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]

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

(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]

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

(b) A Group 2 nitrate exists as a hydrate $\mathbf{M}(NO_3)_2.xH_2O$. 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, $\mathbf{M}(NO_3)_2$. 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, $\mathbf{M}(NO_3)_2$. [1]

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

(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) $\times 2 = 7.621 \times 10^{-3}$
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]

$Li_2CO_3\,(s) \rightarrow CO_2\,(g) + Li_2O\,(s)$

(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]

$SiO_2\,(s) + 2NaOH\,(l)\,/\,(aq) \rightarrow Na_2SiO_3\,(l)\,/\,(aq) + H_2O\,(l)$

(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]

$B_2O_3\,(s) + 6NaOH\,(l)\,/\,(aq) \rightarrow 2Na_3BO_3\,(l)\,/\,(aq) + 3H_2O\,(l)$

[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 $(1.651 \times 10^{-6}) = 2.22$
Higher pH = 14 + log $(1.899 \times 10^{-6}) = 8.28$

$2.22 < pH < 8.28$

(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.

$$\mathrm{k} = \mathrm{A}e^{-\frac{\mathrm{E_a}}{\mathrm{RT}}}$$

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 = 7.97×10^{-5} s^{-1}

Converts both temperatures to Kelvins

$$\mathrm{k}_{873K} = 8.70 \times 10^{-3} = Ae^{-\frac{E_a}{873R}} \quad \text{------ (1)}$$

$$\mathrm{k}_{773K} = 7.97 \times 10^{-5} = Ae^{-\frac{E_a}{773R}} \quad \text{------ (2)}$$

(1) Divided by (2):

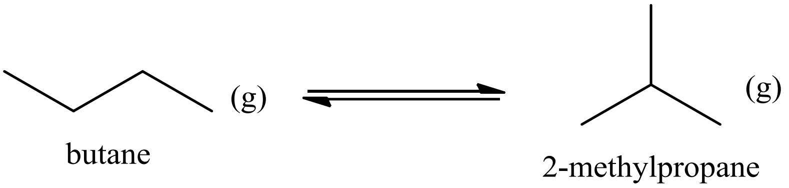
$$109.1593476 = e^{\frac{E_a}{R}(\frac{1}{773}-\frac{1}{873})}$$

$$\frac{E_a}{R}\left(\frac{1}{773}-\frac{1}{873}\right) = \ln(109.1593476)$$

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**
S^o / J K^{-1} mol^{-1}	310	295
ΔH_f^o / kJ mol^{-1}	-127.2	-135.6

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

ΔH_{rxn}^o = -8.40 kJ mol^{-1} ΔS_{rxn}^o = -15 J K^{-1} mol^{-1}
ΔG_{rxn}^o = -8.40 – 298(-0.015) = -3.93 kJ mol^{-1}

2 **(c)** **(ii)** Given that ΔG^o = -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]

