}\,dm^3\,cm^{-1}$. [2]

(ii) From the graph provided on the previous page and the information given in **(a)(i)**, determine the half-life with respect to ClO_3^- and hence the order of reaction with respect to ClO_3^-. [2]

To obtain the full rate law, a further experiment was conducted.

The following graph was obtained.

Assuming that $[ClO_3^-]$ and $[Cl^-]$ are constant,

Initial Rate vs $[H^+]^2$
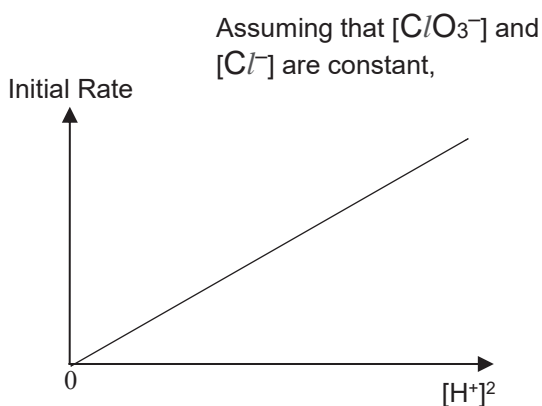
(iii) Using the above data, determine the order of the reaction with respect to H^+. [1]

(iv) Given that the units of k is $mol^{-3}\,dm^9\,s^{-1}$, write the rate equation of the chlorate(V)-chloride reaction. [1]

(v) State a physical property that can be monitored as the reaction progresses. [1]

3 **(b)** Heating solid halides with concentrated H_2SO_4 is one of the ways to obtain hydrogen halides.

However, the halides have different reactivities with concentrated H_2SO_4.

(i) Write an equation to show the reaction of KCl with concentrated H_2SO_4. [1]

(ii) However, when KI is treated with concentrated sulfuric acid, HI will be contaminated with other gaseous products. Identify these gaseous products. [2]

(iii) Suggest another reagent that can be reacted with potassium iodide to obtain pure hydrogen iodide. [1]

The interhalogens are compounds that are made up of two or more different halogens.

ICl and IBr are two such examples.

(c) Even though ICl is more polar than IBr, IBr has a higher boiling point than ICl. Explain this dilemma as clearly as you can. [2]

(d) ICl reacts with water in which water is acting as the nucleophile.

The equation for the reaction is as follows.

$$ICl + H_2O \rightarrow HX + HOY$$

(i) By comparing relative electronegativities, identify **X** and **Y**. [1]

(ii) Hence propose a two-step mechanism for this reaction. Include curly arrows and partial charges. [2]

(e) ICl_3 exists as a planar dimer I_2Cl_6 in solid state. The two iodine atoms are the central atoms.

(i) Draw the structure of the dimer. [1]

(ii) The molten form of ICl_3 is able to conduct electricity because it undergoes auto-ionisation.

One species is square planar and the other is bent with respect to the central iodine atom.
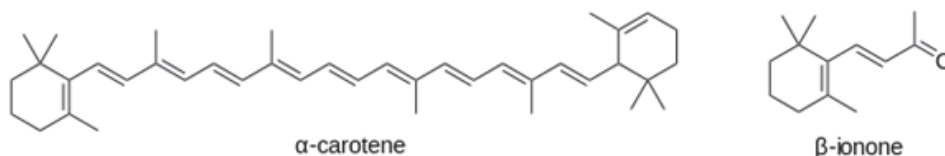
Deduce the formulae of the cation and the anion. [2]

[Total: 19]

**Section B** - Choose <u>either</u> question **4** or **5**. Begin it on a fresh piece of writing paper.

4   α-carotene is a red-orange pigment found in plants and fruits. It is the yellow/orange pigment that gives vegetables and fruits their rich colors. The name "carotene" came about when it was first discovered in carrot roots in 1831.

    (a)   α-carotene is metabolised to form α-ionone and β-ionone, which share the same molecular formula, $C_{13}H_{20}O$.

α-carotene   β-ionone

        (i)   Explain why hot acidified $KMnO_4$ cannot be used in the conversion of α-carotene to β-ionone.   [1]

        (ii)   Based on the structure of α–carotene, draw the structural formula of α-ionone.   [1]

        (iii)   Specify what type of constitutional isomerism is shown between α-ionone and β-ionone.   [1]

        (iv)   Give the structural formula of a constitutional isomer of β-ionone, where neutral iron(III) chloride solution is the <u>only</u> chemical test that can distinguish between itself and β-ionone.   [1]

        (v)   Give the structural formula of a constitutional isomer of β-ionone, which can be distinguished from β-ionone by warm alkaline iodine.   [1]

4 **(b)** β-ionone forms β-damascone via an electrochemical route.
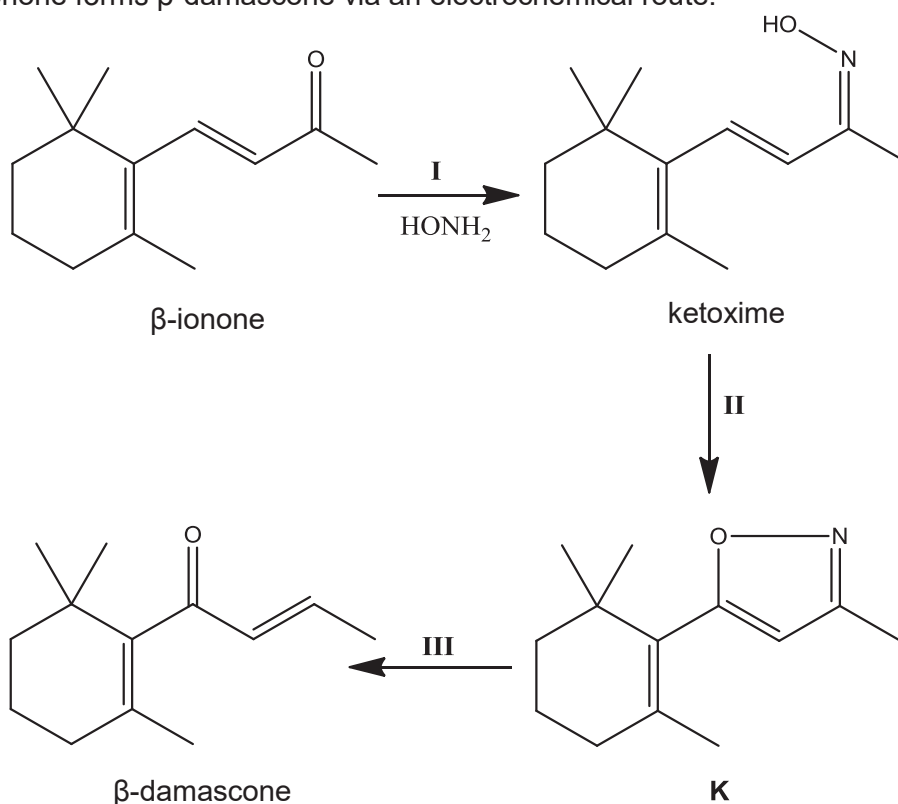
β-ionone — **I** HONH$_2$ → ketoxime

II ↓

K — **III** → β-damascone

It involved the formation of ketoxime in step **I**, followed by an anodic oxidation in step **II**. In the last step, the oxygen-nitrogen bond was cleaved to give β-damascone.

**(i)** Name the type of reaction in step **I**. [1]

(ii) Construct a balanced half-equation for the oxidation of ketoxime in step **II** under acidic conditions.

You are to use "ketoxime" and "**K**" in your half-equation. [1]

(iii) β-damascone exists as a pair of cis-trans isomers. Draw the cis isomer. [1]

4 **(c)** Ethylenediaminetetraacetic acid (EDTA) is a colourless, water-soluble solid. It is on the World Health Organization's List of Essential Medicines.

EDTA can be synthesised via the following reaction route.
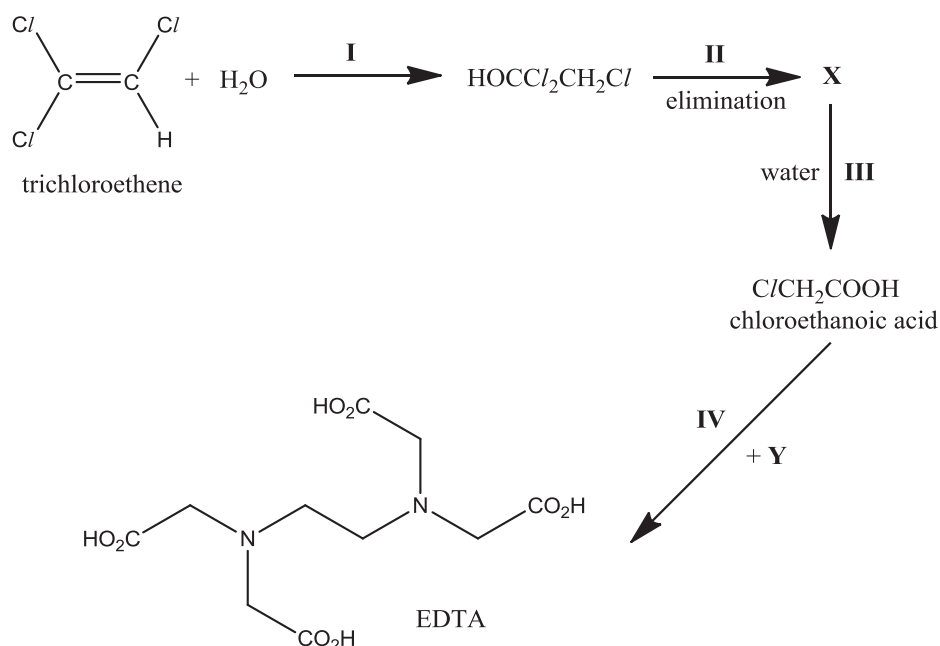
(i) **X** gave a white precipitate when aqueous silver nitrate was added to it. Give the structural formula of **X**. [1]

(ii) Give the structural formula of **Y**. Hence, state a potential problem that might happen when it reacts with chloroethanoic acid. [2]

(d) Chloroethanoic acid can be synthesised from methanal via a three-step route. State the reagents and conditions used in each step and the intermediates involved. [4]

(e) The Kolbe electrolysis involves conversion of carboxylate salts into alkanes. It can be represented by the following half-equation.

$$3 R_1COO^- + 3 R_2COO^- \rightarrow R_1{-}R_1 + R_1{-}R_2 + R_2{-}R_2 + 6CO_2 + 6e^-$$
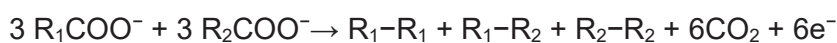
where R_1 and R_2 may not represent the same alkyl group.

In a certain electrolysis, two carboxylate salts were electrolysed, forming three alkanes.

The relative molecular masses are 58.0, 86.0 and 114.0. The alkane with M_r 58.0 is non-chiral. The alkane with M_r 114.0 exists as three stereoisomers - two of which are chiral and the third is non-chiral.

(i) Identify the two carboxylate salts used. [2]

(ii) Draw the stereochemical formula of any of the two chiral stereoisomers. [1]

4 **(e)** In a special application of the Kolbe electrolysis, fumarate was electrolysed into ethyne.

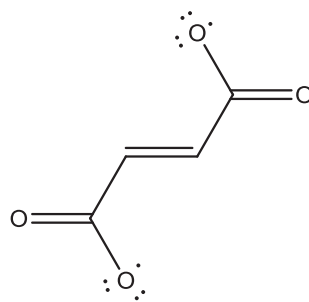fumarate → $2CO_2$ + $2e^-$ + $HC\equiv CH$ ethyne
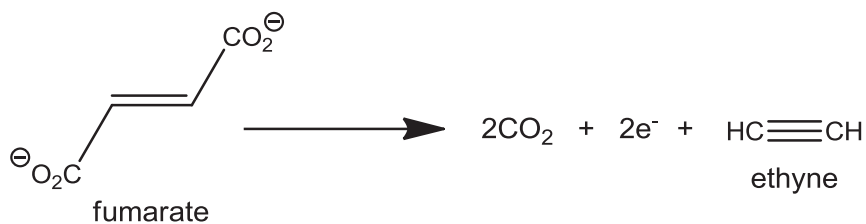
(iii) Kolbe electrolysis proceeds via radical intermediates, which are formed and reacted via homolytic fission and fusion.

Explain the term *homolytic fission*. [1]

(iv) The decomposition of fumarate into ethyne and carbon dioxide happens through two steps – the first of which forms the neutral diradical species below as the intermediate.

Use curly arrows to show how the intermediate decomposes to ethyne and carbon dioxide. [1]

[Total: 20]

5 Melanin is a naturally-occurring organic compound that is responsible for the colour of the skin. The higher the melanin content, the darker the skin is. In the Asian market, skin-lightening lotions have grown to be the most on-demand skin care cosmetic products.

One common ingredient of such lotions is kojic acid, which works by slowing down the rate of formation of melanin. It is obtained from the fermentation of rice malt.

The structure of kojic acid is shown below with the two hydroxyl groups labelled **a** and **b**.

kojic acid

(a) For each of the hydroxyl groups **a** and **b**, explain if it will be substituted with a chlorine atom when one mole of kojic acid is reacted with two moles of PCl_5 at room temperature. [2]

(b) Kojic acid also functions as an antioxidant, scavenging hydroxyl radicals ($^•OH$) that are responsible for ageing. One mole of kojic acid can react with a total of four moles of the radicals to form comenic acid via an intermediate **Z** as shown in the scheme below.

kojic acid   compound **Z**   comenic acid
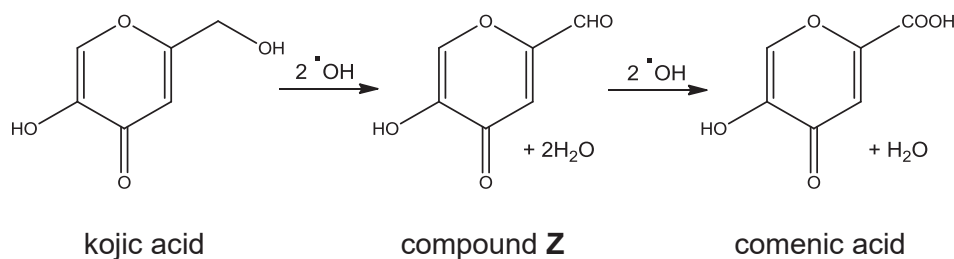
(i) Given the following information, use curly arrows to draw the mechanism for the formation of comenic acid from compound **Z** in two separate steps.

Step 1:
An •OH radical reacts with compound **Z** to form an organic radical intermediate with H_2O being formed as a by-product.
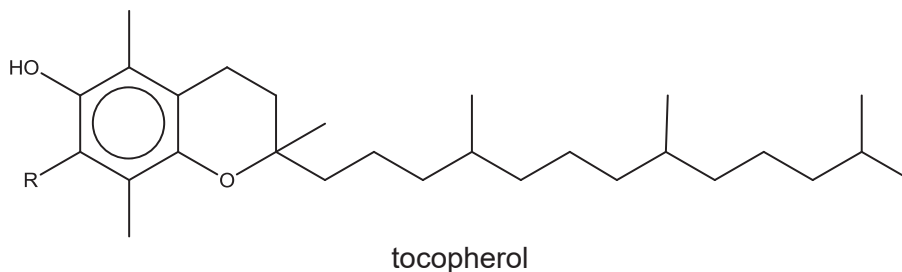
Step 2:
Another •OH radical react with the intermediate formed from the first step. [2]

(ii) Draw another possible organic by-product in the formation of comenic acid from compound **Z**. [1]

5 **(c)** Besides kojic acid, vitamin E is also an essential ingredient that acts as an antioxidant in skin-lightening lotions.

One class of vitamin E is tocopherol, the general structure of which is shown below.

tocopherol

The table below shows the substituent R of two different types of tocopherol, namely α- and β-tocopherol.

	–R
α-tocopherol	$-CH_3$
β-tocopherol	$-H$

Arrange phenol, α-tocopherol and β-tocopherol in an increasing order of pK_a values. Hence, explain the difference in acidity among the three compounds. [3]

(d) To increase the effectiveness and marketability of skin-lightening lotions, titanium dioxide, TiO_2, is often added as a sunscreen agent due to its reflective property.

Solid titanium dioxide reacts with hydrofluoric acid, HF, to form a coordination compound, $H_2[TiF_6]$, and water.

(i) Write a balanced chemical equation, with state symbols, for the above reaction. [1]

(ii) Explain whether the above reaction is a redox reaction. [1]

(iii) State the electronic configuration of titanium in $H_2[TiF_6]$. Hence, explain whether the complex ion is coloured. [3]

5 **(e)** Hydroquinone and catechol are isomers.

Hydroquinone has been used for more than half a century in the formulation of skin lotions to help fade uneven skin tone and dark spots. Catechol, on the other hand, is an important synthetic precursor to pesticides, flavours, and fragrances.

The structures of both compounds, together with their boiling points, are shown below.
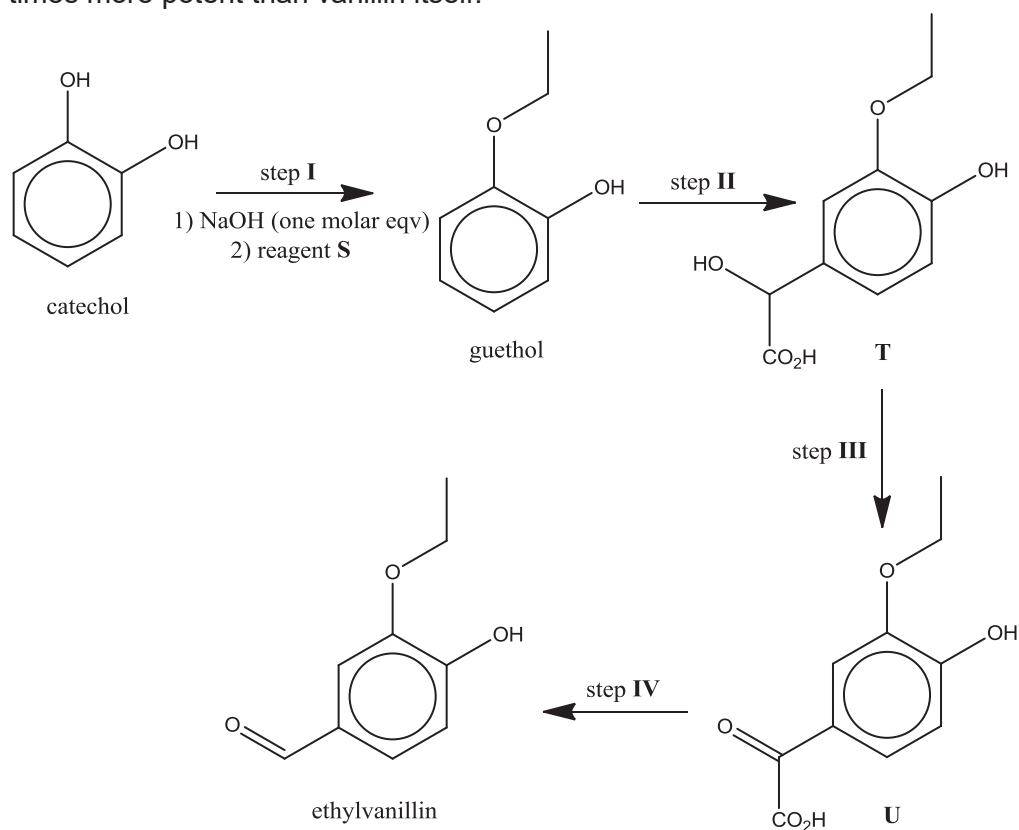

hydroquinone
(boiling point: 287 °C)
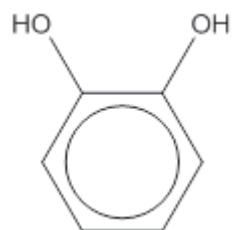
catechol
(boiling point: 246 °C)

(i) Explain why catechol has the lower boiling point. [1]

(ii) Catechol is able to function as a bidentate ligand, but not hydroquinone.

Explain why hydroquinone cannot function as a bidentate ligand. [1]

5 **(f)** Catechol is used industrially to make ethylvanillin, a flavourant reputedly three times more potent than vanillin itself.

OH

OH

catechol

step **I**

1) NaOH (one molar eqv)
2) reagent **S**

O

OH

guethol

step **II**

O

OH

HO

CO₂H **T**

step **III**

O

OH

O

CO₂H **U**

O

OH

O

ethylvanillin

step **IV**

Assume that the ether functional group (R–O–R') is inert.

(i) Explain the purpose of adding NaOH in step **I**. [1]

(ii) Name reagent **S** in step **I**. [1]

(iii) Outline the synthetic pathway to convert ethylvanillin back to compound **T**. Draw the intermediate formed. [3]

[Total: 20]

END OF PAPER

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY 9729/01
Higher 2

Paper 1 Multiple Choice

24 August 2017
1 hour

Additional Materials: Optical Answer Sheet
                         Data Booklet

READ THESE INSTRUCTIONS FIRST

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

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

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

Read the instructions on the Optical Answer Sheet very carefully.

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

Any rough working should be done in this booklet.

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

This document consists of **14** printed pages, including this cover page.

9729/01/Prelim/17   ANGLO-CHINESE JUNIOR COLLEGE
© ACJC 2017   Department of Chemistry   **[Turn over**

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

1 Carbon disulfide is a colourless volatile liquid with the formula CS_2. The compound is used frequently as a building block in organic chemistry as well as an industrial solvent.

It reacts with nitrogen monoxide, NO, to form a yellow solid and two gases. These two gases are formed in equal amounts.

What are these two gases?

A CO_2, NO_2 **B** CO_2, N_2 **C** CO, N_2 **D** CO_2, N_2O

The yellow solid is sulfur.

You cannot balance the equation (with the two product gases in equal amounts) with the three other options.

Balanced equation:

$$CS_2 + 2NO \rightarrow CO_2 + N_2 + 2S$$

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

Which of the following ions will be deflected the **most** in an electric field?

A S^{2-} **B** Br^- **C** F^- **D** O^{2-}

You are to refer to the Data Booklet for the ionic radii (although it is not absolutely necessarily to do so; you can use the Group trend for ionic sizes).

The charge density of the oxide ion is the highest amongst the four.