$K_p = P_{(2\text{-methylpropane})} \ / \ P_{(\text{butane})}$

(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

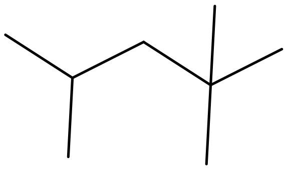
K_p = (1-x)/x

X ($CH(CH_3)_3$) = 0.830

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

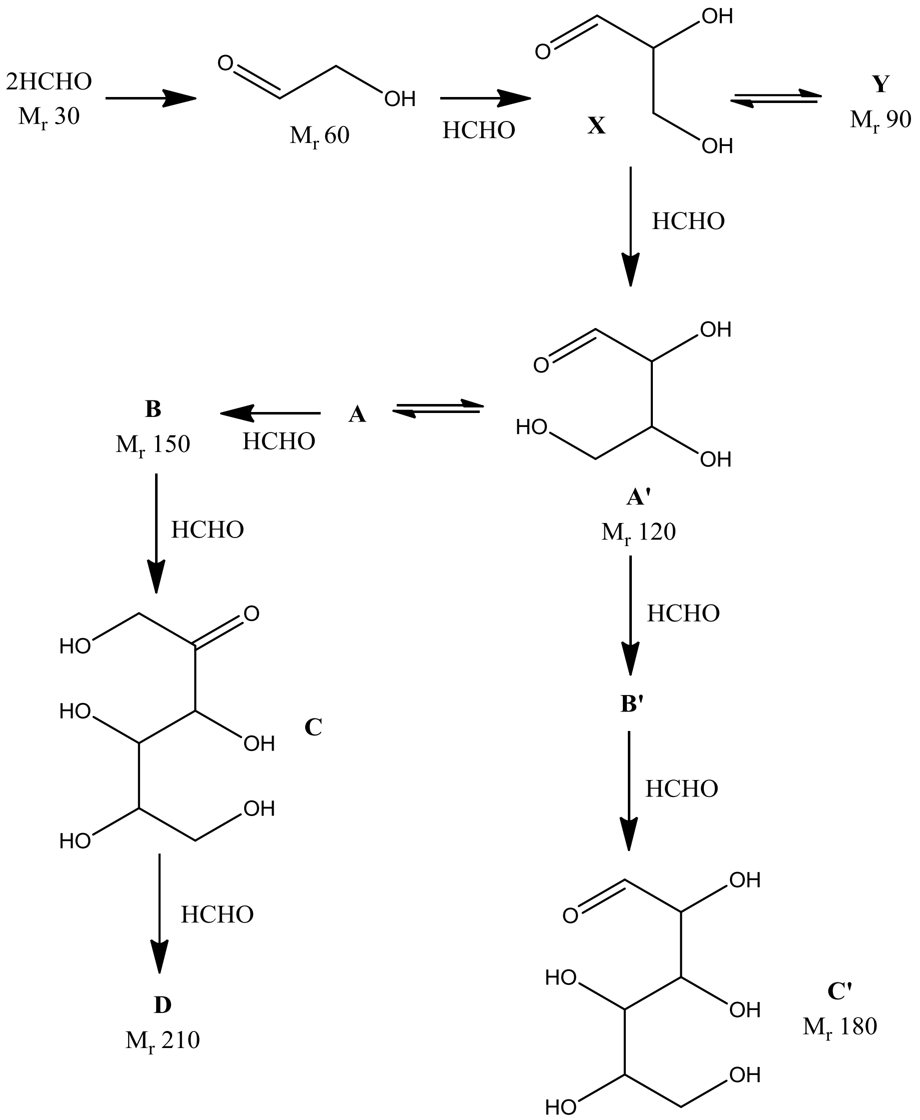
Y has the whole range of carbon atoms; it contains primary, secondary, tertiary and quaternary carbon atoms.

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.

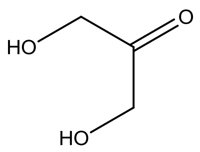
In this reaction, methanal is converted into a vast range of sugars like ribose and from there to RNA, an important hereditary material.



(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**.

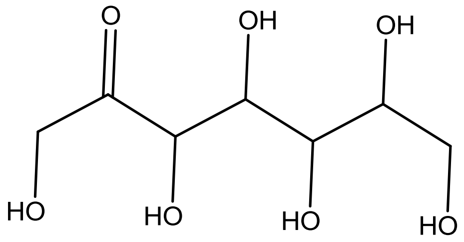
Draw the structural formula of **Y**. [1]



2 **(d)** **(ii)** Suggest a reason why the interconversion of **C** to **C’** cannot 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:

$$2ClO_3^- (aq) + 2Cl^- (aq) + 4H^+ (aq) \rightarrow Cl_2 (g) + 2ClO_2 (aq) + 2H_2O (l)$$

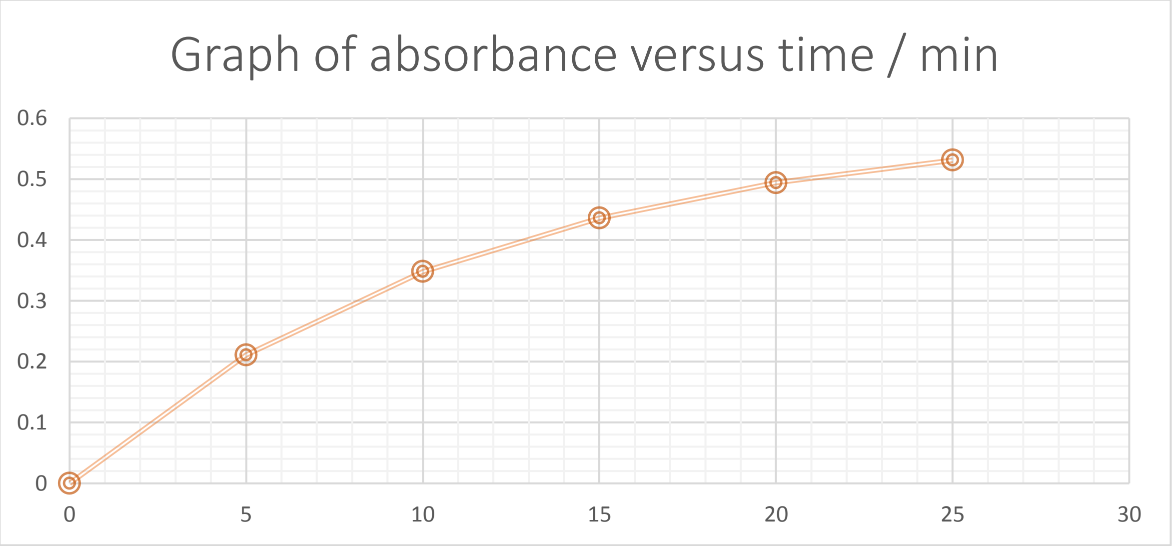
(a) To study the kinetics of chlorate(V)-chloride reaction, an experiment was conducted using a mixture in which the concentrations of the reactants are as follows: 0.000480 mol dm^{-3} of ClO_3^-, 0.1 mol dm^{-3} of Cl^- and 0.4 mol dm^{-3} of H^+.

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.



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.

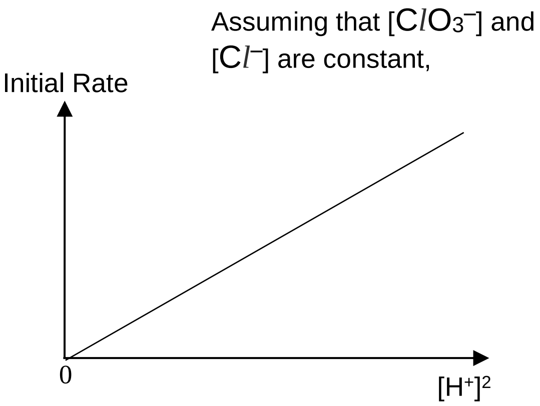
Show that the maximum absorbance value in the above experiment is 0.600, given that ε of ClO_2 is 1250 $mol^{-1}\,dm^3\,cm^{-1}$. [2]

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.



(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 KC*l* 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 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.

IC*l* and IBr are two such examples.

(c) Even though IC*l* is more polar than IBr, IBr has a higher boiling point than IC*l*. 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 IC*l* molecules.

(d) IC*l* reacts with water in which water is acting as the nucleophile.

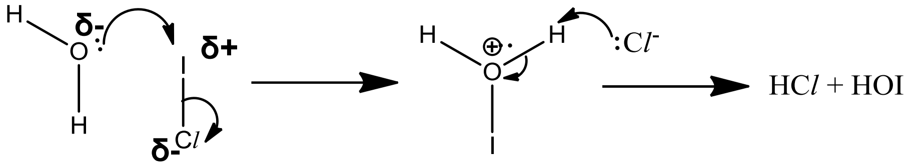
The equation for the reaction is as follows.

$$ICl + H_2O \rightarrow H\mathbf{X} + HO\mathbf{Y}$$

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

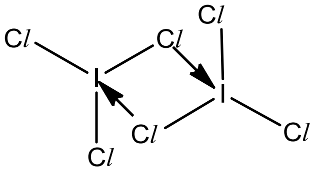
X is chlorine while **Y** is iodine.