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

Nuclear magnetic resonance (NMR) spectroscopy is an analytical technique that uses the magnetic properties of certain atomic nuclei in order to elucidate the structure of an organic molecule.

Atomic nuclei with an even number of protons and an odd number of neutrons (or vice versa) are most suitable for NMR spectroscopy.

Which of the following nuclei is **least** suitable for NMR spectroscopy?

A ^{28}Si **B** ^{31}P **C** ^{103}Rh **D** ^{19}F

A: no. of protons 14 no. of neutrons = 28 – 14 = 14

B: no. of protons 15 no. of neutrons = 31 – 15 = 16

C: no. of protons 45 no. of neutrons = 103 – 45 = 58

D: no. of protons 9 no. of neutrons = 19 – 9 = 10

4 A 25.00 cm^3 sample of a solution of 0.150 mol dm^{-3} MoO$_x^{2-}$ was passed through a Jones reductor (a column of zinc powder). It was reduced to Mo^{3+}. The filtrate required 22.50 cm^3 of 0.100 mol dm^{-3} acidified KMnO$_4$ (aq) to obtain back the original amount of MoO$_x^{2-}$.

What is the value of x?

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

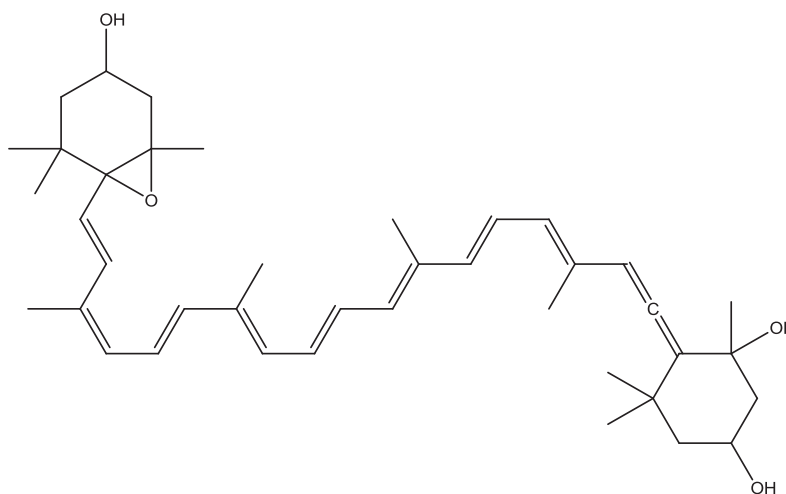Amt of electrons involved = (22.50 X 0.100 / 1000) X 5 = 0.01125

Change in oxidation state in Mo = 0.01125 / (25.00 X 0.150 / 1000) = 3

Original oxidation state of Mo = 3 + 3 = 6

Hence x = 4.

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

5   Neoxanthin is a major xanthophyll found in green leafy vegetables such as spinach.

Which of the following σ bonds are present in neoxanthin?

1   A σ bond formed by sp^2–sp^3 overlap.

2   A σ bond formed by s–p overlap.

3   A σ bond formed by sp–sp^2 overlap.

A   1 and 2 only

B   1 and 3 only

C   2 and 3 only

D   1, 2 and 3

Recall:

Linear Carbon: sp (eg. =C= or –C≡)
Trigonal Planar Carbon: sp^2
Tetrahedral Carbon: sp^3

Bent Oxygen (or Tetrahedral in terms of electron pair geometry) in C-O-C and C-O-H: sp^3

Option 2 is wrong. For s-p overlap, it means that the s orbital belongs to hydrogen, whereas the p orbital (unhybridised) belong to carbon. But the overlaps in the following cases are:
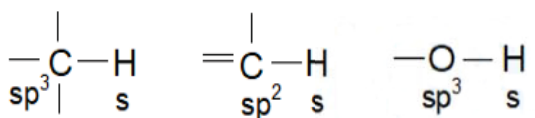
6   The enthalpy changes for the following reactions were measured experimentally:
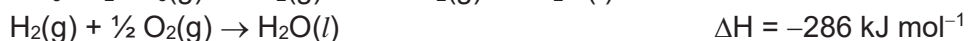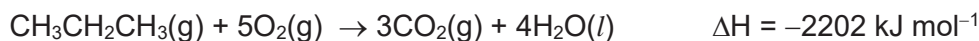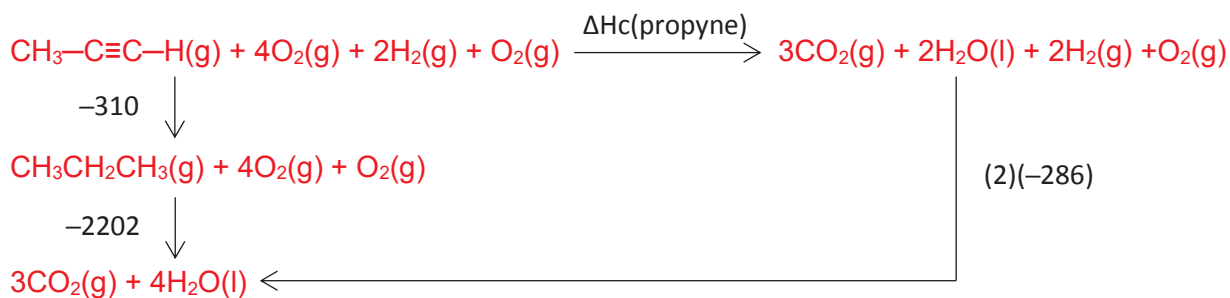
$CH_3CH_2CH_3(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$ $\Delta H = -2202$ kJ mol^{-1}
$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$ $\Delta H = -286$ kJ mol^{-1}
$CH_3-C\equiv C-H(g) + 2H_2(g) \rightarrow CH_3CH_2CH_3(g)$ $\Delta H = -310$ kJ mol^{-1}

What is the enthalpy change of combustion of propyne, $CH_3-C\equiv C-H$, in terms of kJ mol^{-1}?

A   -2226   **B**   -1940   **C**   -1606   **D**   -1320

$CH_3-C\equiv C-H(g) + 4O_2(g) + 2H_2(g) + O_2(g)$ $\xrightarrow{\Delta Hc(propyne)}$ $3CO_2(g) + 2H_2O(l) + 2H_2(g) + O_2(g)$

$-310 \downarrow$

$CH_3CH_2CH_3(g) + 4O_2(g) + O_2(g)$ (2)(–286)

$-2202 \downarrow$

$3CO_2(g) + 4H_2O(l) \longleftarrow$

By Hess' Law,

$\Delta Hc(propyne) = -310 - 2202 - (2)(-286) = -1940$ kJ mol^{-1}

7   35 cm^3 of 0.001 mol dm^{-3} nitric acid solution was added to 35 cm^3 of sulfuric acid solution of the same concentration. What is the resulting pH of the combined solution?

A   1.5   **B**   2.5   **C**   2.8   **D**   3.0

Amount of H$^+$ from HNO_3 = (0.035)(0.001) = 0.000035 mol

Amount of H$^+$ from H_2SO_4 = (2)(0.035)(0.001) = 0.000070 mol

[H$^+$] = (0.000035 + 0.000070) ÷ (0.035 + 0.035) = 0.0015 mol dm^{-3}

pH = $-\log$ [H$^+$] = 2.82

8   In which of the following pairs is the bond angle in the first species smaller than that in the second species?

  1 PBr_3, PBr_4^+

  2 H_2Se, H_2O

  3 SF_2, SCl_2

  A   1 and 2 only

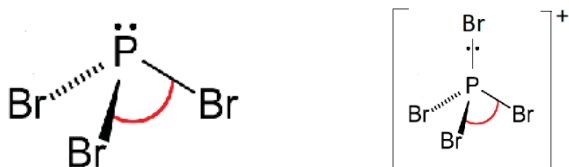 **B**   1 and 3 only

  C   2 and 3 only

  D   1, 2 and 3

Recall: VSEPR model dictates that

"Lone Pair – Lone Pair repulsion > Lone Pair – Bond Pair repulsion > Bond Pair – Bond Pair repulsion"

Option 1

Lone pair on P in PBr_3 is closer to nucleus of P, compared to the Bond Pair in PBr_4^+.

There is stronger repulsion between lone pair and bond pair in PBr_3. Hence the bond angle will be smaller than that in PBr_4^+.

Option 2

Selenium is larger atom than Oxygen. Selenium is also less electronegative than Oxygen. Electron density in Se–H bond is further away from Se, compared to electron density in O–H bond.
There is weaker repulsion between bond pairs in H_2Se. Hence the bond angle will be smaller than that in H_2O.

Option 3

Fluorine is more electronegative than chlorine.
Electron density in S–F bond is further away from S, compared to electron density in S–Cl bond.
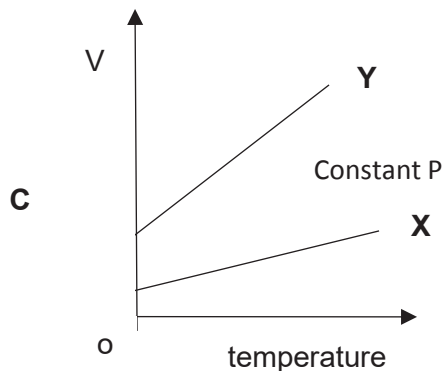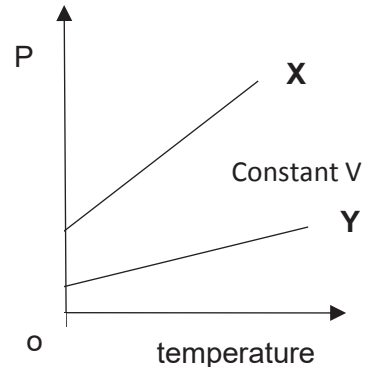There is weaker repulsion between bond pairs in SF_2. Hence the bond angle will be smaller than that in SCl_2.

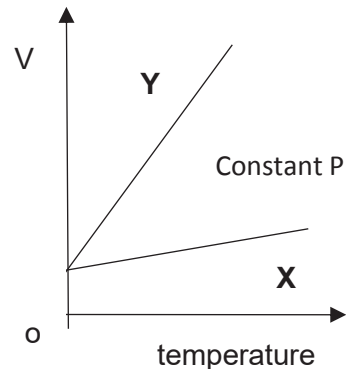9   **X** and **Y** are both ideal gases. **X** has the smaller molecular mass.

Which of the following diagrams correctly describe the behaviour of equal masses of these gases? All temperatures are measured in $^\circ$C.
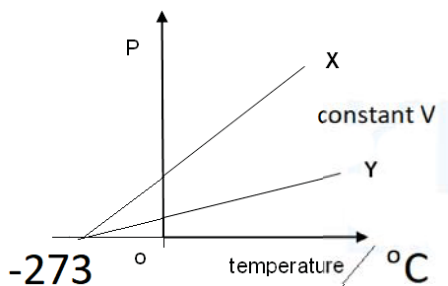
A
P
X
Constant V
Y
O
temperature

B
P
X
Constant V
Y
O
temperature

C
V
Y
Constant P
X
O
temperature

D
V
Y
Constant P
X
O
temperature
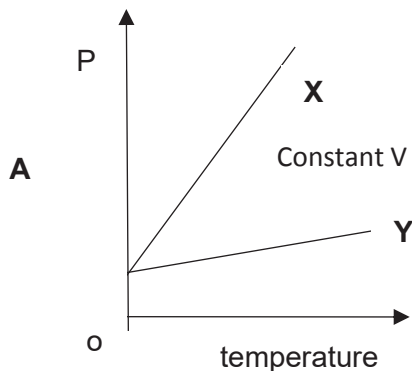
For Ideal Gas, PV = nRT

PV = (m / M_r) RT

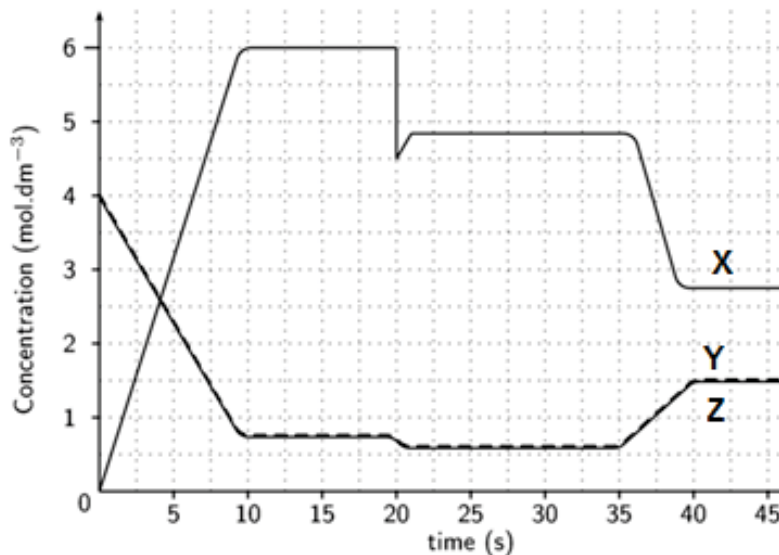At constant Volume, P = (m R / VM_r) T

where Gradient of Line = (m R / VM_r)

X has smaller M_r than Y. Hence the line for X has a steeper gradient than Y.

P
X
constant V
Y
-273   O   temperature $^\circ$C

10 **X** exists in equilibrium with **Y** and **Z**.

$$2X\ (g) \rightleftharpoons Y\ (g) + Z\ (g)$$

The concentrations of **X**, **Y** and **Z** varies across time as shown below. Note that the dotted line refers to both concentrations of **Y** and **Z**.

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

A   The equilibrium constant is dimensionless.

B   **X**(g) was taken out of the system at 20 s.

C   Given that the temperature was decreased at 35 s, it can be concluded that the forward reaction is endothermic.

D   Temperature has no effect on the spontaneity of this reaction.

Option A

$Kp = (P_y\ P_z) / P_x^2$ atm . atm / atm^2

Hence Kp is dimensionless.

Option B

Sudden decrease in [X], but [Y] and [Z] both decrease over time at t = 20s.

This implies that X(g) is taken out of the system at t = 20s.

Option C

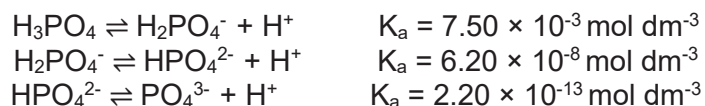If $\Delta H_{forward}$ = +ve, temperature must increase for the POE to shift right.

Option D

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

$\Delta S = 0$ because there is no change in total amount of gaseous particles in the system, regardless of the system shifting left or right.
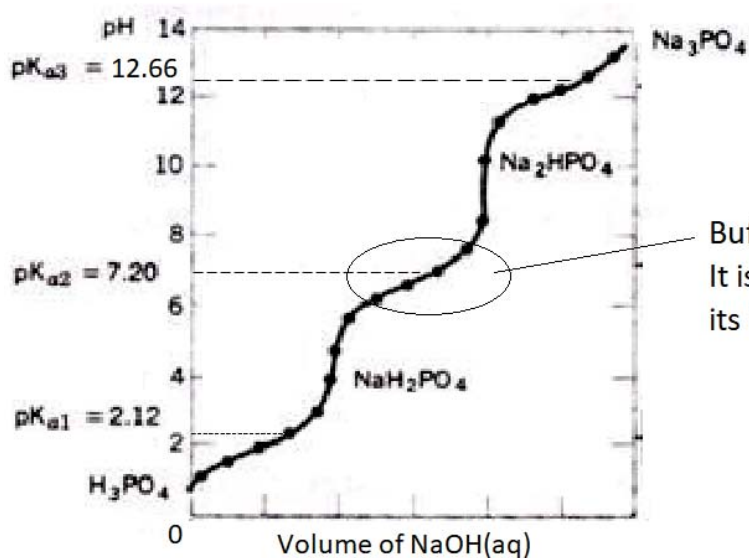Assumption: Temperature is not low enough for liquefaction of gases to occur.

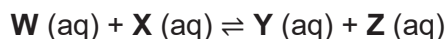**11** The stepwise dissociation equations of phosphoric acid and the corresponding equilibrium constants are shown below.

$$H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+ \qquad K_a = 7.50 \times 10^{-3} \text{ mol dm}^{-3}$$
$$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+ \qquad K_a = 6.20 \times 10^{-8} \text{ mol dm}^{-3}$$
$$HPO_4^{2-} \rightleftharpoons PO_4^{3-} + H^+ \qquad K_a = 2.20 \times 10^{-13} \text{ mol dm}^{-3}$$

A phosphate buffer with pH 7 needs to be prepared.

Which is the best way to prepare such a solution?

A Dissolving Na_3PO_4 alone in water.

B Dissolving H_3PO_4 and NaH_2PO_4 in water.

C Dissolving Na_2HPO_4 and Na_3PO_4 in water.

D Dissolving Na_2HPO_4 and NaH_2PO_4 in water.

Buffer with pH = 7 lies within this region. It is made up of $H_2PO_4^-$ (weak acid) and its HPO_4^{2-} (conjugate base).

12 An equilibrium can be represented by the equation below.

$$W \text{ (aq)} + X \text{ (aq)} \rightleftharpoons Y \text{ (aq)} + Z \text{ (aq)}$$

In 0.50 dm^3 of a certain mixture, the concentrations of these substances at equilibrium were as shown:

Species	W	X	Y	Z
Concentration / mol dm^{-3}	1.00	2.00	2.00	1.00

A certain amount of **Y** was added to this equilibrium mixture.

What is the number of moles of **Y** added such that the new equilibrium [**W**] is 1.20 mol dm^{-3}?

Assume that the temperature remained constant throughout.

A 0.10   **B** 0.20   **C** 0.75   **D** 1.50

At initial equilibrium, Kc = [Y(aq)] [Z(aq)] ÷ [W(aq)] [X(aq)]

Kc = (2.00)(1.00) ÷ (1.00)(2.00)

Kc = 1

	W (aq) +	**X** (aq) ⇌	**Y** (aq) +	**Z** (aq)
Initial Conc	1.00	2.00	2.00 + a	1.00
Change	+0.20	+0.20	−0.20	−0.20
Eqm Conc	1.20	2.20	1.80 + a	0.80

For the new equilibrium,   Kc = (1.80 + a)(0.80) ÷ (1.20)(2.20) = 1

Upon solving,   a = 1.5 mol dm^{-3}

Since it is 0.5 dm^3 solution, therefore the amount added = (1.5)(0.5) = 0.75 mol

13 A sample of washing powder which contains a mixture of Na_2CO_3 and $NaHCO_3$ was titrated with aqueous hydrochloric acid and the following titration curve was obtained.
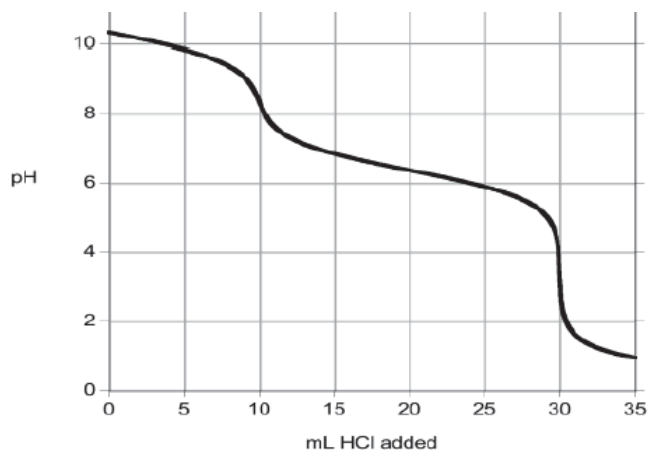
What is the mole ratio of HCO_3^- to CO_3^{2-} in the washing powder?

A   1:1   **B**   1:2   **C**   2:1   **D**   3:1

The first 10 cm³ of HCl is used for: $H^+(aq) + CO_3^{2-}(aq) \rightarrow HCO_3^-(aq)$

The next (30 – 10) = 20 cm³ of HCl is used for: $H^+(aq) + HCO_3^-(aq) \rightarrow H_2CO_3(aq)$

But this $HCO_3^-(aq)$ comes from the original sample, and from the first reaction.

Hence the $HCO_3^-(aq)$ from original sample should correspond to (20 – 10) = 10 cm³ of HCl.

Amount of $HCO_3^-(aq)$: Amount of $CO_3^{2-}(aq)$

≡ Volume of HCl reacting with $HCO_3^-(aq)$ in original sample : Volume of HCl reacting with $CO_3^{2-}(aq)$ in sample

= 10 cm³ : 10 cm³

= 1 : 1

14 The table below contains the standard reduction potential values for some cobalt and mercury species.

half-equation	E$^\circ$/ V
Co^{3+} (aq) + e $\rightleftharpoons$ Co^{2+} (aq)	+1.82
Co^{2+} (aq) + 2e $\rightleftharpoons$ Co (s)	-0.28
Hg^{2+}(aq) + e $\rightleftharpoons$ Hg^+(aq)	+0.91
Hg^+(aq) + e $\rightleftharpoons$ Hg(l)	+0.80

Which one of the following predictions is correct?

A   Both Co^{2+} and Hg^+ will disproportionate.

B   Neither Co^{2+} nor Hg^+ will disproportionate.

C   Only Co^{2+} will disproportionate.

D   Only Hg^+ will disproportionate.

For $Co^{2+} \rightarrow Co^{3+} + Co$

$E^{\ominus}_{cell} = E^{\ominus}_{red} + E^{\ominus}_{ox}$ = (−0.28) + (−1.82) = −2.10 V

Since $E^{\ominus}_{cell}$ < 0, the reaction is NOT spontaneous.

For $Hg^+ \rightarrow Hg^{2+} + Hg$

$E^{\ominus}_{cell} = E^{\ominus}_{red} + E^{\ominus}_{ox}$ = (+0.80) + (−0.91) = −0.11 V
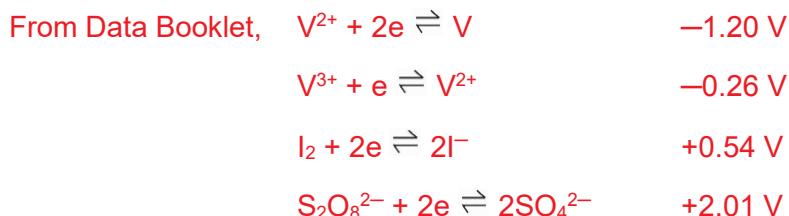
Since $E^{\ominus}_{cell}$ < 0, the reaction is NOT spontaneous.