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]

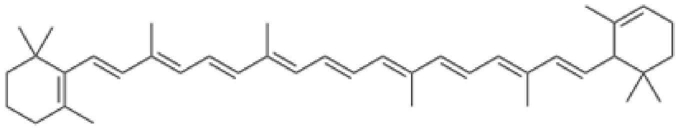
ICl_4^- and ICl_2^+

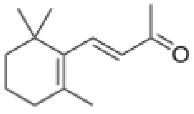
[Total: 19]

Section B - Choose either 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.

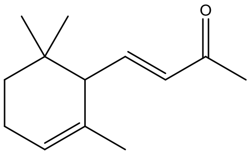
(a) α-carotene is metabolised to form α-ionone and β-ionone, which share the same molecular formula, $C_{13}H_{20}O$.


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]



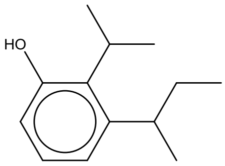
(iii) Specify what type of constitutional isomerism is shown between α-ionone and β-ionone. [1]

Positional isomers.

(iv) Give the structural formula of a constitutional isomer of β-ionone, where neutral iron(III) chloride solution is the only 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.

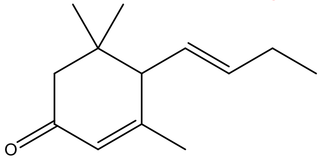
Example:



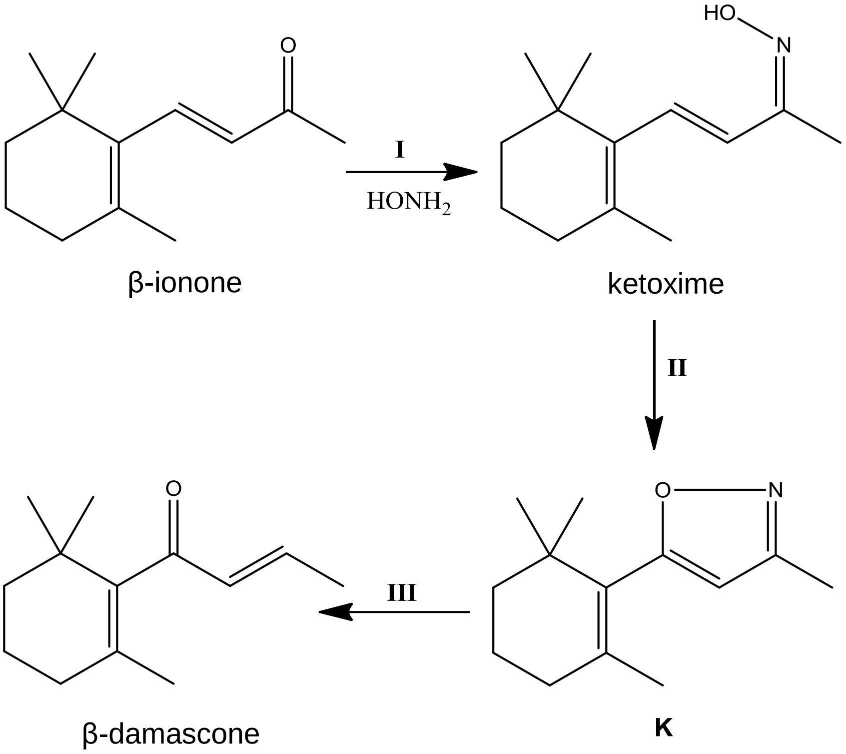
4 **(a)** **(v)** Give the structural formula of a constitutional isomer of β-ionone, which can be distinguished from β-ionone by warm alkaline iodine. [1]

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]

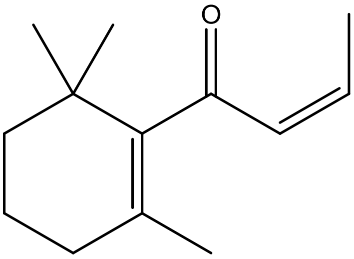
condensation or addition elimination

(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]