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

The reaction between iodide and peroxydisulfate ($S_2O_8^{2-}$) is slow due to its high activation energy.

Which of the following cannot function as a catalyst for the above mentioned reaction?

A V^{2+} **B** Mn^{2+} **C** Mn^{3+} **D** Co^{3+}
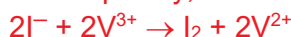
From Data Booklet, $V^{2+} + 2e \rightleftharpoons V$ −1.20 V

$V^{3+} + e \rightleftharpoons V^{2+}$ −0.26 V

$I_2 + 2e \rightleftharpoons 2I^-$ +0.54 V

$S_2O_8^{2-} + 2e \rightleftharpoons 2SO_4^{2-}$ +2.01 V

Case 1: $S_2O_8^{2-}$ react first with V^{2+}.

$S_2O_8^{2-} + 2V^{2+} \rightarrow 2SO_4^{2-} + 2V^{3+}$
$E^{\ominus}_{cell} = E^{\ominus}_{red} + E^{\ominus}_{ox} = (+2.01) + (+0.26) = +2.27$ V
Since $E^{\ominus}_{cell} > 0$, the reaction is spontaneous.

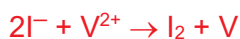Subsequently, V^{3+} must react to form V^{2+} again, for V^{2+} to function as a catalyst.
$2I^- + 2V^{3+} \rightarrow I_2 + 2V^{2+}$
$E^{\ominus}_{cell} = E^{\ominus}_{red} + E^{\ominus}_{ox} = (-0.26) + (-0.54) = -0.80$ V
Since $E^{\ominus}_{cell} < 0$, the reaction is NOT spontaneous.

Hence V^{2+} cannot function as a catalyst in this reaction.

Case 2: I^- react first with V^{2+}.

$2I^- + V^{2+} \rightarrow I_2 + V$
$E^{\ominus}_{cell} = E^{\ominus}_{red} + E^{\ominus}_{ox} = (-1.20) + (-0.54) = -1.76$ V
Since $E^{\ominus}_{cell} < 0$, the reaction is NOT spontaneous.

16 The decomposition of hydrogen peroxide is a first order reaction.

It takes 20 minutes for a 0.140 mol dm^{-3} solution of hydrogen peroxide to halve its concentration.

How much time (in minutes) does it take for a 0.280 mol dm^{-3} solution of hydrogen peroxide to halve its concentration?

A   80   **B**   40   **C**   20   **D**   10

Half-life is the time required for a quantity to reduce to half its initial value.

"Half its initial value" means that it is 50% of its initial value. It is about percentage or ratio, not about the absolute amount.

For 1st order reaction, $k\, t_{1/2} = \ln 2$. Since temperature is constant, the rate constant (k) will be constant, and hence the half-life ($t_{1/2}$) will be constant.
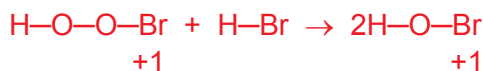
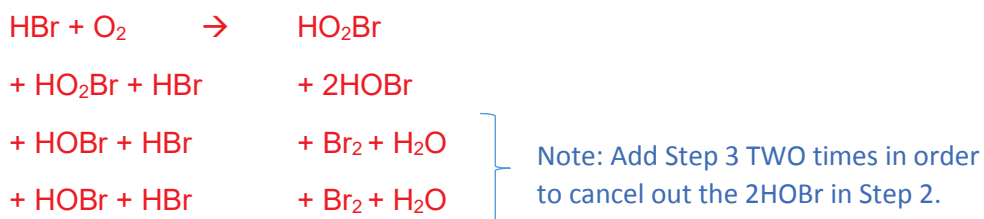**17**   The reaction mechanism between O_2 and HBr is as proposed:
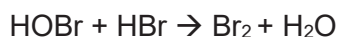
HBr + O_2 → HO_2Br (slow)

HO_2Br + HBr → 2HOBr

HOBr + HBr → Br_2 + H_2O

Which of the following statements is true?

A   The bromine in HO_2Br is oxidised in the second step.

B   The overall equation is O_2 + 4HBr → $2Br_2$ + $2H_2O$.

C   The half-life of this reaction is constant.

D HO_2Br is the only intermediate.

Option A

H—O—O—Br + H—Br → 2H—O—Br

　　　　+1　　　　　　　　　+1

Option B: Add up all the elementary steps to get the overall equation.

HBr + O_2　　　→　　　HO_2Br

+ HO_2Br + HBr　　　+ 2HOBr

+ HOBr + HBr　　　+ Br_2 + H_2O　　　Note: Add Step 3 TWO times in order

+ HOBr + HBr　　　+ Br_2 + H_2O　　　to cancel out the 2HOBr in Step 2.

Option C

Rate = k $[HBr]^1$ $[O_2]^1$

This is not a first-order reaction.

Note: We need to assume that the HBr is NOT in large excess. Otherwise, Rate = k" $[O_2]^1$

This is a pseudo first-order reaction. Then the half-life will be constant.

Similarly, we assume that O_2 is NOT in large excess.

Option D

HOBr is another intermediate.

18 The numerical values of the solubility products at 25 °C for $PbCl_2$ and PbI_2 are 1.70×10^{-5} and 9.80×10^{-9} respectively.

What is the value of the equilibrium constant for the reaction below?

$$PbI_2 \text{ (s)} + 2Cl^- \text{ (aq)} \rightleftharpoons PbCl_2 \text{ (s)} + 2I^- \text{ (aq)}$$
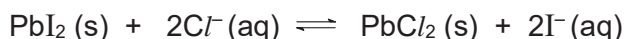
A 3.01×10^6

B 1.73×10^3

C 5.76×10^{-4}

D 3.32×10^{-7}

K_{sp} of $PbCl_2 = [Pb^{2+}][Cl^-]^2 = 1.70 \times 10^{-5} \rightarrow [Cl^-]^2 = 1.70 \times 10^{-5} / [Pb^{2+}]$

K_{sp} of $PbI_2 = [Pb^{2+}][I^-]^2 = 9.80 \times 10^{-9} \rightarrow [I^-]^2 = 9.80 \times 10^{-9} / [Pb^{2+}]$

$K_c = [I^-]^2 / [Cl^-]^2 = (9.80 \times 10^{-9}) / (1.70 \times 10^{-5}) = \underline{\textbf{5.76} \times \textbf{10}^{-4}}$

19 Mohr's salt is named after the German chemist Karl Friedrich Mohr, who made many important advances in the methodology of titration in the nineteenth century.

It is a double salt because it contains two cations and an anion.

Heating solid Mohr's salt with sodium hydroxide liberated a colourless gas. A green precipitate is also formed. It was insoluble in excess sodium hydroxide. On standing in air the solid turned brown.

What is the formula of Mohr's salt?

A $AgCr(CO_3)_2$

B $Ag_2Fe(CO_3)_2$

C $Fe(NH_4)(SO_4)_2$

D $Fe(NH_4)_2(SO_4)_2$

Heating the solid with NaOH liberated a colourless gas of ammonia, thus NH_4^+ is present.

The green precipitate of $Fe(OH)_2$ was formed, which was insoluble in excess sodium hydroxide and turned brown due to oxidation by air to $Fe(OH)_3$, thus Fe^{2+} is present.

Given the above deduction, the answer can be narrowed down to options C or D. To ensure that the overall compound is electrically neutral, there must be one mole of Fe^{2+}, two moles of NH_4^+ and two moles of SO_4^{2-} per mole of the salt. Hence, $\underline{\textbf{Fe(NH}_4\textbf{)}_2\textbf{(SO}_4\textbf{)}_2}$ must be the salt.

20 Photographic film contains silver halides, which absorb light to form silver metal and halogens are formed. Different silver halides have different sensitivity to light and will undergo this process to a different extent.

During the development of the film, a solution of aqueous ammonia or sodium thiosulfate is used to dissolve the unreacted silver halides. However, sodium thiosulfate is preferred, as some silver halides are not soluble in aqueous ammonia.

Which statements concerning the above processes are correct?

1 Metallic silver forms a very stable complex with thiosulfate, hence silver halides are soluble.

2 The decomposition of the silver halide to metallic silver and the respective halogen is easier for AgBr than for AgCl because bromide is more reducing than chloride.

3 AgBr is less soluble than AgCl in aqueous ammonia, as solubility product of AgCl is of a higher value.

A 1 and 2 only

B 1 and 3 only

C 2 and 3 only

D 1, 2 and 3

1: False. It is silver ion (Ag^+), not metallic silver, that complexes with thiosulfate.

2: True. Going down Group 17, the reducing power of the halides increases. It is true that bromide is more reducing than chloride.

3: True. Given that both AgCl and AgBr are binary salts, their K_{sp} values can be compared directly to determine which is more soluble. Since AgBr is less soluble than AgCl in aqueous ammonia, its K_{sp} value must be lower than that of AgCl.

Hence, statements **2 and 3 only are correct**.

21   *Use of the Data Booklet is relevant to this question.*
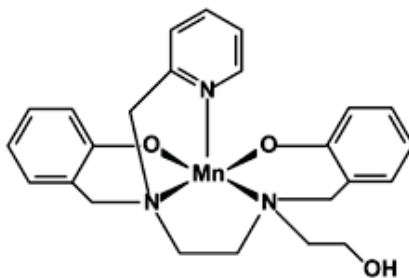
Which of the following statements about the above complex is **false**?

A   There are no 4s electrons in manganese in this complex.

B   This complex contains five ligands.

C   The coordination number of this complex is 5.

D   The oxidation number of manganese in this complex is +2.

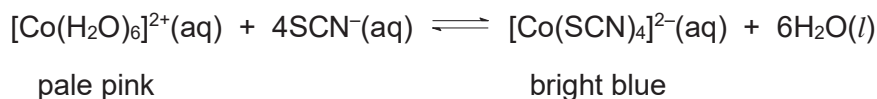**A:** True. Mn^{2+}: $[Ar]3d^5$. The two 4s electrons have been removed in the formation of Mn^{2+} from Mn.

B: False. The complex **does not contain five ligands**. There is only one polydentate ligand.

C: True. As there are five dative covalent bonds formed into the Mn^{2+} ion, the coordination number is 5.

D: True. As the complex is electrically neutral overall, the central metal ion must be Mn^{2+} as it is bonded to two O^-.

22 Cobalt forms many coloured complexes with ligands such as H_2O and SCN^-.

A 100 cm^3 solution of Co^{2+}(aq) turns from pink to bright blue when 10 cm^3 of NaSCN(aq) is added to the solution.

$$[Co(H_2O)_6]^{2+}(aq) + 4SCN^-(aq) \rightleftharpoons [Co(SCN)_4]^{2-}(aq) + 6H_2O(l)$$

pale pink   bright blue

At equilibrium, $[Co(H_2O)_6]^{2+}$ and $[Co(SCN)_4]^{2-}$ are found to be present in a mole ratio of 1:10.

Given that lg K_c for the equilibrium is 3.00, which of the following statements is **false**?

A   At equilibrium, $[SCN^-] = 3.16 \times 10^{-1}$ mol dm^{-3}.

B $[Co(SCN)_4]^{2-}$ is more stable than $[Co(H_2O)_6]^{2+}$.

C   The units of K_c is mol^{-4} dm^{12}.

D   Dilution of the reaction mixture decreases the ratio of $[Co(H_2O)_6]^{2+}$ to $[Co(SCN)_4]^{2-}$ at equilibrium.

A: True.

$$K_c = 1000 = \frac{[[Co(SCN)_4]^{2-}]}{[[Co(H_2O)_6]^{2+}][SCN^-]^4} = \frac{(10/0.11)}{(1/0.11)[SCN^-]^4}$$

∴ $[SCN^-] = 0.316$ mol dm^{-3}

B: True. SCN^- is a stronger ligand than H_2O, thus $[Co(SCN)_4]^{2-}$ is more stable than $[Co(H_2O)_6]^{2+}$. This can also be concluded from the fact that at equilibrium, the mole ratio $[Co(SCN)_4]^{2-}$: $[Co(H_2O)_6]^{2+}$ = 10 : 1.

C: True. $K_c = \dfrac{[[Co(SCN)_4]^{2-}]}{[[Co(H_2O)_6]^{2+}][SCN^-]^4}$ (mol dm^{-3})$^{-4}$ → mol^{-4} dm^{12}

D: False. By Le Chatelier's Principle, dilution of the reaction mixture causes the position of equilibrium to shift to the left, resulting in an **increase in the ratio of $[Co(H_2O)_6]^{2+}$ to $[Co(SCN)_4]^{2-}$ at equilibrium**.

23 Carbon disulfide, CS_2, can be electrolysed into carbon subsulfide, C_3S_2, an unusual compound.

The boiling points of these two compounds are 46.2 °C and 90.0 °C respectively.

$$CS_2(l) \xrightarrow[\text{electrolysis}]{\textbf{I}} ZnS(l) \ + \ S{=}C{=}C{=}C{=}S \ (l) \xrightarrow[Br_2]{\textbf{II}}$$

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

1 Bromine is acting as a reducing agent in **II**.

2 C_3S_2 has the higher boiling point because there are more covalent bonds to be broken than in CS_2.

3 The carbon atoms in C_3S_2 do not share a common oxidation state.

A 2 and 3 only

B 1 and 3 only
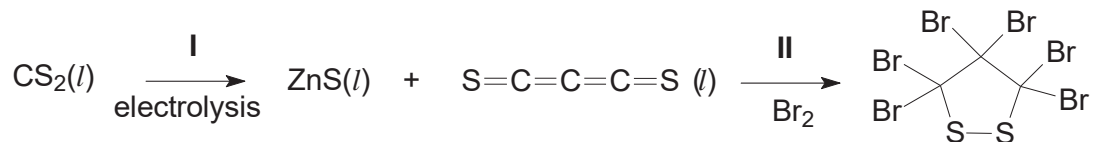
C 1 and 2 only

D 1, 2 and 3

1: False. Bromine is acting as an oxidising agent in **II**.

2: False. The boiling point of a simple covalent molecule depends on the intermolecular forces of attraction, not the number or strength of the covalent bonds.

3: True. Each of the carbon atoms directly bonded to sulfur is +3, while the other carbon not directly bonded to sulfur is +2.

Hence, statements **1 and 2 only are false**.

24 L-lyxose and D-xylose are monosaccharides.
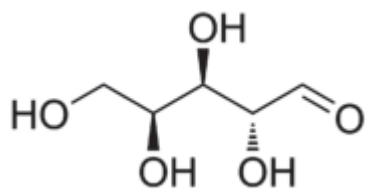
L-xylose   D-xylose
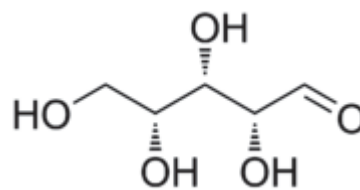
Which of the following statements are true?

1 They have the same melting point.

2 The same volume of hydrogen gas is produced when excess sodium is added to equal amounts of each of them under the same conditions.

3 Both compounds undergo intramolecular nucleophilic substitution to form cyclic esters.

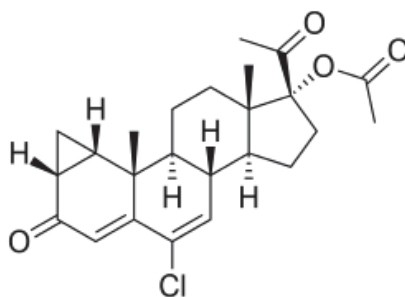**A** 1 and 2 only

B 1 and 3 only

C 2 and 3 only

D 2 only

1: False. L-xylose and D-xylose are not enantiomers (they are diastereomers), thus they have different physical properties, such as melting point.

2: True. Both L-xylose and D-xylose have four hydroxyl groups each. One mole of the monosaccharide produces two moles of hydrogen gas when reacted with sodium.

3: False. Ester is formed from the reaction between a carboxylic acid (or acyl halide) and an alcohol functional group. There is no carboxylic acid functional group in either monosaccharides.

Hence, statement **2 only is correct**.

25 Cyproterone acetate (abbreviated as CPA) is a drug that is used in the treatment of androgen-related conditions like acne and prostate cancer.

Which of the following statements about CPA are correct?

1   One mole of CPA undergoes condensation with three moles of 2,4-dinitrophenylhydrazine.

2   Two moles of yellow precipitate is formed when one mole of CPA is warmed with alkaline iodine solution.

3   CPA does not cause a colour change in hot acidified potassium dichromate(VI).

A   1 and 3 only

B   1 and 2 only

C   2 and 3 only

D   3 only

1: False. One mole of CPA undergoes condensation with only two moles of 2,4-DNPH.

2: False. Only one mole of yellow precipitate is formed when one mole of CPA is subjected to iodoform test.

3: True. Alkenes can only be oxidised by hot acidified potassium manganate(VII), while the alcohol formed from the cleavage of the ester bond is a tertiary alcohol and thus cannot be oxidised.

Hence, statement **3 only is correct**.

26 Xantocillin was first isolated from *Penicillium notatum* in the 1950s. It is used as an antibiotic.
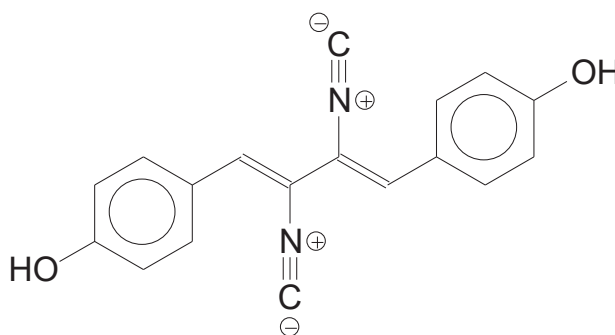
xantocillin

Which of the following statements about xantocillin is **false**?

A   It is a nitrile.

B   It exists as three cis-trans isomers.

C   There are four sp hybridised atoms.

D   It gives a violet colouration on adding neutral iron(III) chloride.

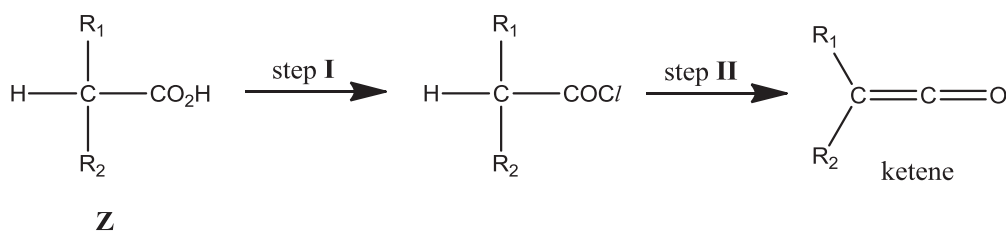**A:** False. It is **<u>not a nitrile</u>** (–CN), but rather contains isocyanide (–NC) functional groups.

B: True. As xantocillin is symmetrical and there are two C=C double bonds, there are the cis-cis, cis-trans (or trans-cis) and trans-trans isomers.

C: True. Each of the two isocyanide (–NC) functional groups contains one sp carbon atom and one sp nitrogen atoms. Hence, there are four sp hybridised atoms in total.

D: True. Phenol reacts with neutral iron(III) chloride to give a violet colouration.

27 Ketenes are important reagents in organic synthesis. They can be formed from carboxylic acids via the synthetic route below.

Which of the following statements about the above reaction are correct?

1 The ketene will always be non-chiral, no matter which **Z** is used as the starting reactant.

2 Hydrochloric acid can be used as the reagent in step **I**.

3 The ketene can be converted back into **Z** by using water under suitable conditions.

A 1 and 2 only

B 1 and 3 only

C 2 and 3 only

D 1, 2 and 3

1: True. There is no chiral carbon in the ketene (C=C=O) functional group.

2: False. Such conversion can be achieved through the use of PCl_3, PCl_5 or $SOCl_2$ instead of HCl.

3: True. Water acts as a nucleophile to convert ketene back into **Z**.

Hence, statements **1 and 3 only are correct**.

28 Aqueous silver nitrate can be used to test for the presence of halogens in organic compounds. Which of the following compounds produces a precipitate most readily when aqueous silver nitrate is added?
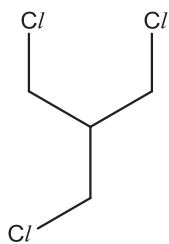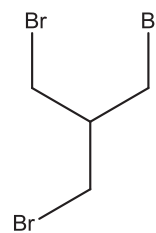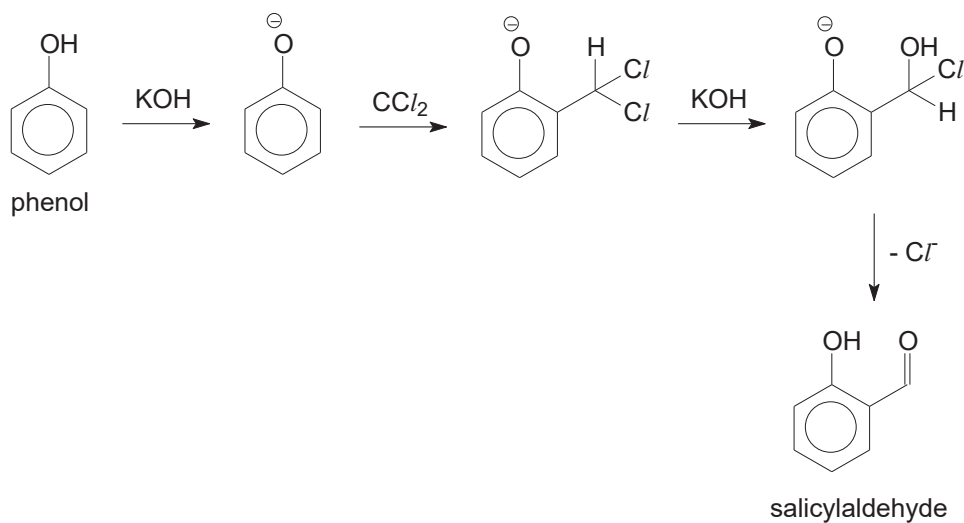
A
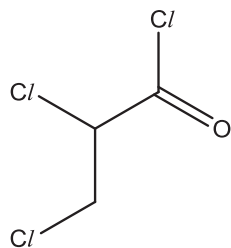
B
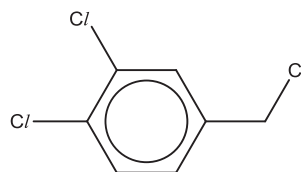
C

D

As acyl chloride is the easiest to hydrolyse, the compound in option **A** will produce a precipitate most readily upon the addition of aqueous silver nitrate.

29 The Reimer–Tiemann reaction is a chemical reaction used for the ortho-formylation of phenols, with the simplest example being the conversion of phenol to salicylaldehyde.

Which of the following types of reaction are involved in the above reaction scheme?

1 Nucleophilic substitution

2 Electrophilic substitution

3 Elimination

A 1 and 2 only

B 1 and 3 only

C 2 and 3 only

D 1, 2 and 3

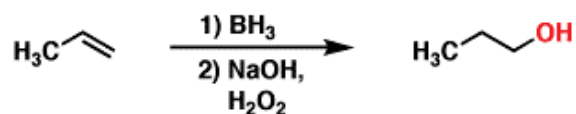**1:** True. Step 3 involves nucleophilic substitution of –Cl to –OH.

2: True. Step 2 involves electrophilic substitution on the 2-position of the phenyl ring.

3: True. Step 4 involves elimination of Cl^-.

Hence, statements **1, 2 and 3 are correct**.

30   Hydroboration is one of the many methods to hydrate alkenes to alcohols. An example is shown below.

Which of the following alcohols cannot be formed via hydroboration?

A   Butan-2-ol from but-1-ene

B   2-methylpropan-1-ol from 2-methylpropene

C   3-methylpentan-2-ol from 3-methylpent-2-ene

D   4-methylhexan-3-ol from 3-methylhex-3-ene

As seen from the example, hydroboration is an anti-Markovnikov electrophilic addition reaction. It means a hydrogen atom is added to the more substituted carbon atom instead of the less substituted carbon atom.

As such, subjecting but-1-ene to hydroboration should result in the formation of butan-1-ol instead of butan-2-ol.

Index No.	Name		Form Class	Tutorial Class	Subject Tutor

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY   **9729/02**
Higher 2

Paper 2   Structured Questions   **15 August 2017**
                                                   2 hours

Candidates answer on the Question Paper
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, index number, form class, tutorial class and subject tutor's name on all the work you hand in.
Write in dark blue or black pen.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions.
A Data Booklet is provided.

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

For Examiner's Use	
Question no.	**Marks**
1	/ 7
2	/ 13
3	/ 9
4	/ 11
5	/ 5
6	/ 9
7	/ 14
8	/ 7
TOTAL	**/ 75**

This document consists of **21** printed pages, including this cover page.

For more than two millenia human ingenuity has turned natural and synthetic poisons into weapons of war. World War I was especially hailed by historians as the "Chemists' War" because it was the first war in which chemical weapons were used on such an enormous scale, even on civilians. Chemicals were used to bring widespread destruction and death. It set the precedence for World War II. On the bright side, chemicals were used to save millions of soldiers' lives in World War II.

Question 1 examines how chemical weapons were used to kill in World War I, while Question 2 examines the use of chemicals as medicine in the battlefields of World War II.

1 A range of different chemicals - chlorine, phosgene and mustard "gas" - were used as weapons throughout World War I.

Their melting and boiling points are tabulated below.

Gas	Melting point / ^{0}C	Boiling point / ^{0}C
chlorine	-101.5	-34.0
phosgene	-118	8.3
mustard "gas"	14.4	217.0

Chlorine was first used on a large scale by the German forces at Ypres in April 1915. It reacts with water in the lungs to form hydrochloric acid, which can quickly lead to death. At lower concentrations, it can cause coughing, vomiting, and irritation to the eyes.

(a) Phosgene is a colourless gas, with an odour likened to that of 'musty hay'.

Phosgene is known to react violently with water to give hydrochloric acid and carbonic acid. Give the equation of the reaction between phosgene and water.

$COCl_2 + 2H_2O \rightarrow H_2CO_3 + 2HCl$

[1]

(b) The Germans introduced another chemical weapon – mustard "gas". It was fired into enemy positions by cannons.

(i) How is the name mustard "gas" misleading?

It is actually a liquid at room temperature because its melting point is lower than room temperature and its boiling point is higher than room temperature.

[1]

1 (b) The structural formula of mustard "gas" is $ClCH_2CH_2SCH_2CH_2Cl$.

Unlike alkyl halides, mustard "gas" reacts instantly with water to form hemi-mustard, $ClCH_2CH_2SCH_2CH_2OH$.

(ii) The following intermediate is thought to be formed by mustard "gas" itself via an intramolecular nucleophilic substitution before the attack of water.
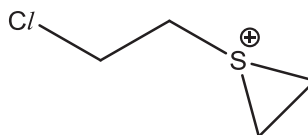

How does this intermediate make the hydrolysis of mustard "gas" easier than that of alkyl halides?

The presence of angle/ring strain in this intermediate makes it more susceptible to nucleophilic attack than the mustard gas molecule itself.

[1]

(iii) The conversion of the intermediate in **b(ii)** to hemi-mustard involves two steps, the first involving the attack by water and the second involving deprotonation.
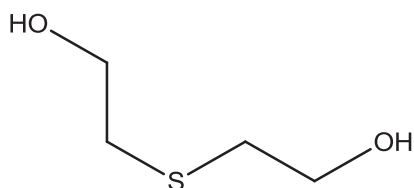
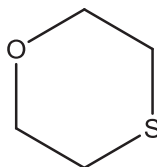Use electron arrows to show how the intermediate in **b(ii)** is converted into hemi-mustard.
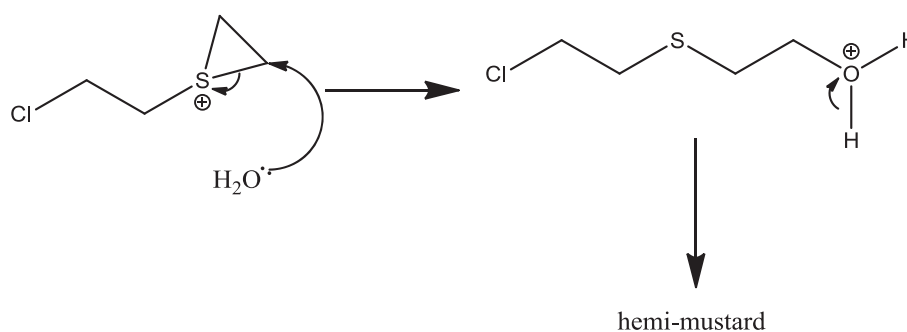
hemi-mustard

[2]

1 (b) (iv) Hemi-mustard can be further attacked by water to form **J**, $C_4H_{10}SO_2$.

Draw the structure of **J**.

[1]

(v) On reaction with concentrated sulfuric acid at 140 °C, hemi-mustard can be converted into **K**, C_4H_8SO, which does not decolourise bromine.
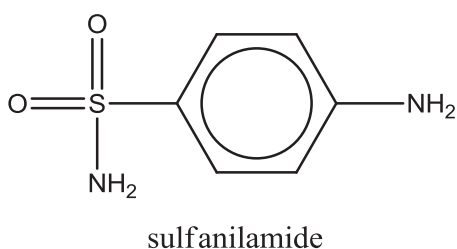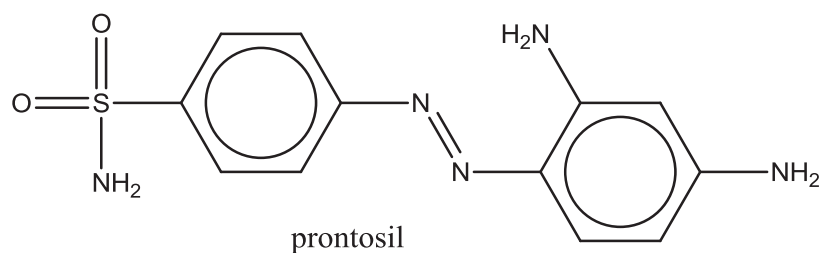
Draw the structure of **K**.

[1]

[Total: 7 marks]

2 **(a)** Prontosil and sulfanilamide are anti-bacterial drugs.

prontosil

sulfanilamide

These two drugs saved many soldiers in World War II.

The photo below is that of a **sulfanilamide kit** issued by the United States Army to its soldiers during World War II.

One source states that the maximum daily dosage of sulfanilamide is 6.5 g per kg of patient. An average US army soldier may be assumed to weigh about 70 kg.

Sulfanilamide has many side-effects – itching, headache, diarrhoea, pale skin, vomiting, dizziness, fatigue.

Is it safe for a wounded US army soldier to consume as many as 30 **kits** worth of tablets in a single day? Justify with calculations.

Yes.
Mass of drug in 30 kits = 30(12)0.5 g < 6.5(70) g

[1]

2 (b) Prontosil was found to be active in *vivo* (in human bodies) while sulfanilamide was found to be active both in *vivo* and in *vitro* (in bacterial cultures grown in petri dishes).

It was later proven that intestinal enzymes break down prontosil to sulfanilamide in the human intestine – in this reaction, the oxidation states of certain nitrogen atoms are altered.

There are a few classes of enzymes as listed below.

Transferases catalyse group transfer reactions.

Hydrolases catalyse reactions that involve hydrolysis.

Ligases are used in catalysis where two substrates are litigated and the formation of carbon-carbon, carbon-sulfide, carbon-nitrogen, and carbon-oxygen bonds due to condensation reactions.

Reductases catalyse reduction reactions.

Oxidases catalyse oxidation reactions.

(i) Suggest the type of intestinal enzyme which catalyses the conversion of prontosil to sulfanilamide.

Reductase

[1]

(ii) Name the side-product in the conversion of prontosil to sulfanilamide.

1,2,4-triaminobenzene or benzene-1,2,4-triamine

[1]

To analyse the sulfanilamide content in a pill, it was dissolved in HC*l* (aq).

(c) Sulfanilamide is not very soluble in water. Explain why sulfanilamide is not soluble in water but is soluble in HC*l* (aq).

Sulfanilamide is not very soluble in water due to limited hydrogen bonding due to the presence of benzene / hydrophobic nature of benzene.

However, in acid, sulfanilamide is a base / will be protonated by acid / becomes ionic, so interactions with water change from hydrogen bonding to the more favorable / stronger ion-dipole interactions.

[2]

2 A 0.350 g sample of an antibiotic powder containing sulfanilamide was dissolved to form an aqueous solution.

The solution was diluted and made up to the mark in a 100 cm³ graduated flask. A 25.0 cm³ aliquot was transferred into a conical flask, in which 25.0 cm³ of 0.0200 mol dm⁻³ $KBrO_3$ was added. About 10 g of solid KBr was then added.
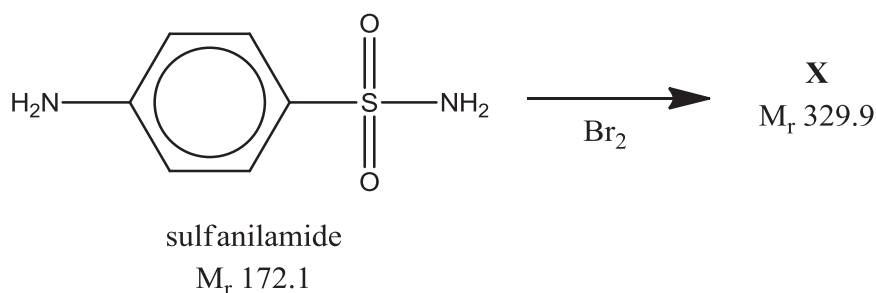
BrO_3^- reacts with bromide according to the equation:

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

(d) **(i)** Calculate the amount of Br_2 formed.

Amount of Br_2 = 3 * (25.0 * 0.0200 / 1000) = 0.00150 mol

[1]

The bromine formed then reacts with the sulfanilamide to form **X**.

Note that the following equation is not balanced.

sulfanilamide
M_r 172.1

(ii) By comparing the M_r of sulfanilamide and **X**, show that **X** is a dibrominated compound.
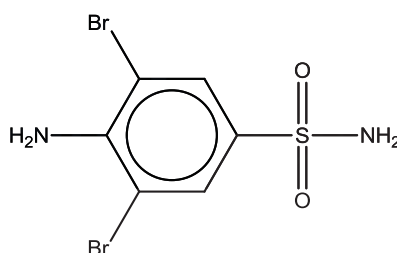
The A_r of bromine is 79.9 to the nearest 1 dp.

Observing the 0.9 in the M_r of **X**, we can conclude there are two bromine atoms in **X**.
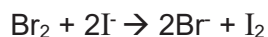
Or

329.9 + 2 – (172.1) = 159.8 = 2(79.9)

[1]

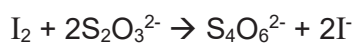**(iii)** Draw the structure of **X**, ignoring the directing effects of the $-SO_2NH_2$ group.

[1]

2 (e) After ten minutes, an excess of KI was added.

$$Br_2 + 2I^- \rightarrow 2Br^- + I_2$$

The liberated iodine was then titrated with 18.00 cm^3 of 0.0900 mol dm^{-3} Na$_2$S$_2$O$_3$.

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

Calculate the amount of bromine which reacted with the KI.

Amt of iodine = 0.5 * (18.00 * 0.0900 / 1000) = 8.10 $\times 10^{-4}$ mol = amount of bromine reacted with KI.

[1]

(f) Using your answers to **(d)** and **(e)**, calculate the amount of sulfanilamide which reacted with the bromine.

Amt of bromine reacted with sulfanilamide
$= (1.50 \times 10^{-3}) - (8.10 \times 10^{-4}) = 6.90 \times 10^{-4}$ mol

amt of sulfanilamide which reacted with the bromine $= 3.45 \times 10^{-4}$ mol

[2]

(g) Hence, calculate the percentage mass of sulfanilamide in the sample.

Mass of sulfanilamide in sample = 3.45 $\times 10^{-4} \times 4 \times 172 = 0.2374$ g

Percentage mass of sulfanilamide in sample = $\frac{0.2374\,g}{0.350g} \times 100\% = 67.8\%$

[2]

[Total: 13 marks]

3 Hydrazine (N_2H_4) was first used as rocket fuel in World War II, and has since been used as a propellent for maneuvering spacecraft, as it decomposes rapidly and exothermically into hydrogen gas and nitrogen gas.

Hydrazine may be produced industrially by the Olin-Rashig process from NH_2Cl and ammonia.

$$NH_2Cl \text{ (g)} + NH_3 \text{ (g)} \rightleftharpoons HCl \text{ (g)} + N_2H_4 \text{ (g)}$$
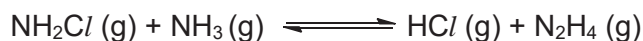
The values of K_c are tabulated below with the corresponding temperatures.

T / K	298	304	503
K_c	1.525×10^6	1.230×10^5	2.201×10^4

(a) State the value of K_p at 304 K. Justify your answer.
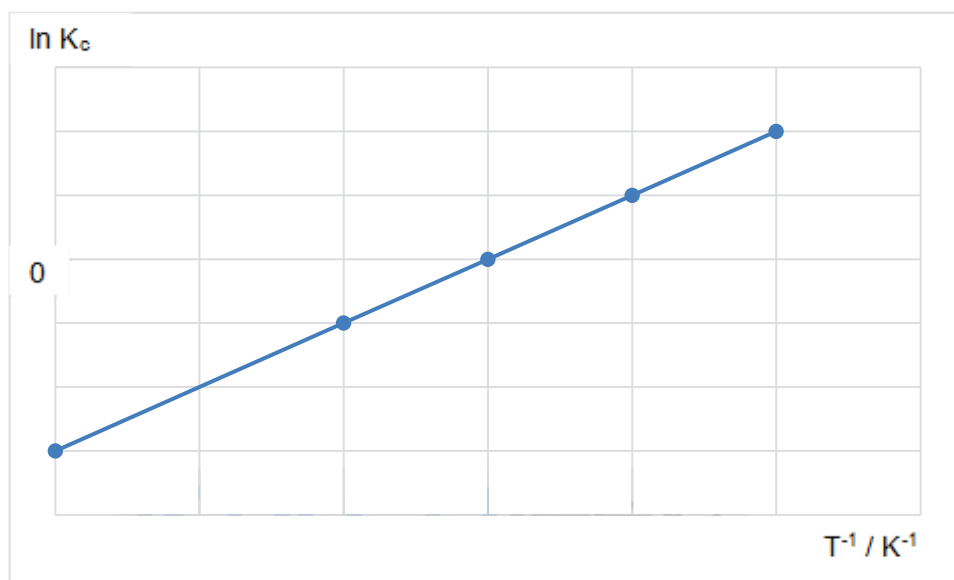
1.230×10^5

As the <u>unit of K_c is dimensionless</u> OR <u>there are equal amounts of gaseous reactants and products in the equation</u>, the value of K_c is the same as the value of K_p.

[2]

(b) By manipulating the relationship of $K_c = e^{\frac{-\Delta G}{RT}}$, we obtain

$$R \ln K_c = \frac{1}{T}(-\Delta H) + \Delta S.$$

The graph below was plotted with $\ln K_c$ as the y-axis and $\frac{1}{T}$ as the x-axis.

(i) Describe how you would obtain the value of ΔS from the above graph.

Read off the y-intercept and then multiply it by R

[1]

3 (b) (ii) Another way to find the standard entropy change of a reaction is to consider the standard molar entropies of the species involved.

Species	HCl (g)	N$_2$H$_4$ (g)	NH$_2$Cl (g)	NH$_3$ (g)
Standard molar entropy / J mol^{-1} K^{-1}	187	239	201	193

Calculate the standard entropy change of the Olin-Rashig process.

Standard entropy change
$= \sum S \, (products) - \sum S \, (reactants)$
= 187 + 239 – (201+193)
= + 32 J mol^{-1} K^{-1}

[1]

(iii) Hence, using your answer to **b(ii)** and the equation in **(b)**, calculate the standard enthalpy change of the Olin-Rashig reaction, including its units.

$$R \ln K_c = \frac{1}{T}(-\Delta H) + \Delta S$$

8.31 ln (1.525 * 10^6) = (1/298)(-ΔH) + 32

ΔH = - 25.7 kJ mol^{-1}

[1]

(c) The pK$_a$ and pK$_b$ values of the two reactants – monochloramine (NH$_2$Cl) and ammonia - are tabulated below.

Product	NH$_2$Cl	NH$_3$
pK$_a$	14	32.5
pK$_b$	15	4.75

Explain these differences as much as you can.

NH$_2$Cl has an Cl atom which is more electronegative than H in NH$_3$.

The presence of the more electronegative chlorine atom in NH$_2$Cl compared to hydrogen in NH$_3$ causes the lone pair on the nitrogen in monochloramine to be less available than the lone pair in ammonia. Hence, monochloramine is the weaker base as shown by the bigger pK$_b$.

The presence of the more electronegative chlorine atom in NH$_2$Cl compared to hydrogen in NH$_3$ causes the conjugate base of monochloramine to be more stable than the conjugate base of ammonia. Hence monochloramine is the stronger acid as shown by the bigger pK$_a$.

[2]

3 (d) Monochloramine is an oxidising agent.
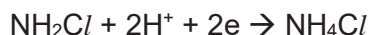
$$NH_2Cl + 2H^+ + 2e \rightarrow NH_4Cl$$

The reduction potentials of the above half-reaction is +1.45 V.

However, in alkaline medium, the reduction potential is + 0.74 V.

Explain the difference between these two reduction potentials.

In alkaline medium, concentration of H^+ will be lower, thus backward reaction is favoured.

The tendency of monochloramine to be reduced decreases, and hence the reduction potential decreases.

[2]

[Total: 9 marks]

4 (a) Ethanoic acid, a weak monobasic acid, is the main component in vinegar.

When a 20.0 cm³ sample of vinegar was titrated against 0.05 mol dm⁻³ aqueous potassium hydroxide using a pH meter, the following graph was obtained.
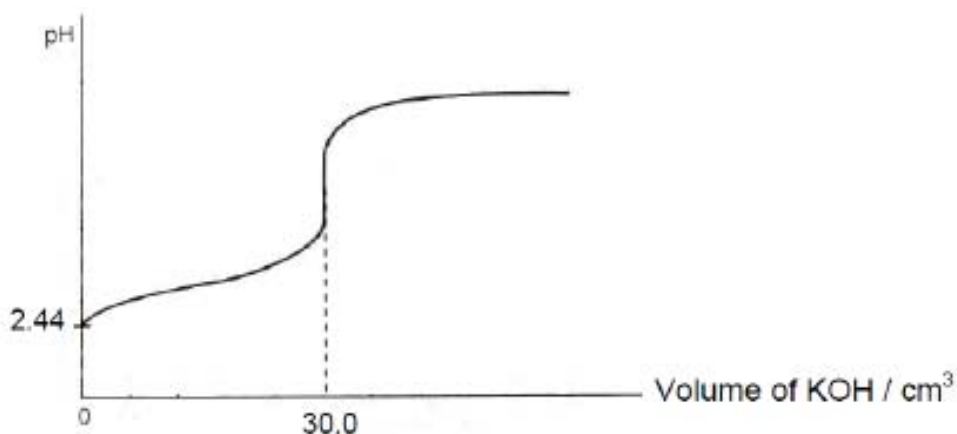
(i) Show that the concentration of the ethanoic acid solution is 0.0750 mol dm⁻³.

Amount of KOH
= 30.0/1000 * 0.05

Concentration of ethanoic acid solution
= (30.0/1000 * 0.05) / (20.0/1000) = 0.0750 M (shown)

[1]

(ii) Hence **use your answer and the initial pH to show** that ethanoic acid is a weak acid.

If ethanoic acid were a strong acid where dissociation is complete (100%),
$[H^+]$ = 0.0750 M, pH = – log (0.0750) = 1.12

However, it is a weak acid where dissociation is partial, the $[H^+]$ dissociated is low, the actual pH would be higher than 1.12.
OR

$[H^+]$ = 10⁻²·⁴⁴ = 0.003631 M < 0.0750M, dissociation of acid is not complete, it is a weak acid.

[2]

4 (a) (iii) Show that the acid dissociation constant of ethanoic acid has a numerical value of 1.85×10^{-4}.

$[H^+] = 0.003631$ M
$K_a = (0.003631)^2 / (0.0750 - 0.003631) = 1.85 \times 10^{-4}$ M

[2]

(iv) Calculate the value of the pH after 15.00 cm³ of aqueous potassium hydroxide has been added.