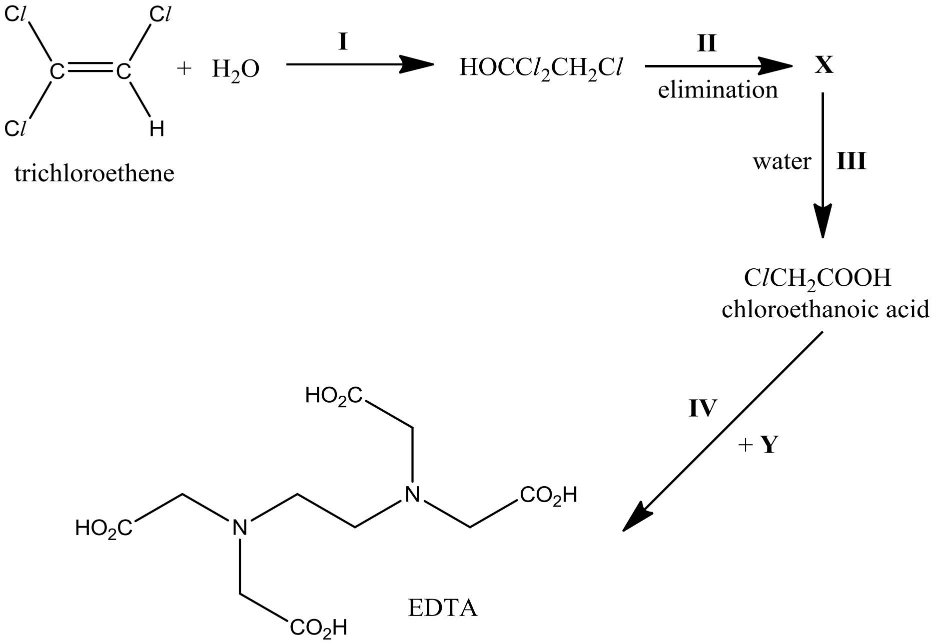
ketoxime $\rightarrow$ **K** + $2H^+$ + 2e

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]

$ClCH_2COCl$

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

$H_2N(CH_2)_2NH_2$

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]

$HCHO \rightarrow HOCH_2CN \rightarrow ClCH_2CN \rightarrow ClCH_2CO_2H$
Step I: HCN, trace amt of NaCN, 10 to 20 ^0C
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.

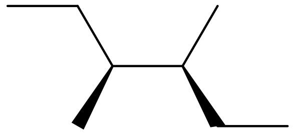
The relative molecular masses are 58.0, 86.0 and 114.0.

The alkane with M_r 58.0 is non-chiral.

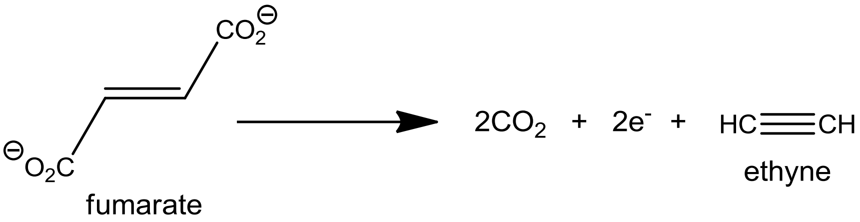
The alkane with M_r 114.0 exists as three stereoisomers - two of which are chiral and the third is non-chiral.

(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.

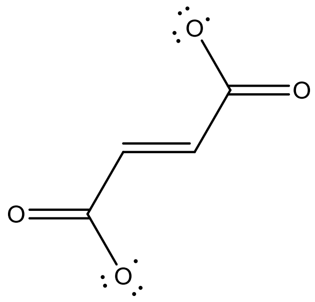


4 **(e)** **(iii)** Kolbe electrolysis proceeds via radical intermediates, which are formed and reacted via homolytic fission and fusion.

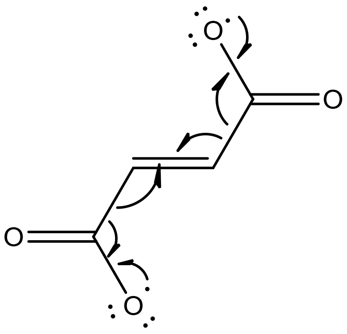
Explain the term *homolytic fission*. [1]

Homolytic fission is the process in which the two electrons in a covalent bond are divided equally 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]

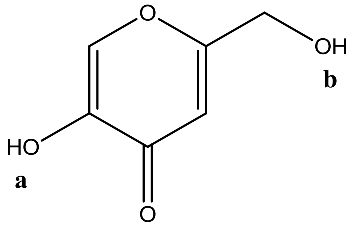


[Total: 20]

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**.