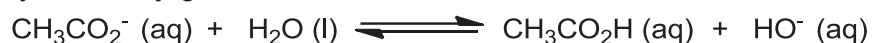When 15.00 cm³ of KOH is added, half of the weak acid would have reacted. It is a maximum buffering capacity.

$pH = pK_a = 3.73$

[1]

(v) Write a suitable chemical equation, with state symbols, to explain why the equivalence pH is above 7.

Hydrolysis of conjugate base:
$$CH_3CO_2^- \text{ (aq)} + H_2O \text{ (l)} \rightleftharpoons CH_3CO_2H \text{ (aq)} + HO^- \text{ (aq)}$$

[1]

(b) (i) Solution **A** was prepared by adding 10.00 cm³ of the potassium hydroxide solution to 25.0 cm³ of the ethanoic acid solution.

Calculate the pH of solution **A**.

Amt of ethanoic acid remaining = $\frac{25 \times 0.0750}{1000} - \frac{10 \times 0.0500}{1000} = 0.001375$ mol
Amt of ethanoate = 0.0005
$pH = pK_a + \lg \left(\frac{[salt]}{[acid]}\right)$
$= -\lg (1.85 \times 10^{-4}) + \lg (0.0005/0.001375) = 3.29$

[2]

(ii) When a small amount of acid or base is added to solution **A**, its pH remained relatively constant. Explain, with the aid of equations, why this is so.

Solution **A** is buffer as there are large reservoirs of ethanoic acid (weak acid) and ethanoate ions (conjugate base).

When a small amount of acid is added,

$$CH_3CO_2^- + H^+ \rightarrow CH_3CO_2H$$

The formation of CH_3CO_2H is insignificant compared to the large reservoir of CH_3CO_2H. Hence, the pH does not decrease significantly.

When a small amount of base is added,

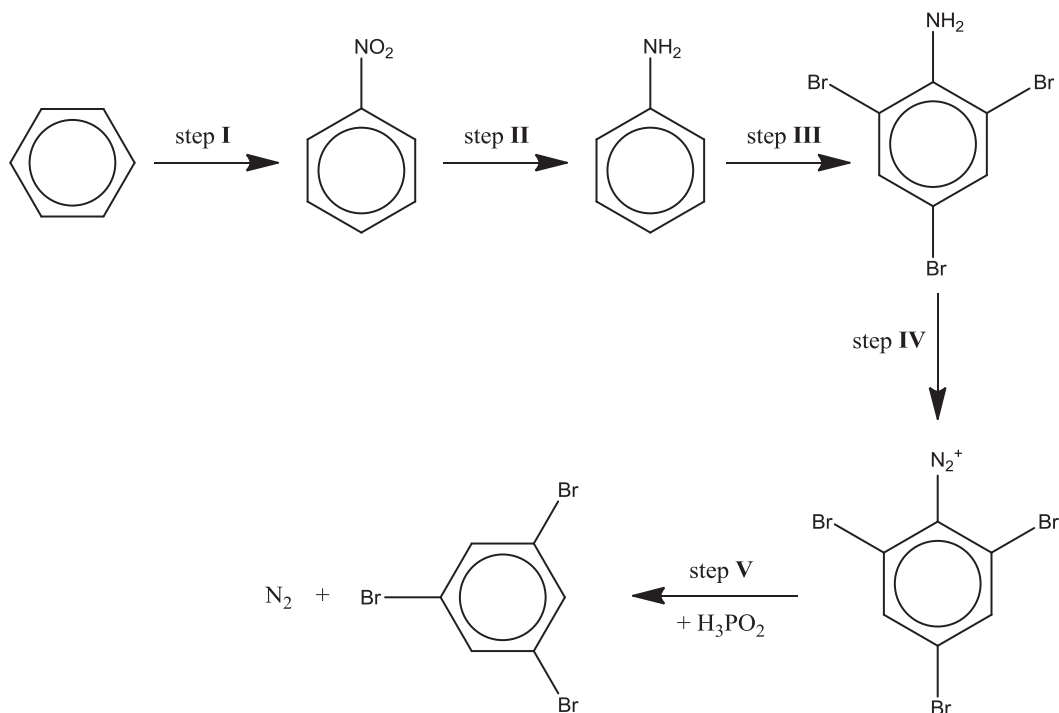$$CH_3CO_2H + OH^- \rightarrow CH_3CO_2^- + H_2O$$

The formation of $CH_3CO_2^-$ is insignificant compared to the large reservoir of $CH_3CO_2^-$. Hence, the pH does not increase significantly.

[2]

[Total: 11 marks]

5 Study the synthetic route from benzene to 1,3,5-tribromobenzene, shown below.

(a) State the reagents and conditions used in steps **I** and **II**.

step **I** : Conc. HNO_3, conc. H_2SO_4, 55 -60 ^{0}C
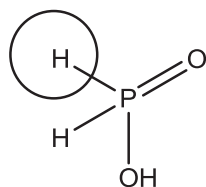step **II** : Sn, conc HCl , heat under reflux

[2]

(b) By examining the positions of the bromine atoms, suggest why 1,3,5-tribromobenzene cannot be made directly from benzene with bromine.

Bromine is a 2,4-director.

[1]

(c) Phosphinic acid, H_3PO_2, is used in step **V**. Only one out of its three hydrogen atoms is acidic. A non-acidic hydrogen substituted on the benzene to liberate nitrogen gas.

Draw the structure of phosphinic acid and circle the hydrogen atom which substitutes on the benzene.
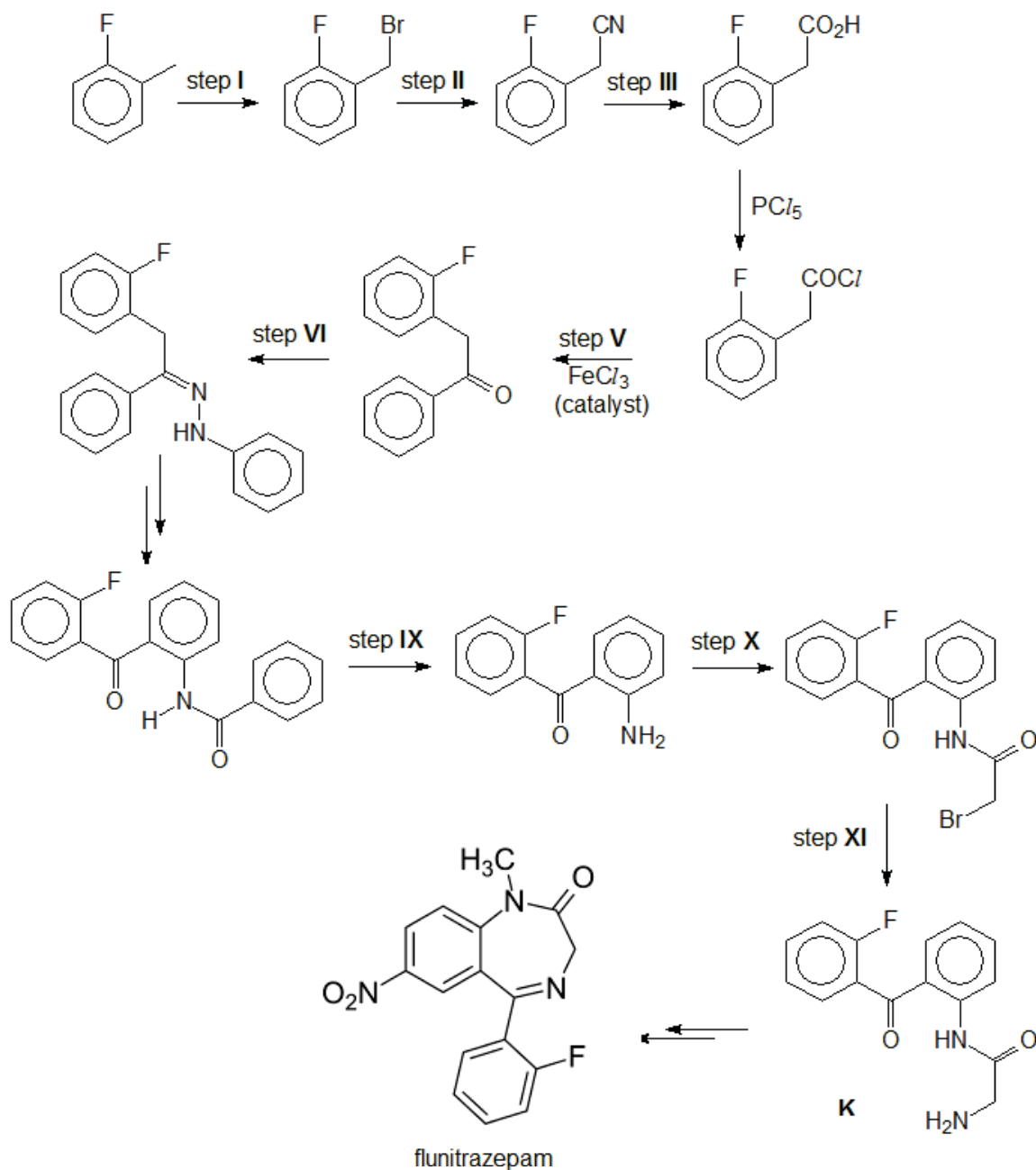

[2]

[Total: 5 marks]

6 (a) Flunitrazepam is a drug used in the short-term treatment of insomnia and as a pre-medication in surgical procedures and for inducing anaesthesia.

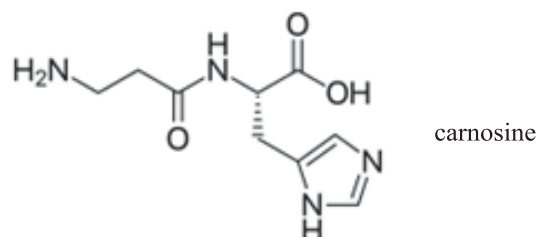Study the synthetic route to flunitrazepam shown below.

flunitrazepam

6 (a) Fill in the table below with the appropriate reagents and conditions.

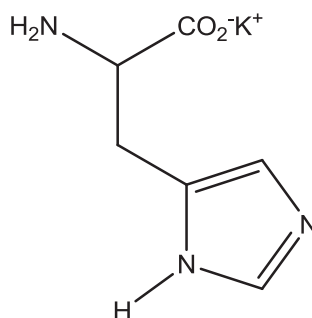| Step	Reagents and conditions
I	Limited Br_2, UV or high temp
II	KCN, ethanol, heat under reflux
III	H_2SO_4 (aq) (or HCl), heat under reflux
V	Benzene
VI	Phenylhydrazine ($C_6H_5NHNH_2$)
XI	excess ammonia, ethanol, heat in sealed tube. Or concentrated ammonia, heat at high pressure

[6]

6 (b) Carnosine is a dipeptide health supplement. It first appeared in the mainstream health community around a decade ago in the form of supplements, eye-drops and skin creams.

carnosine

(i) One of the products is β–alanine (structure shown below) when carnosine is hydrolysed with hot KOH (aq).

Draw the structural formula of the other product.

(ii) α-alanine is one of the twenty essential amino acids. It is a constitutional isomer of β–alanine. Unlike β–alanine, it is chiral. Draw the skeletal formula of α-alanine.

OR

(iii) Sarcosine is another constitutional isomer of β–alanine. It is an α-amino acid, just like α-alanine. Draw the structural formula of sarcosine.

OR

[3]

[Total: 9 marks]

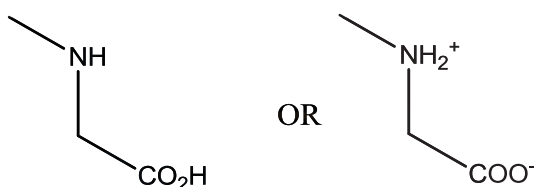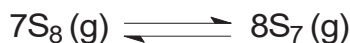**7** Sulfur forms many cyclic allotropes with different ring sizes. In the solid state, the most stable allotrope of sulfur is the form of S_8. In the gas phase, all ring sizes from S_3 to S_{12} have been detected.

(a) In the gas phase, the different ring sizes are in equilibrium. The equation for the equilibrium between $S_7(g)$ and $S_8(g)$ is given below:

$$7S_8\,(g) \rightleftharpoons 8S_7\,(g)$$

(i) Give the expression for the equilibrium constant, K_c, for the reaction between S_7 and S_8 as written above.

$$K_c = [S_7]^8 / [S_8]^7$$

[1]

When dissolved in an organic solvent, S_6, S_7 and S_8 were all detected in equilibrium in the following proportions by mass:

Allotrope	S_6	S_7	S_8
% by mass	1.5	0.5	98.0

(ii) Calculate the amount of S_7 and S_8 at equilibrium when 1.00 g of sulfur is dissolved in 1.00 dm^3 of solvent.

Amount of S_7 = 0.005 / (7 X 32.1) = 2.23 X 10^{-5} mol
Amount of S_8 = 0.98 / (8 X 32.1) = 3.82 X 10^{-3} mol

[2]

(iii) Calculate the value of the equilibrium constant in **(i)**.

$$K_c = \frac{(2.23\times10^{-5})^8}{(3.82\times10^{-3})^7} = 5.15 \text{ X } 10^{-21} \text{ mol dm}^{-3}$$

[1]

(b) In the solid phase, S_8 crystallises in two well-known allotropic forms: orthorhombic and monoclinic.

Both combust in excess oxygen to form liquid SO_3. The standard enthalpy changes of combustion of these two forms are as follows:

$$\Delta H_c\,(S_8, \text{orthorhombic}) = -296.8 \text{ kJ mol}^{-1}$$
$$\Delta H_c\,(S_8, \text{monoclinic}) = -297.1 \text{ kJ mol}^{-1}$$

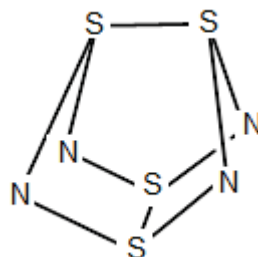Draw an energy level diagram to conclude which is the more stable form.

Orthorhombic [1]
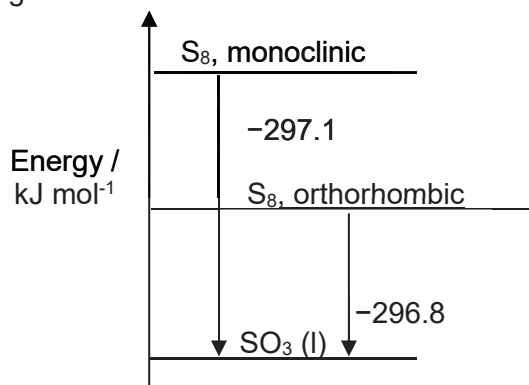
S$_8$, monoclinic

Energy / kJ mol^{-1}

−297.1

S$_8$, orthorhombic

−296.8

SO$_3$ (l)

[2]

7 (c) Sulfur also forms an interesting cage-like compound with nitrogen, S_4N_4.

(i) There are π bonds in S_4N_4 which are alternating.

The π bonds are omitted in the structural formula shown above.

Fill in the missing π bonds onto the structural formula above.

[1]
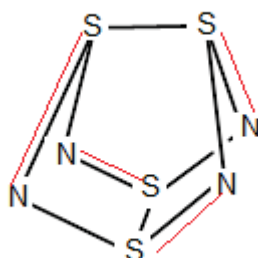
S_4N_4 reacts with hot NaOH(aq) to give thiosulfate ($S_2O_3^{2-}$) and trithionate ($S_3O_6^{2-}$) in 1:2 ratio. Ammonia is the gaseous side-product.

(ii) Suggest what makes this reaction spontaneous.

An increase in entropy with the formation of gas.

[1]

(iii) The skeletal equation is as such:
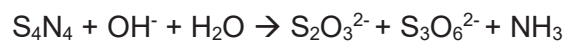
$$S_4N_4 + OH^- + H_2O \rightarrow S_2O_3^{2-} + S_3O_6^{2-} + NH_3$$

Balance the ionic equation.

$2S_4N_4 + 6OH^- + 9H_2O \rightarrow S_2O_3^{2-} + 2S_3O_6^{2-} + 8NH_3$

[1]

7 (d) There are two possible structures of the metabisulfite ion ($S_2O_5^{2-}$), as shown below.

Y   Z

(i) Using appropriate values from the Data Booklet, calculate the enthalpy changes of atomisation of **Y** and **Z**. Hence deduce which is more stable.

ΔH_{atom}**Y** = 4(S-O) + 2(S=O) = 4(360) + 2(500) = + 2440 kJ mol^{-1}

ΔH_{atom} **Z** = 2(S-O) + 2(S=O) + (S-S) = 2(360) + 3(500) + 264
= + 2484 kJ mol^{-1}

Z is the more stable one.

[2]

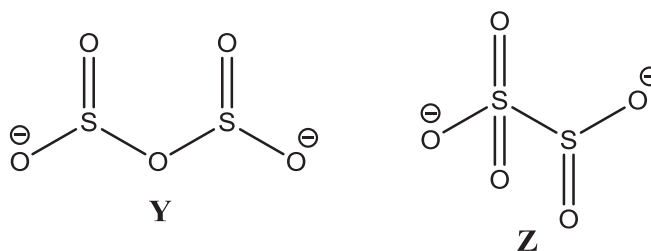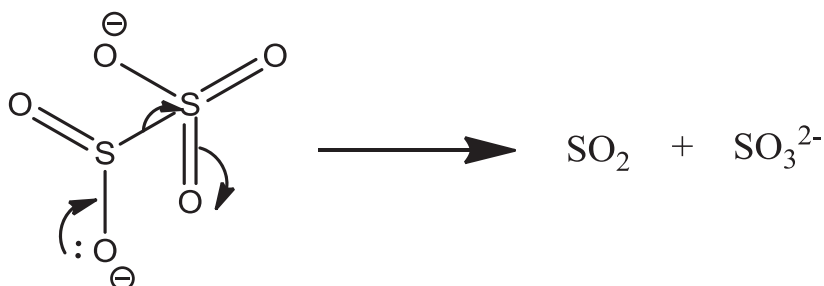**(ii)** Metabisulfite (structure **Z**) decomposes to SO_2 and sulfite (SO_3^{2-}) in a single step. Draw curly arrows to show the electron movement in this decomposition.

SO_2 + SO_3^{2-}

[1]

7 (d) (iii) Potassium metabisulfite, $K_2S_2O_5$, is a white crystalline powder.

It is chemically very similar to sodium metabisulfite, $Na_2S_2O_5$, with which it is sometimes used interchangeably. Potassium metabisulfite is generally preferred out of the two as a food preservative as it does not contribute sodium to the diet.

Explain why potassium metabisulfite decomposes at a higher temperature on heating than sodium metabisulfite.
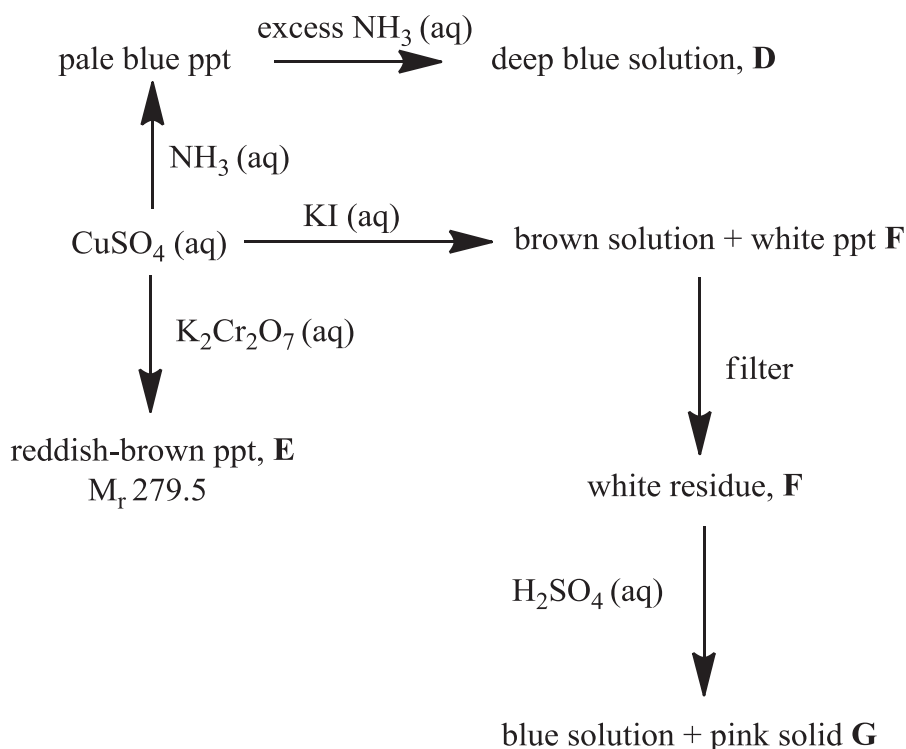
K^+ has the lower polarising power due to its lower charge density as compared to Na^+.

Hence, the covalent bonds in the metabisulfite ion in $K_2S_2O_5$ is weakened to the lesser extent. [1]

[2]

[Total: 14 marks]

8 (a) Copper(II) sulfate can undergo a series of reactions as shown in the reaction scheme below.

pale blue ppt $\xrightarrow{\text{excess } NH_3 \text{ (aq)}}$ deep blue solution, **D**

$\uparrow$ NH_3 (aq)

$CuSO_4$ (aq) $\xrightarrow{\text{KI (aq)}}$ brown solution + white ppt **F**

$\downarrow$ $K_2Cr_2O_7$ (aq)

reddish-brown ppt, **E**
M_r 279.5

filter $\downarrow$

white residue, **F**

$\downarrow$ H_2SO_4 (aq)

blue solution + pink solid **G**

Identify **D**, **E**, **F** and **G**.

D: $Cu(NH_3)_4(H_2O)_2^{2+}$ or $Cu(NH_3)_4^{2+}$ **F**: CuI or Cu_2I_2

E: $CuCr_2O_7$ **G**: Cu

[4]

(b) Ionisation isomerism is a special type of constitutional isomerism in which the isomers form different ions in solution.

There is a pair of cobalt(III) ionisation isomers, **K** and **L**. They have molecular formula $CoBrSO_4(NH_3)_4$. **K** is red while **L** is dark violet.

On addition of aqueous barium nitrate, only **K** gave a white precipitate.
On addition of aqueous silver nitrate, only **L** gave an off-white precipitate.

(i) Give the structural formulae of the cations in **K** and **L**.