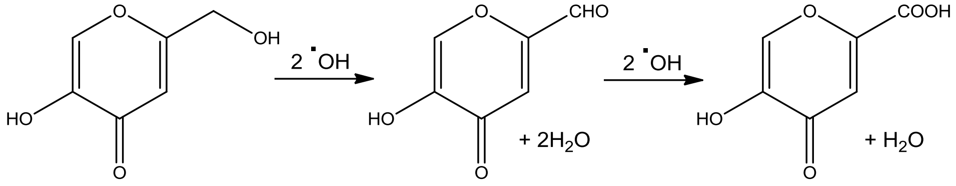
kojic acid

(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 (•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.



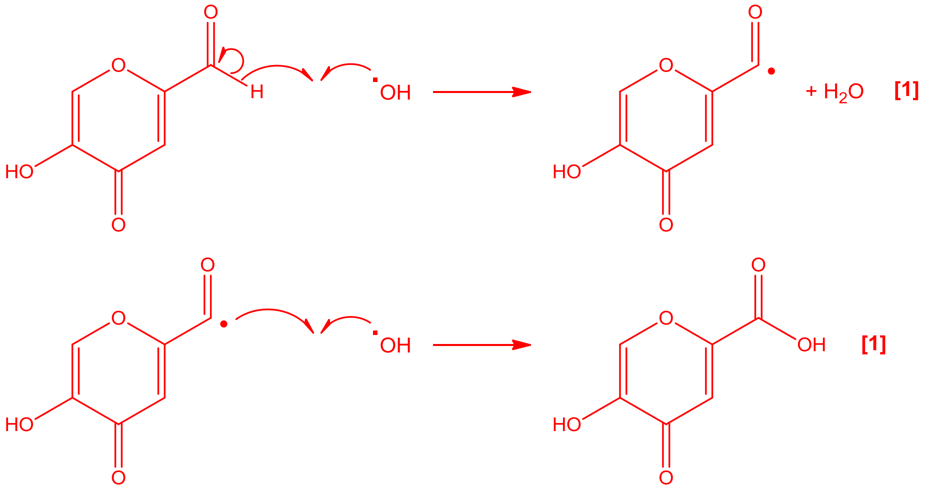
kojic acid compound **Z** comenic acid

(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.

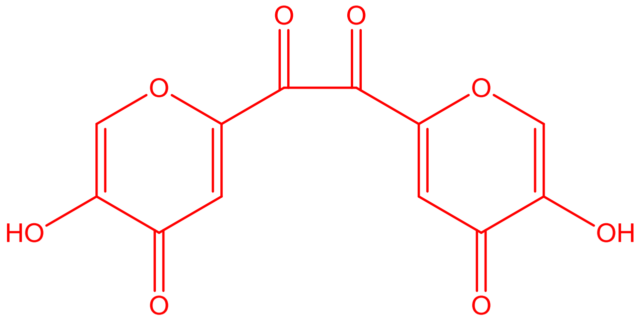
Step 1:
An •OH radical reacts with compound **Z** to form an organic radical intermediate with H_2O being formed as a by-product.

Step 2:
Another •OH radical react with the intermediate formed from the first step.

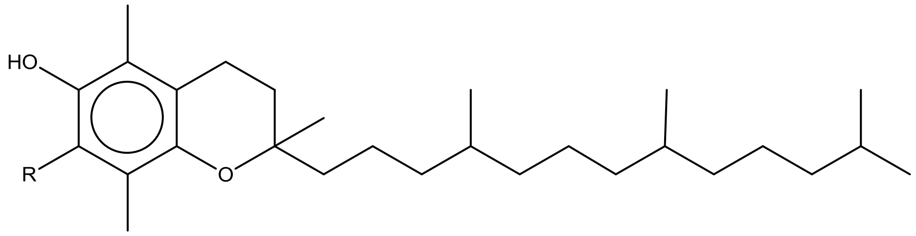
[2]