K: $[CoBr(NH_3)_4]^{2+}$ or $[Co(H_2O)Br(NH_3)_4]^{2+}$
L: $[CoSO_4(NH_3)_4]^+$ or $[Co(H_2O)SO_4(NH_3)_4]^+$

[2]

(ii) Explain briefly why **K** and **L** exhibit different colours.

Different ligands will split the energy of the d orbitals by different extents, hence visible light of different wavelengths will be absorbed, leading to different colours.

[1]

[Total: 7 marks]

END OF PAPER

CHEMISTRY 9729/03
Higher 2

Paper 3

18 August 2017
2 hours

Additional Materials: Writing Paper
Data Booklet
Cover Page

READ THESE INSTRUCTIONS FIRST

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

Answer **all** questions in Section **A**.
Answer **either** question 4 or 5 in Section **B**.
Start each question on a new sheet of writing paper.

A Data Booklet is provided.
The use of an approved calculator is expected, where appropriate.
You are reminded of the need for good English and clear presentation in your answers.

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

This document consists of **17 printed pages**, including this cover page.

9729/03/Prelim/17   ANGLO-CHINESE JUNIOR COLLEGE

Section A – Answer **ALL** questions. Begin each question on a fresh piece of writing paper.

1 This question is about Period 3 and Group 2 elements.

(a) Phosphorus sulfide, P_4S_3, is used in small amounts in the tip of a matchstick. On striking a matchstick, this compound burns to form sulfur dioxide and phosphorus pentoxide.

(i) Write the equation for this reaction. [1]

$$P_4S_3 + 8O_2 \rightarrow 3SO_2 + P_4O_{10}$$

(ii) The melting points of the two oxides formed in **(a)(i)** differ significantly from that of silicon(IV) oxide (SiO_2). Account for this difference in terms of structure and bonding of each oxide. [2]

The two above-mentioned oxides are simple covalent molecules while SiO_2 has a giant covalent structure. Overcoming weak IMF between P_4O_{10} and SO_2 molecules versus strong covalent bonds between Si and O atoms. SiO_2 has the highest melting point.
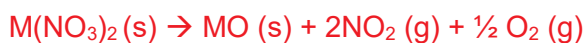
(iii) The solid oxide formed in **(a)(i)** dissolves in water to give an acidic solution.

Write the equation for this reaction and give an approximate pH of the solution formed. [2]

$$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4 \quad \text{pH 2 or 3}$$

(b) A Group 2 nitrate exists as a hydrate $M(NO_3)_2.xH_2O$. On heating, 1.80 g of this hydrate lost 0.55 g in the form of steam, as it was converted into the anhydrous nitrate, $M(NO_3)_2$. Subsequent heating to constant mass produced a white residue and mixture of two gases. The gases produced were passed through aqueous sodium hydroxide. The remaining gas occupied 95 cm³ at 101 kPa and 30 °C.

(i) Write an equation, with state symbols, representing the thermal decomposition of Group 2 nitrates, $M(NO_3)_2$. [1]

$$M(NO_3)_2 \text{ (s)} \rightarrow MO \text{ (s)} + 2NO_2 \text{ (g)} + \tfrac{1}{2} O_2 \text{ (g)}$$

(ii) Assuming that the gas behaves ideally, calculate the amount of remaining gas formed. [1]

3.81×10^{-3}

(iii) Hence, **calculate the value of** x **and deduce the identity of** metal **M**. [3]

No. of moles of nitrate present = (ii) $\times$ 2 = 7.621×10^{-3}
No. of moles of water = 0.55 / 18.0 = 3.056×10^{-2}

$$x = \frac{3.056 \times 10^{-2}}{7.621 \times 10^{-3}} = 4$$

A_r of **M** = 40.0

Calcium

(c) Calcium oxide is the key ingredient for the process of making cement.

When 1.50 g calcium is burned in air, calcium oxide is formed together with a red brown solid.

The red brown solid has the following composition by mass: Ca, 81.1%; N, 18.9%.

Adding water to the red brown solid produces calcium hydroxide and 19.2 cm^3 of ammonia gas at room temperature and pressure.

(i) Deduce the formula of the red brown solid. [2]

	Mass percentage / A_r	Simplest ratio
Ca	2.0275	3
N	1.35	2

Ca_3N_2

(ii) Write the chemical equation for the reaction between the red brown solid with water. [1]

$Ca_3N_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2NH_3$

(iii) Write the chemical equation for the reaction of calcium with O_2 and hence calculate the mass of CaO formed when 1.5 g of calcium is burnt in O_2. [2]

$2Ca\ (s) + O_2\ (g) \rightarrow 2CaO\ (s)$
n(calcium) = 0.0374
n(calcium oxide) = 0.0374
m(calcium oxide) = 0.0374 x (40 + 16) = 2.10 g

1 **(d)** A diagonal relationship is said to exist between certain pairs of diagonally adjacent elements in the second and third Periods of the Periodic Table.

For instance, lithium shows similar chemical properties to magnesium.

(i) Write the equation for the thermal decomposition of lithium carbonate. [1]

$$Li_2CO_3 \text{ (s)} \rightarrow CO_2 \text{ (g)} + Li_2O \text{ (s)}$$

(ii) Explain why this is unlike that of the other Group 1 carbonates. [1]

The charge densities (or polarising power) of Li^+ and Mg^{2+} are similar.
or
The electronegativities of lithium and magnesium are similar.

(e) Lithium nitride, Li_3N, is a red solid. It is the only stable Group 1 nitride. The nitrides of all the Group 2 elements are known.

Li_3N is currently investigated as a storage medium for hydrogen gas.

$$Li_3N + 2H_2 \rightleftharpoons 2LiH + LiNH_2$$

State the role of hydrogen. [1]

Electrophile / Proton donor / Acid / Bronsted acid / Lewis acid

(f) A diagonal relationship also exists between boron and silicon.

B_2O_3 is acidic, like SiO_2 but unlike the oxides of the other Group 13 elements.

(i) Write a balanced chemical equation, with state symbols, that illustrates the acidic nature of SiO_2. [1]

$$SiO_2 \text{ (s)} + 2NaOH \text{ (l) / (aq)} \rightarrow Na_2SiO_3 \text{ (l) / (aq)} + H_2O \text{ (l)}$$

(ii) Write a balanced chemical equation, with state symbols, that illustrates the acidic nature of B_2O_3, given that it forms a similar anion as in **(i)**. [1]

$$B_2O_3 \text{ (s)} + 6NaOH \text{ (l) / (aq)} \rightarrow 2Na_3BO_3 \text{ (l) / (aq)} + 3H_2O \text{ (l)}$$

[Total: 20]

2 **(a)** Divalent metal cations like tin and cadmium form insoluble precipitates with NaOH (aq).

The K_{sp} of $Sn(OH)_2$ is 5.45×10^{-27} mol^3 dm^{-9}.

(i) If the concentration of $Cd(OH)_2$ in a saturated solution is 1.217×10^{-5} mol dm^{-3}, determine the solubility product of $Cd(OH)_2$. [1]

$4(1.217 \times 10^{-5})^3 = 7.21 \times 10^{-15}$ mol^3 dm^{-9}

(ii) Calculate the molar solubility of $Sn(OH)_2$ in a solution of pH 8. [2]

$[OH^-] = 10^{-6}$ mol dm^{-3}

No. of moles of $Sn(OH)_2$ that can dissolve in 1 dm^3 water
$= \frac{5.45 \times 10^{-27}}{10^{-12}} = 5.45 \times 10^{-15}$ mol

(iii) A certain solution has 0.002 mol dm^{-3} each of Cd^{2+} and Sn^{2+}.

Calculate the pH range over which the two cations can be effectively separated. [2]

$$\frac{5.45 \times 10^{-27}}{0.002} < [OH^-]^2 < \frac{7.21 \times 10^{-15}}{0.002}$$
$$1.651 \times 10^{-12} < [OH^-] < 1.899 \times 10^{-6}$$

Lower pH = 14 + log (1.651×10^{-6}) = 2.22
Higher pH = 14 + log (1.899×10^{-6}) = 8.28

2.22 < pH < 8.28

(b) Propanone, also known as "acetone", is one of the most important solvents in organic chemistry – it can be used to dissolve many things from fats and waxes to airplane glue and nail polish.

It decomposes to **H** and ketene ($H_2C=C=O$). At 600 °C, the decomposition rate constant is 8.7×10^{-3} s^{-1}.

(i) Suggest the identity of **H**.   methane or CH_4 [1]

(ii) Determine the half-life of the reaction at 600 °C.   79.7 s [1]

(iii) How much time is required for 75% of a sample of propanone to decompose at 600 °C? [1]

2 X 79.7 = 159 seconds

(iv) The Arrhenius equation links different parameters (its activation energy, the absolute temperature, and its rate constant at that temperature) of a reaction together.

$$k = Ae^{-\frac{E_a}{RT}}$$

Given that the half-life of the reaction at 500 °C is 8700 s and using your answer to **(ii)**, calculate the activation energy (including its units) of this reaction. [2]

Rate constant at 500 °C = 7.97 X 10^{-5} s^{-1}

Converts both temperatures to Kelvins

$k_{873K} = 8.70 \times 10^{-3} = Ae^{-\frac{E_a}{873R}}$ ------ (1)

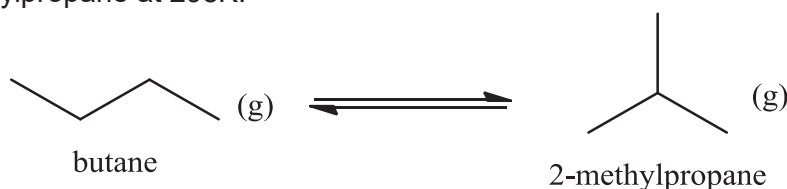$k_{773K} = 7.97 \times 10^{-5} = Ae^{-\frac{E_a}{773R}}$ ------ (2)

(1) Divided by (2):

109.1593476 = $e^{\frac{E_a}{R}(\frac{1}{773}-\frac{1}{873})}$

$\frac{E_a}{R}\left(\frac{1}{773} - \frac{1}{873}\right) = \ln(109.1593476)$

E_a = 8.31 x ln (109.1593476) / (1.48186 X 10^{-4}) = + 263165 J mol^{-1}

E_a = + 264 kJ mol^{-1}

2 **(c)** Under appropriate conditions, butane can be made to isomerise reversibly to 2-methylpropane at 298K.

butane   2-methylpropane

	butane	2-methylpropane
S°/ J K^{-1} mol^{-1}	310	295
ΔH$_f$°/ kJ mol^{-1}	-127.2	-135.6

(i) Calculate the ΔG° for the forward isomerisation reaction. [2]

ΔH$_{rxn}$° = -8.40 kJ mol^{-1} ΔS$_{rxn}$° = -15 J K^{-1} mol^{-1}
ΔG$_{rxn}$° = -8.40 – 298(-0.015) = -3.93 kJ mol^{-1}

2 **(c)** **(ii)** Given that $\Delta G^\circ = -RT \ln K_p$, calculate the equilibrium constant, K_p, for the isomerisation reaction. [1]

$K_p = e^{\frac{3930}{8.31(298)}} = 4.89$

(iii) Write the K_p expression for the isomerisation equilibrium. [1]

$K_p = P_{(2\text{-methylpropane})} / P_{(butane)}$

(iv) Determine the mole fractions of the two gases at equilibrium. [3]

Let the mole fraction of butane be x.
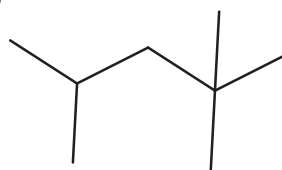
Mole fraction of 2-methylpropane = 1 – x

$K_p = (1-x)/x$

$X (CH(CH_3)_3) = 0.830$

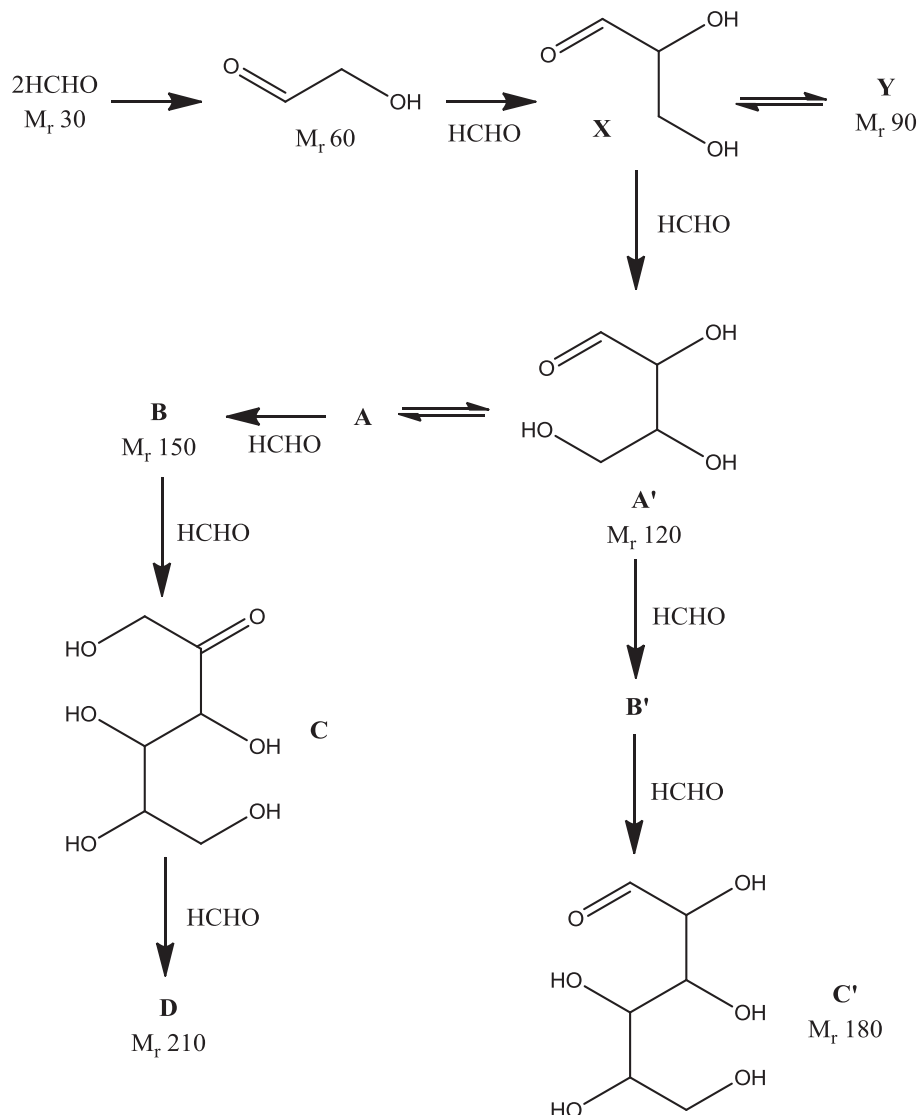**(v)** In the industry, 2-methylpropane is used to make compound **Y**, C_8H_{18}.

Y has the whole range of carbon atoms; it contains primary, secondary, tertiary and quaternary carbon atoms.

Draw the structural formula of **Y**, assuming that the original carbon skeleton did not rearrange. [1]

2 **(d)** Life in the universe is widely thought to have originated from methanal, HCHO, through the Formose reaction.

In this reaction, methanal is converted into a vast range of sugars like ribose and from there to RNA, an important hereditary material.
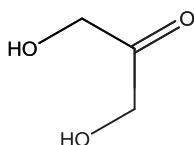

(i) **X** and **Y** are functional group isomers.

Y does not rotate the plane of plane-polarised light. Fehling's and Tollens' tests are the only tests which can differentiate between **X** and **Y**.

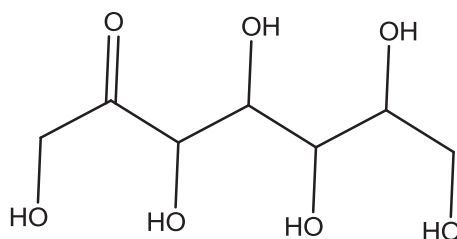Draw the structural formula of **Y**. [1]

2 **(d)** **(ii)** Suggest a reason why the interconversion of **C** to **C'** <u>cannot</u> be done in a single step. [1]

- You cannot simultaneously reduce the aldehyde and oxidise the secondary alcohol in C'.
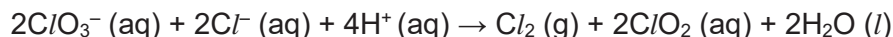- You cannot simultaneously reduce the ketone and oxidise the primary alcohol in C.

(iii) Draw the structural formula of **D**. [1]

[Total: 21]

3 This question is on Group 17, the halogens.

Chlorate(V), ClO_3^-, reacts with chloride according to the equation:

$$2ClO_3^- \text{ (aq)} + 2Cl^- \text{ (aq)} + 4H^+ \text{ (aq)} \rightarrow Cl_2 \text{ (g)} + 2ClO_2 \text{ (aq)} + 2H_2O \text{ (l)}$$
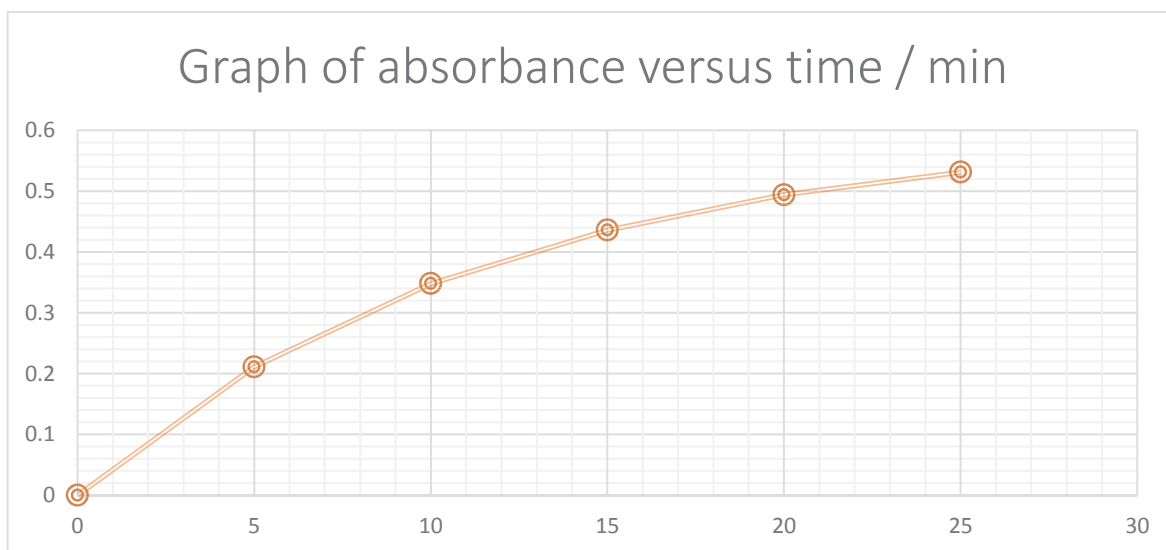
(a) To study the kinetics of chlorate(V)-chloride reaction, an experiment was conducted using a mixture in which the concentrations of the reactants are as follows: 0.000480 mol dm^{-3} of ClO_3^-, 0.1 mol dm^{-3} of Cl^- and 0.4 mol dm^{-3} of H^+.

At five-minute intervals, small samples of the reaction mixture were withdrawn, quenched and placed into the UV-vis spectrometer to record its absorbance value. The absorbance value corresponds to the concentration of the product ClO_2.

The results of the above experiment are shown below.

Time/min	0	5	10	15	20	25
Absorbance/A	0.000	0.211	0.348	0.436	0.494	0.531

The graph of absorbance/A against time/min is plotted below.

Graph of absorbance versus time / min

3 **(a)** **(i)** Beer-Lambert's Law states that the absorbance values, A, is directly proportional to the concentration of absorbing species, c, as shown below.

$$A = \varepsilon c l$$

where ε is the molar extinction coefficient and l is the path length, which is usually 1.0 cm.

This equation can be used to calculate the absorbance value when maximum amount of ClO_2 was formed.

Show that the maximum absorbance value in the above experiment is 0.600, given that ε of ClO_2 is 1250 mol^{-1} dm^3 cm^{-1}. [2]

Recognises that chlorate(V) is the limiting reagent.
A = 1250(1.0)(0.000480) = 0.600

3 (a) (ii) From the graph provided on the previous page and the information given in **(a)(i)**, determine the half-life with respect to ClO_3^- and hence the order of reaction with respect to ClO_3^-. [2]

Half-lives roughly constant at x min (acceptable range from 7 to 9 min)
1st order wrt ClO_3^-

To obtain the full rate law, a further experiment was conducted.
The following graph was obtained.

Assuming that $[ClO_3^-]$ and $[Cl^-]$ are constant,
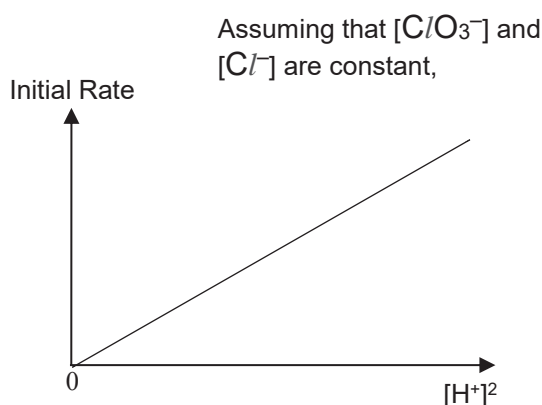
(iii) Using the above data, determine the order of the reaction with respect to H$^+$. [1]
2nd order

(iv) Given that the units of k is mol^{-3} dm^9 s^{-1}, write the rate equation of the chlorate(V)-chloride reaction. [1]

Rate = k[chloride][chlorate(V)][H$^+$]^2

(v) State a physical property that can be monitored as the reaction progresses. [1]

Change in pH or change in Electrical conductivity or change in mass
Change in pressure (constant volume) or
Change in volume (constant pressure)

3 **(b)** Heating solid halides with concentrated H_2SO_4 is one of the ways to obtain hydrogen halides.

However, the halides have different reactivities with concentrated H_2SO_4.

(i) Write an equation to show the reaction of KCl with concentrated H_2SO_4. [1]

$$KCl + H_2SO_4 \rightarrow KHSO_4 + HCl$$

(ii) However, when KI is treated with concentrated sulfuric acid, HI will be contaminated with other gaseous products. Identify these gaseous products. [2]

$$SO_2 \text{ and } H_2S$$

(iii) Suggest another reagent that can be reacted with potassium iodide to obtain pure hydrogen iodide. Conc. phosphoric acid or conc. H_3PO_4 [1]

The interhalogens are compounds that are made up of two or more different halogens.

ICl and IBr are two such examples.

(c) Even though ICl is more polar than IBr, IBr has a higher boiling point than ICl. Explain this dilemma as clearly as you can. [2]

Based on the relative strengths of pdpd alone, IBr should have the lower boiling point. However, the electron cloud size of the IBr is big enough such that its idid is stronger than the IMF present between ICl molecules.

(d) ICl reacts with water in which water is acting as the nucleophile.
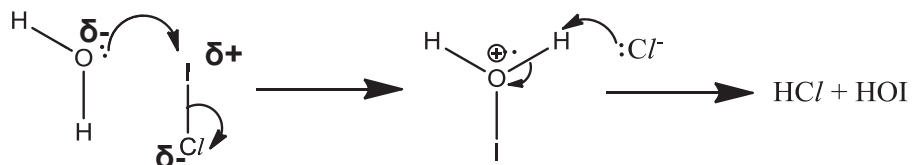
The equation for the reaction is as follows.

$$ICl + H_2O \rightarrow H\mathbf{X} + HO\mathbf{Y}$$

(i) By comparing relative electronegativities, identify **X** and **Y**. [1]
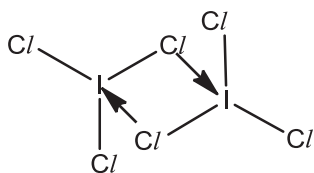
X is chlorine while **Y** is iodine.

3 **(d)** **(ii)** Hence propose a two-step mechanism for this reaction. Include curly arrows and partial charges. [2]

(e) ICl_3 exists as a planar dimer I_2Cl_6 in solid state. The two iodine atoms are the central atoms.

(i) Draw the structure of the dimer. [1]

(ii) The molten form of ICl_3 is able to conduct electricity because it undergoes auto-ionisation.

One species is square planar and the other is bent with respect to the central iodine atom.
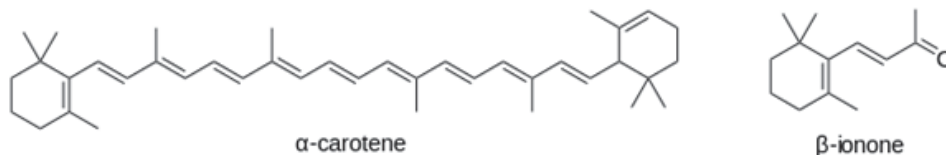
Deduce the formulae of the cation and the anion. [2]

ICl_4^- and ICl_2^+

[Total: 19]

**Section B** - Choose <u>either</u> question **4** or **5**. Begin it on a fresh piece of writing paper.

4 α-carotene is a red-orange pigment found in plants and fruits. It is the yellow/orange pigment that gives vegetables and fruits their rich colors. The name "carotene" came about when it was first discovered in carrot roots in 1831.

(a) α-carotene is metabolised to form α-ionone and β-ionone, which share the same molecular formula, $C_{13}H_{20}O$.

α-carotene   β-ionone

(i) Explain why hot acidified $KMnO_4$ cannot be used in the conversion of α-carotene to β-ionone. The alkenes will be oxidised too. [1]

(ii) Based on the structure of α–carotene, draw the structural formula of α-ionone. [1]
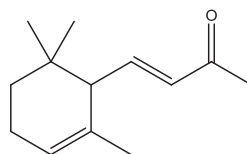
(iii) Specify what type of constitutional isomerism is shown between α-ionone and β-ionone. [1]

Positional isomers.

(iv) Give the structural formula of a constitutional isomer of β-ionone, where neutral iron(III) chloride solution is the <u>only</u> chemical test that can distinguish between itself and β-ionone. [1]

Proposed structure has to be a phenol and seven carbons outside the benzene, without rings and π bonds.

Example:
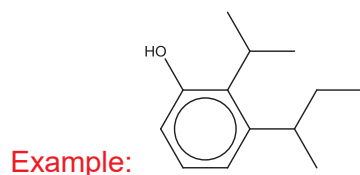
4 **(a)** **(v)** Give the structural formula of a constitutional isomer of β-ionone, which can be distinguished from β-ionone by warm alkaline iodine. [1]

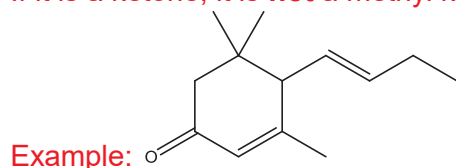Proposed structure <u>need not necessarily be a ketone</u>.
If it is a ketone, it is **not** a methyl ketone.
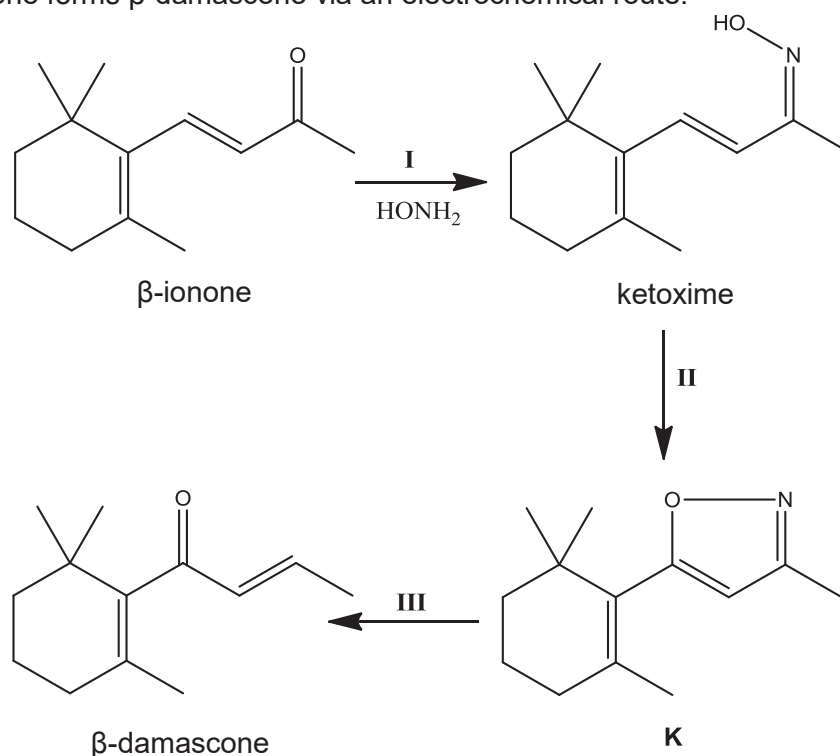
Example:

(b) β-ionone forms β-damascone via an electrochemical route.

It involved the formation of ketoxime in step **I**, followed by an anodic oxidation in step **II**. In the last step, the oxygen-nitrogen bond was cleaved to give β-damascone.

(i) Name the type of reaction in step **I**. [1]

condensation or addition elimination

(ii) Construct a balanced half-equation for the oxidation of ketoxime in step **II** under acidic conditions.

You are to use "ketoxime" and "**K**" in your half-equation. [1]

ketoxime → K + 2H⁺ + 2e

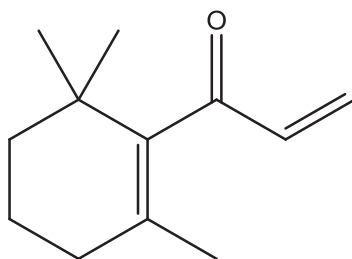**4** **(b)** **(iii)** β-damascone exists as a pair of cis-trans isomers. Draw the cis isomer. [1]

(c) Ethylenediaminetetraacetic acid (EDTA) is a colourless, water-soluble solid. It is on the World Health Organisation's List of Essential Medicines.

EDTA can be synthesised via the following reaction route.

(i) **X** gave a white precipitate when aqueous silver nitrate was added to it. Give the structural formula of **X**. [1]

C*l*CH₂COC*l*

ClCH₂COCl

(ii) Give the structural formula of **Y**. Hence, state a potential problem that might happen when it reacts with chloroethanoic acid. [2]

H₂N(CH₂)₂NH₂
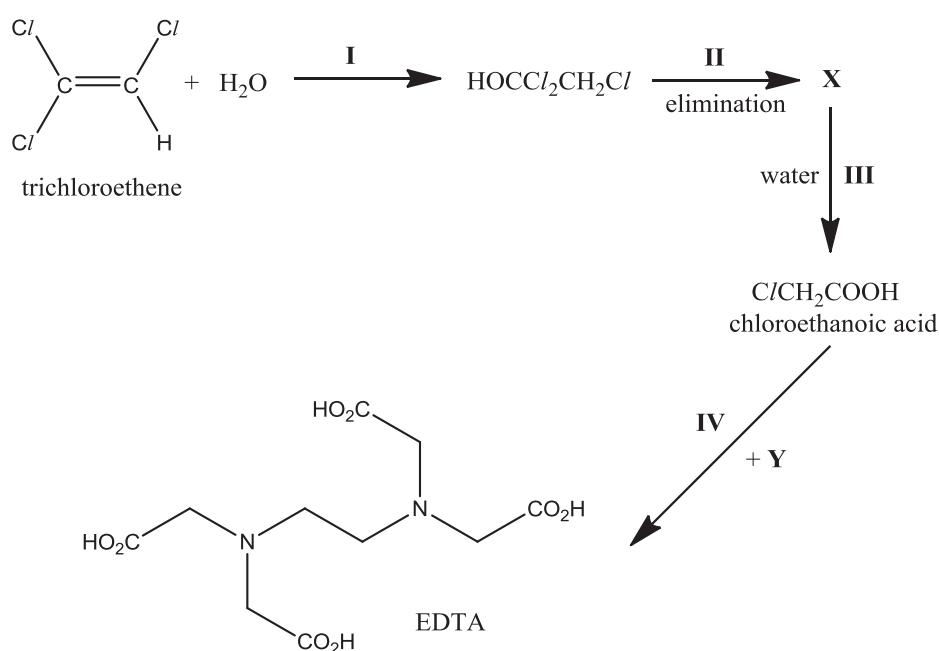
H₂N(CH₂)₂NH₂

Form the salt / acid-base reaction rather than nucleophilic (acyl) substitution / condensation

4 **(d)** Chloroethanoic acid can be synthesised from methanal via a three-step route. State the reagents and conditions used in each step and the intermediates involved. [4]

HCHO → HOCH$_2$CN → ClCH$_2$CN → ClCH$_2$CO$_2$H
Step I: HCN, trace amt of NaCN, 10 to 20 ^{0}C
Step II: SOCl_2 / PCl_5 / PCl_3
Step III: heat with aqueous acid

(e) The Kolbe electrolysis involves conversion of carboxylate salts into alkanes. It can be represented by the following half-equation.

$$3\ R_1COO^- + 3\ R_2COO^- \rightarrow R_1{-}R_1 + R_1{-}R_2 + R_2{-}R_2 + 6CO_2 + 6e^-$$

where R$_1$ and R$_2$ may not represent the same alkyl group.

In a certain electrolysis, two carboxylate salts were electrolysed, forming three alkanes.

The relative molecular masses are 58.0, 86.0 and 114.0.

The alkane with M$_r$ 58.0 is non-chiral.

The alkane with M$_r$ 114.0 exists as three stereoisomers - two of which are chiral and the third is non-chiral.

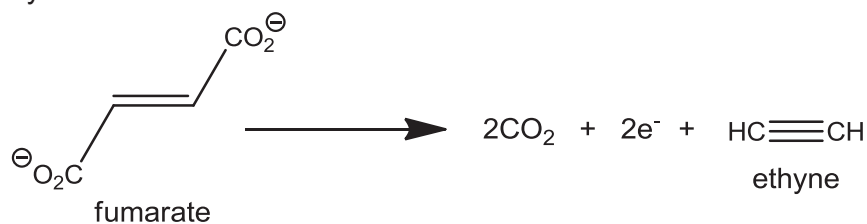**(i)** Identify the two carboxylate salts used. [2]
Propanoate and 2-methylbutanoate

(ii) Draw the stereochemical formula of any of the two chiral stereoisomers. [1]

In a special application of the Kolbe electrolysis, fumarate was electrolysed into ethyne.

fumarate

$$2CO_2 + 2e^- + HC\equiv CH$$

ethyne

4   (e)   (iii)   Kolbe electrolysis proceeds via radical intermediates, which are formed and reacted via homolytic fission and fusion.

Explain the term *homolytic fission*. [1]

Homolytic fission is the process in which the two electrons in a <u>covalent</u> bond are divided <u>equally</u> between the two atoms when the bond breaks.

(iv)   The decomposition of fumarate into ethyne and carbon dioxide happens through two steps – the first of which forms the neutral diradical species below as the intermediate.

Use curly arrows to show how the intermediate decomposes to ethyne and carbon dioxide. [1]

[Total: 20]

5 Melanin is a naturally-occurring organic compound that is responsible for the colour of the skin. The higher the melanin content, the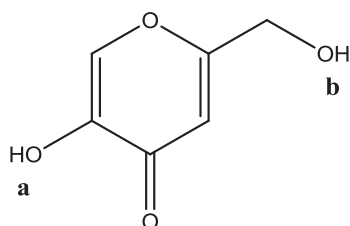 darker the skin is. In the Asian market, skin-lightening lotions have grown to be the most on-demand skin care cosmetic products.

One common ingredient of such lotions is kojic acid, which works by slowing down the rate of formation of melanin. It is obtained from the fermentation of rice malt.

The structure of kojic acid is shown below with the two hydroxyl groups labelled **a** and **b**.

kojic acid

(a) For each of the hydroxyl groups **a** and **b**, explain if it will be substituted with a chlorine atom when one mole of kojic acid is reacted with two moles of PCl_5 at room temperature. [2]

For **a**, the C-O bond possesses a partial double bond character due to the overlap of the p orbital of the oxygen with that of the sp^2 carbon. As such, the bond is not easily broken, disallowing the substitution of 'a'.

For **b**, the C-O bond is not as strong, thus the nucleophilic substitution will take place more readily.

(b) *Kojic acid* also functions as an antioxidant, scavenging hydroxyl radicals ($^{\bullet}OH$) that are responsible for ageing. One mole of *kojic acid* can react with a total of four moles of the radicals to form *comenic acid* via an intermediate **Z** as shown in the scheme below.

kojic acid   compound **Z**   comenic acid

(i) Given the following information, use curly arrows to draw the mechanism for the formation of comenic acid from compound **Z** in two separate steps.

Step 1:
An $^{\bullet}$OH radical reacts with compound **Z** to form an organic radical intermediate with H_2O being formed as a by-product.

Step 2:
Another $^{\bullet}$OH radical react with the intermediate formed from the first step.

[2]

+ H_2O **[1]**

OH   **[1]**

5   **(b)**   **(ii)** Draw another possible organic by-product in the formation of comenic acid from compound **Z**.

[1]

5 **(c)** Besides kojic acid, vitamin E is also an essential ingredient that acts as an antioxidant in skin-lightening lotions. One class of vitamin E is tocopherol, the general structure of which is shown below.

tocopherol

The table below shows the substituent R of two different types of tocopherol, namely α- and β-tocopherol.

	–R
α-tocopherol	–CH$_3$
β-tocopherol	–H

Arrange phenol, α-tocopherol and β-tocopherol in an increasing order of pK_a values. Hence, explain the difference in acidity among the three compounds. [3]
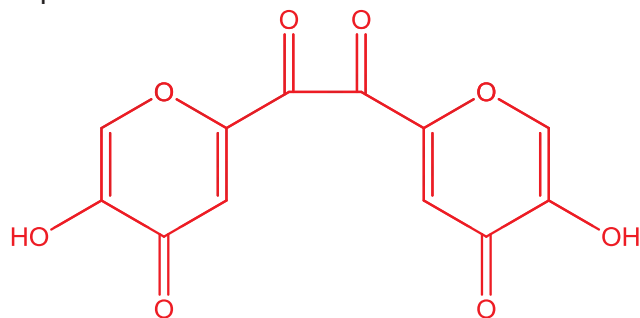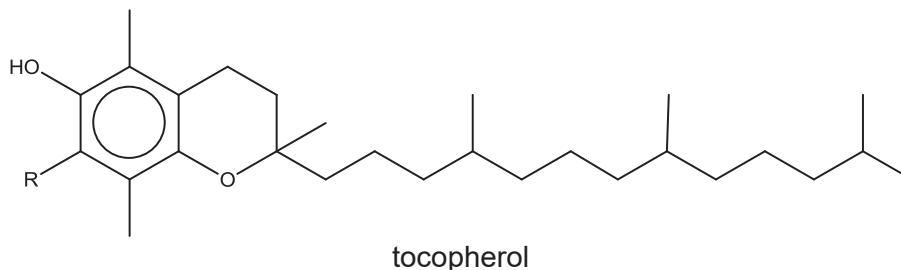
pK_a of phenol < β-tocopherol < α-tocopherol

Phenol is the strongest acid as its conjugate base is the most stable due to the fact that there are no electron-donating groups attached to the benzene ring to intensify the negative charge on the oxygen atom.

α-tocopherol is a weaker acid compared to β-tocopherol as the former has one additional electron-donating alkyl / methyl group that destabilises its conjugate base.

(d) To increase the effectiveness and marketability of skin-lightening lotions, titanium dioxide, TiO$_2$, is often added as a sunscreen agent due to its reflective property.

Solid titanium dioxide reacts with hydrofluoric acid, HF, to form a coordination compound, H$_2$[TiF$_6$], and water.

(i) Write a balanced chemical equation, with state symbols, for the above reaction. [1]

TiO$_2$ (s) + 6HF (aq) → H$_2$[TiF$_6$] (aq) + 2H$_2$O (l)

(ii) Explain **whether the above reaction is a redox reaction.** [1]

It is not a redox reaction since the oxidation state of titanium remains the same at +4 in TiO$_2$ and H$_2$[TiF$_6$].

5 **(d)** **(iii)** State the electronic configuration of titanium in $H_2[TiF_6]$. Hence, explain whether the complex ion is coloured. [3]

Ti^{4+} : $1s^2 2s^2 2p^6 3s^2 3p^6$

As there are <u>no electrons in the 3d subshell</u> of Ti^{4+}, there is <u>no d-d transition</u> to promote an electron from a lower energy d orbital to a higher energy d orbital. As such, the complex ion is <u>colourless</u>.

(e) Hydroquinone and catechol are isomers.

Hydroquinone has been used for more than half a century in the formulation of skin lotions to help fade uneven skin tone and dark spots. Catechol, on the other hand, is an important synthetic precursor to pesticides, flavours, and fragrances.

The structures of both compounds, together with their boiling points, are shown below.

hydroquinone
(boiling point: 287 °C)
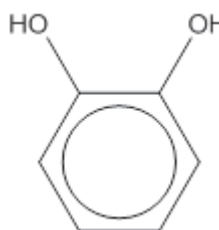
catechol
(boiling point: 246 °C)

(i) Explain why catechol has the lower boiling point. [1]

The presence of <u>intramolecular hydrogen bonding</u> between the two phenolic / -OH groups in catechol makes its <u>intermolecular hydrogen bonding less extensive</u> than that between hydroquinone molecules, thus catechol requires less heat energy to overcome the intermolecular hydrogen bonding.

(ii) Catechol is able to function as a bidentate ligand, but not hydroquinone.

Explain why hydroquinone cannot function as a bidentate ligand. [1]

The <u>oxygen atoms / phenolic / -OH groups</u> in hydroquinone <u>point to opposite directions</u>, thus they <u>cannot form dative bonds to the same central metal species</u>.

5 **(f)** Catechol is used industrially to make ethylvanillin, a flavourant reputedly three times more potent than vanillin itself.
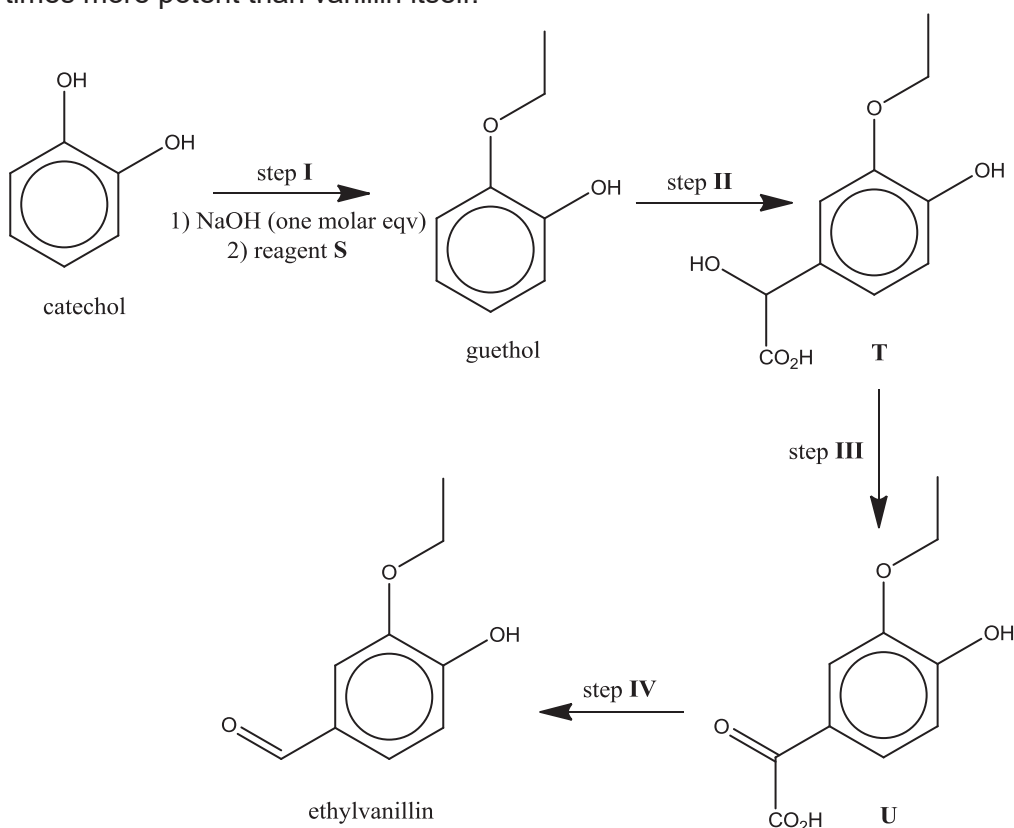
Assume that the ether functional group (R–O–R') is inert.

(i) Explain the purpose of adding NaOH in step **I**. [1]
To <u>deprotonate the phenol functional group</u> to make it a **better nucleophile**.

(ii) Name reagent **S** in step **I**. Chloroethane / bromoethane / iodoethane [1]

(iii) Outline the synthetic pathway to convert ethylvanillin back to compound **T**. Draw the intermediate formed. [3]

ethylvanillin   intermediate [1]   compound **T**
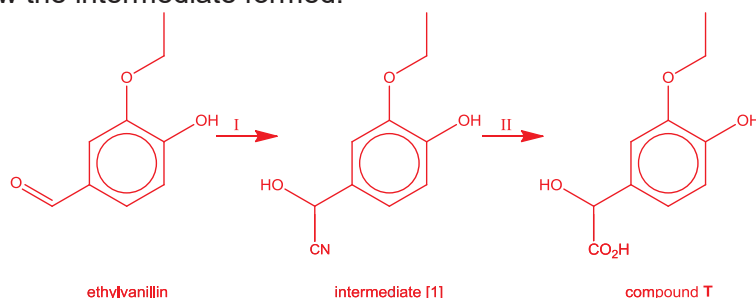
Step I: HCN, trace amount of KCN / NaCN, 10-20 °C
Step II: dilute HCl / H$_2$SO$_4$, heat

[Total: 20]

END OF PAPER

Question 1

In this experiment, you are required to find the concentration in mol dm^{-3} of sodium thiosulfate, $Na_2S_2O_3$, in solution **FA 1**.

You are provided with:
FA 1 contains sodium thiosulfate, $Na_2S_2O_3$.
FA 2 is potassium manganate (VII) containing 1.83 g dm^{-3} $KMnO_4$.
FA 3 is 1 mol dm^{-3} sulfuric acid, H_2SO_4.
FA 4 is 10% potassium iodide containing 4 g dm^{-3} KI.

You are also provided with starch indicator.

Dilution of FA 2

(a) By using a burette measure between 41.00 cm^3 and 42.00 cm^3 of **FA 2** into the 250 cm^3 graduated flask.

Record your burette readings and the volume of **FA 2** added to the flask in the space below.

Final burette reading / cm^3	41.50
Initial burette reading / cm^3	0.00
Volume of **FA2** used / cm^3	41.50

[2]

Make up the contents of the flask to the 250 cm^3 mark with distilled water. Stopper and mix the contents thoroughly by slowly inverting the flask a number of times. Label this solution **FA5**.

Titration

Filll a second burette with **FA 1**, the solution containing sodium thiosulfate.

Use a measuring cylinder to transfer 10 cm^3 of **FA 3** and 10 cm^3 of **FA 4** into a conical flask. Pipette 25.0 cm^3 of **FA 5** into the conical flask containing the mixture of **FA 3** and **FA 4**. The potassium manganate (VII) oxidises potassium iodide to iodine, I_2.

Titrate the liberated iodine with **FA 1** as follows. Run the solution from the burette into the conical flask until the initial brown colour of the iodine becomes pale yellow. Then add 1 cm^3 of the starch indicator and continue to add **FA 1** drop by drop until the blue-black colour of the starch-iodine complex disappears, leaving a colourless solution. This is the end-point of the titration.

Record your titration results in the space below. Make certain that your recorded results show the precision of your working. Repeat your experiment to obtain consistent results.

	1	2
Final burette reading / cm^3	24.20	24.20
Initial burette reading / cm^3	0.00	0.00
Volume of **FA1** used / cm^3	24.20	24.20

[6]

(b) From your titration results obtain a suitable volume of **FA 1** to be used in your calculations. Show clearly how you obtained this volume.

Average titre = (24.20 + 24.20) / 2 = <u>24.20 cm^3</u>

Volume of **FA1** = ………………… [1]

Calculations

Show your working and appropriate significant figures in all of your calculations.

(c) Calculate how many moles of $KMnO_4$ are contained in the **FA 2** run into the graduated flask. [A_r: K, 39.1; O, 16.0; Mn, 54.9]

No. of moles of $KMnO_4$ added into the graduated flask = $\dfrac{41.50}{1000}$ X $\dfrac{1.83}{158.0}$

= <u>4.81 x 10^{-4}</u>

No. of moles of $KMnO_4$ added into the graduated flask = ……………………… [1]

(d) Calculate how many moles of $KMnO_4$ are then pipetted from the 250 cm^3 graduated flask into the titration flask.

No. of moles of $KMnO_4$ pipetted into the titration flask = 4.81 x 10^{-4} x $\dfrac{25.0}{250}$

= <u>4.81 x 10^{-5}</u>

No. of moles of $KMnO_4$ pipetted into the titration flask = ……………………… [1]

(e) Use this answer to calculate how many moles of iodine molecules, I_2 are formed when the manganate (VII) ions react with an excess of iodide ions in the titration flask.

$$MnO_4^- \ + \ 8H^+ \ + \ 5e \ \rightarrow \ Mn^{2+} \ + \ 4H_2O$$
$$I^- \ \rightarrow \ \tfrac{1}{2} I_2 \ + \ e$$
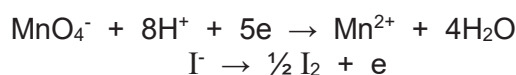
No. of moles of I_2 formed = 4.81 x 10^{-5} x 2.5 = <u>1.20 x 10^{-4}</u>

No. of moles of iodine molecules, I_2 formed = ……………………… [1]

(f) Use this answer to calculate how many moles of sodium thiosulfate, $Na_2S_2O_3$ react with the iodine molecules formed.

$$2S_2O_3{}^{2-} \rightarrow S_4O_6{}^{2-} + 2e$$
$$\tfrac{1}{2} I_2 + e \rightarrow I^-$$
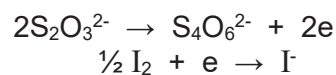
No. of moles of $Na_2S_2O_3$ reacted = 1.20 x 10^{-4} x 2 = <u>2.40 x 10^{-4}</u>

No. of moles of thiosulfate ions reacted = ……………………… [1]

(g) Calculate the concentration in mol dm^{-3} of the sodium thiosulfate, $Na_2S_2O_3$, in **FA 1**.

Concentration of $Na_2S_2O_3$ in FA1 = 2.40 x 10^{-4} x $\frac{1000}{24.20}$ = 9.93 x 10^{-3} mol dm^{-3}
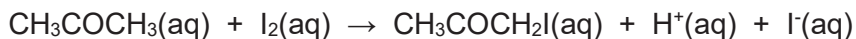
Concentration of sodium thiosulfate = …………………….. [1]

[Total: 14 marks]

Question 2

The derivation of rate equations is an important part of the process of discovering a reaction mechanism.

The experiment detailed in this question is part of an investigation into the mechanism of the iodination of propanone:

$$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + H^+(aq) + I^-(aq)$$

The reaction is catalysed by hydrogen ions and hence the rate equation can be expressed as

$$Rate = k [CH_3COCH_3]^a [H^+]^b [I_2]^c$$

where a, b and c are the orders with respect to the species shown in the rate equation.

FA 1 contains sodium thiosulfate, $Na_2S_2O_3$ (from Question 1)
FA 3 is 1 mol dm^{-3} sulfuric acid, H_2SO_4 (from Question 1)
FA 6 is 1 mol dm^{-3} aqueous propanone
FA 7 is 0.02 mol dm^{-3} I_2 in KI solution (5 g of I_2 and 33 g of KI in 1 dm^3 solution)
**FA 8** is 1 mol dm^{-3} $NaHCO_3$

Procedure

1. Pipette 25.0 cm^3 of **FA 3** into a conical flask.
2. Using the same pipette deliver 25.0 cm^3 of **FA 6** into the same conical flask.
3. Using a measuring cylinder, collect 50 cm^3 of **FA 7**.
4. Transfer the **FA 7** into the conical flask containing the mixture of **FA 3** and **FA 6** as quickly as possible and at the same time start the stop watch. Swirl the mixture in the conical flask to ensure complete mixing.
5. When the reaction has been going on for 3 minutes, pipette 10.0 cm^3 of the reaction mixture into another conical flask containing 10 cm^3 of **FA 8**, noting the exact time at which this was done.
6. Mix the solution thoroughly and titrate the mixture against **FA 1** from a burette until the solution turns yellow. Using the plastic dropper add 1 cm^3 of starch and continue titration until the solution becomes colourless.
7. Repeat **steps 5 – 6**, at times of 6, 9, 12 and 15 minutes.
8. Record yours results in the table below:

Results

Time when reaction mixture was added to $NaHCO_3$					
Final Volume / cm^3					
Initial Volume / cm^3					
Vol. of **FA1** used / cm^3					

[6]

(a) Plot a graph of the volume of **FA 1** used against time.

- *Labelled axes of appropriate scale*
- *Straight line (best fit)*
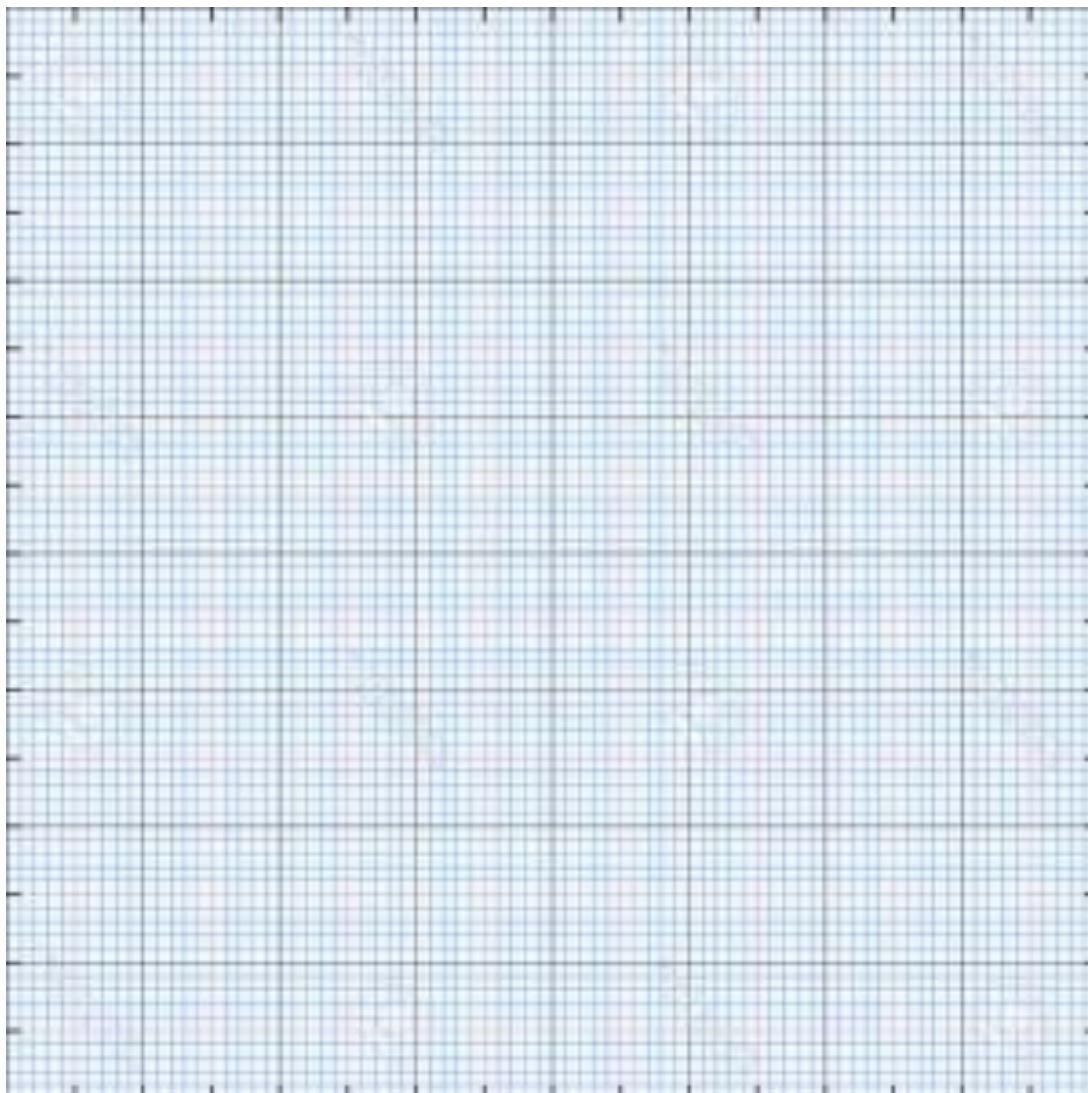
[2]

(b) What is the purpose of adding the reaction mixture to **FA 8** in Step 5. Explain.

NaHCO₃ neutralises the acid and hence stops the reaction so that the amount of iodine remaining at that instant can be determined

[1]

(c) The acid **(FA 3)** and the propanone **(FA 6)** are used in large excess in the reaction. Explain why this is necessary.

To ensure that the concentration of propanone and H⁺ remains approximately constant during the duration of the reaction

[1]

(d) Based on your graph, what conclusion can your draw about how the rate of reaction depends on the reactant of interest in this investigation?

Whilst iodine concentration is decreasing with time, the graph is a straight line and hence rate is constant throughout the reaction [1]. Reaction is independent of iodine concentration [1].

[2]

In another similar experiment at the same temperature, the volume of propanone used was halved but the total volume was kept constant by adding water to the reaction mixture. When a similar graph was plotted, the gradient at each point was half that obtained from the first graph.

(e) Why must water be added to the reaction mixture to keep total volume constant in the second experiment?

To ensure that the concentration of propanone varies directly with its volume

[1]

(f) What conclusion can you draw from the above information?

1st order with respect to propanone as halving the concentration cause the rate of reaction to halve as well.

[1]

Planning

The **method of initial rates** allows the values of these orders to be found by running the reaction multiple times under controlled conditions and measuring the rate of the reaction in each case. All variables are held constant from one run to the next, except for the concentration of one reactant. The order of that reactant concentration in the rate law can be determined by observing how the reaction rate varies as the concentration of that one reactant is varied. This method is repeated for each reactant until all the orders are determined. The initial rate experiment involves measuring the time taken for some easily recognisable event to happen very early on in a reaction. In using the initial rate method, time interval for the reaction to proceed to a given point must be kept short, otherwise the rate will become more of an average rate rather than the initial (instantaneous rate).

For the reaction investigated in Question 2, you are to design a plan that will allow you to determine the rate equation by the **initial rate method**.

In your plan, you should include details of
- Step-wise procedure that must be followed
- Details of type of apparatus used
- Results to be tabulated
- Processing of results
- Interpretation of results

[10]

Considerations

Using the initial rate method
- In using the initial rate method, time interval for the reaction to proceed to a given point must be kept reasonably short. Since the time taken for the iodine colour to be discharged is used as a measure of the reaction rate, the amount of iodine used in the reaction must be small.
- Hence, set up reaction mixtures with different amount of the reactant of interest keeping the rest constant, will allow for the concentration of the reactant that we are interested in to be varied and hence understand how the rate varies with it.

Procedure
- Into a clean dry conical flask, place 5 cm^3 of sulfuric acid, 4cm^3 of iodine solution and 11 cm^3 of deionized water. All volumes can be measured using different measuring cylinders of appropriate capacity.
- Instill 3 drops of starch solution into the conical flask.
- Using another measuring cylinder, collect 5 cm^3 of the propanone.
- Pour the propanone into the conical flask and start the stop watch immediately.
- Swirl the reaction mixture and place it on a white tile.
- Record the time taken for the dark blue colour of the reaction mixture to disappear.
- Repeat the experiment for the other mixtures as shown in the table below.

Expt	Vol of propanone / cm^3	Vol of H_2SO_4 / cm^3	Vol of iodine / cm^3	Vol of water / cm^3	Time taken / s
1	5	5	4	11	
2	10	5	4	6	
3	5	10	4	6	
4	5	5	2	13	

Processing of Results
- Rate of reaction α (Vol of I_2 used / time taken)
- Compute the rate for each of the four experiments
- Comparing Expt 1 & 2, deduce order w.r.t. propanone
- Comparing Expt 1 & 3, deduce order w.r.t H^+
- Comparing Expt 1 & 4, deduce order w.r.t I_2

Interpretation of Results
- If rate remains unchanged when the concentration of the reactant under investigation is changed, then reaction is 0 order with respect to that reactant
- If rate is doubled when concentration of reactant of interest is doubled, then reaction is 1st order with respect to that reactant
- If rate is quadruples when concentration of reactant of interest is doubled, then reaction is 2nd order with respect to that reactant

[Total: 24 marks]

Question 3

You are to perform the tests given in the following table on each of **FA 9**, **FA 10** and **FA 11** to identify, where possible, the cation and anion present in each solution.

Record details of colour changes observed, formation of any precipitate and the solubility of any such precipitate in an excess of the reagent added.

Where gases are released, they should identified by a test, described in the appropriate place in your table. You should indicate clearly at what stage in a test a change occurs.

Marks are **not** given for chemical equations. **No additional tests for ions present should also be attempted**.

Test		Observations [7]		
		FA 9	**FA 10**	**FA11**
(a)	To 1 cm depth of solution in a test-tube, add aqueous sodium hydroxide drop-by-drop, until it is in excess.	White precipitate is formed, soluble in excess of NaOH	No precipitate is formed, hence no observable change	White precipitate is formed, soluble in excess of NaOH
(b)	To 1 cm depth of solution in a test-tube, add aqueous ammonia drop-by-drop, until it is in excess.	White precipitate is formed, soluble in excess of aqueous NH_3	No precipitate is formed, hence no observable change	White precipitate is formed, insoluble in excess of aqueous NH_3
(c)	To 1 cm depth of solution in a test-tube, add aqueous barium chloride,

then | No precipitate is formed, hence no observable change | No precipitate is formed, hence no observable change | White precipitate is formed |
| | add dilute hydrochloric acid. | | | White precipitate is insoluble in dilute HCl |
| **(d)** | To 1 cm depth of solution in a test-tube, add 2 cm depth of water and 1 cm depth of aqueous silver nitrate,

then divide the resultant solution into 2 parts. | No precipitate is formed, hence no observable change | Yellow precipitate is formed | No precipitate is formed, hence no observable change |

To 1 part of solution, add dilute nitric acid.		Yellow precipitate is insoluble in dilute HNO_3	<u>No precipitate is formed</u>, hence no observable change
To 1 part of solution, add aqueous ammonia.		Yellow precipitate is insoluble in aqueous NH_3	White precipitate is formed, insoluble in excess of aqueous NH_3

(e) For each of the solutions **FA 9**, **FA 10** and **FA 11**, summarise the evidence from the tests performed to identify the cations and/or anions present.

FA 9 contains **Zn^{2+}**

Supporting evidence

White precipitate is formed when **FA 9** is added to NaOH & aqueous NH_3. White precipitate is observed to be soluble in excess of both NaOH & aqueous NH_3.

FA 10 contains **I^-**

Supporting evidence

Yellow precipitate of AgI is formed when **FA 10** is added to a solution of $AgNO_3$. AgI remains insoluble in dilute HNO_3 & aqueous NH_3.

FA 11 contains **Al^{3+}** and **SO_4^{2-}**

Supporting evidence

When NaOH & aqueous NH_3 are added to sample of **FA 11**, a white precipitate is formed, but white precipitate is soluble in excess NaOH & but insoluble in excess aqueous NH_3.

White precipitate of $BaSO_4$ is formed when $BaCl_2$ is added to sample of **FA 11**, and white precipitate is insoluble in dilute HC*l*.

[4]

(f) **Do not perform the tests for the following ions.**

It is believed that when testing a solution containing both NH_4^+ ions and NO_3^- ions, students should identify the NH_4^+ ion before attempting to identify the NO_3^- ion. Suggest a reason for the experimental procedure to be as such.

To test for the presence of NO_3^-, NaOH, A*l* strip/foil and heat are required for the liberation of NH_3 gas. Similarly, NaOH & heat are required to test for the presence of NH_4^+.

Hence it is necessary for students to identify the NH_4^+ ion before identifying NO_3^-, since test for NO_3^- will also yield similar experimental observations.

[1]

Planning

You are given aqueous solutions of the following acids:

$CH_3CH_2COCOOH$; CH_3COCH_2COOH; $CH_3CH(OH)CH_2COOH$ and $CH_3CH_2CH(OH)COOH$

Outline a sequence of simple chemical tests, by which you could identify each of the above acids.

[5]

EITHER
- Iodoform reaction on all four
  - Positive for CH_3COCH_2COOH and $CH_3CH(OH)CH_2COOH$
- Oxidation with H^+/MnO_4^- or $H^+/Cr_2O_7^{2-}$
  - Positive for $CH_3CH(OH)CH_2COOH$ and $CH_3CH_2CH(OH)COOH$

	Iodoform	Oxidation
$CH_3CH_2COCOOH$	-	-
CH_3COCH_2COOH	+	-
$CH_3CH(OH)CH_2COOH$	+	+
$CH_3CH_2CH(OH)COOH$	-	+

OR
- Brady's test on all four
  - Positive for CH_3COCH_2COOH and $CH_3CH_2COCOOH$
- Iodoform reaction on all four
  - Positive for $CH_3CH(OH)CH_2COOH$ and CH_3COCH_2COOH

	Brady's test	Iodoform
$CH_3CH_2COCOOH$	+	-
CH_3COCH_2COOH	+	+
$CH_3CH(OH)CH_2COOH$	-	+
$CH_3CH_2CH(OH)COOH$	-	-

Procedure
To each of the 4 acids in a test tube, add a few drops of 2,4 dinitrophenylhydrazine.
- The ones that give a yellow ppt contain carbonyl functional groups whilst those that do not probably contain the alcohol functional groups

To a second sample of the 4 acids in separate test tubes add a mixture of iodine in aqueous sodium hydroxide and warm.
- The one that gives a pale yellow ppt will be CH_3COCH_2COOH or $CH_3CH(OH)CH_2COOH$

Tabulate the results to deduce their identity:

	TEST 1	TEST 2
A		
B		
C		
D		

[Total: 17 marks]

~ END OF PAPER~