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]

$$TiO_2\ (s) + 6HF\ (aq) \rightarrow H_2[TiF_6]\ (aq) + 2H_2O\ (l)$$

(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]

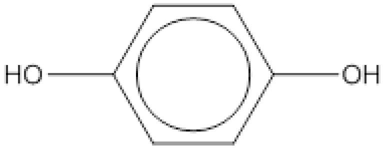
Ti^{4+} : $1s^2 2s^2 2p^6 3s^2 3p^6$

As there are no electrons in the 3d subshell of Ti^{4+}, there is no d-d transition to promote an electron from a lower energy d orbital to a higher energy d orbital. As such, the complex ion is colourless.

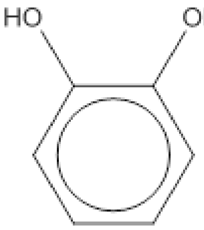
(e) Hydroquinone and catechol are isomers.

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]

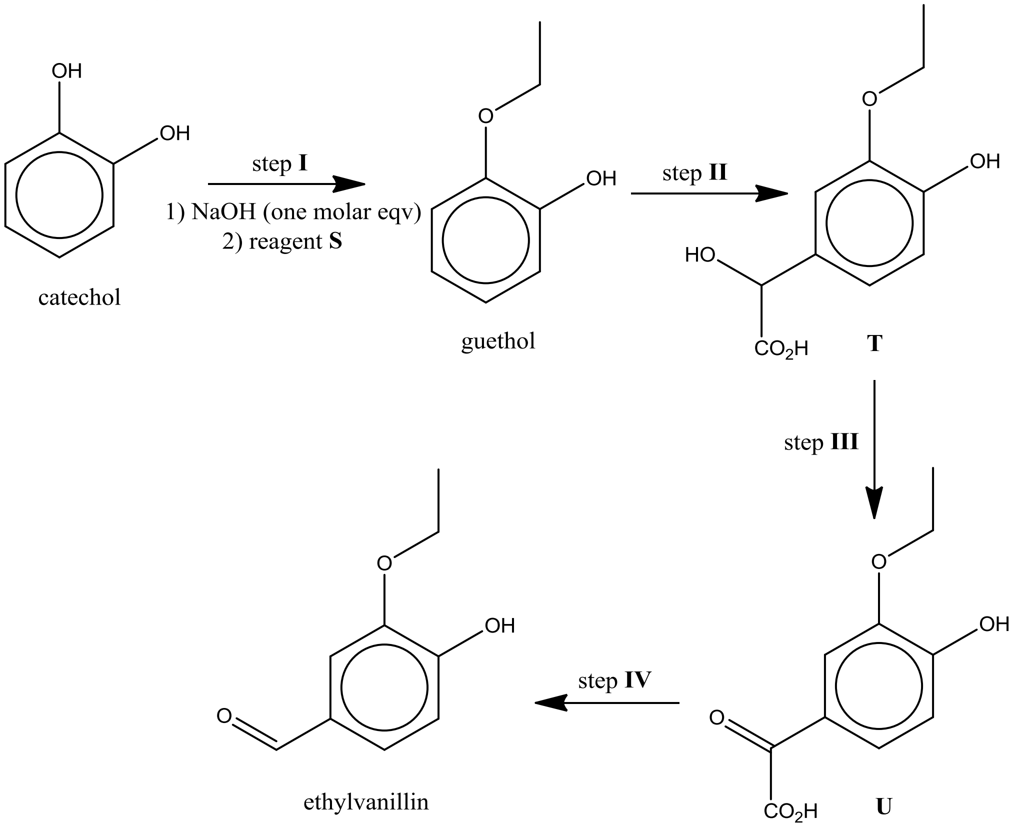
The presence of intramolecular hydrogen bonding between the two phenolic / -OH groups in catechol makes its intermolecular hydrogen bonding less extensive than that between hydroquinone molecules, thus catechol requires less heat energy to overcome the intermolecular hydrogen bonding.

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

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

The oxygen atoms / phenolic / -OH groups in hydroquinone point to opposite directions, thus they cannot form dative bonds to the same central metal species.

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

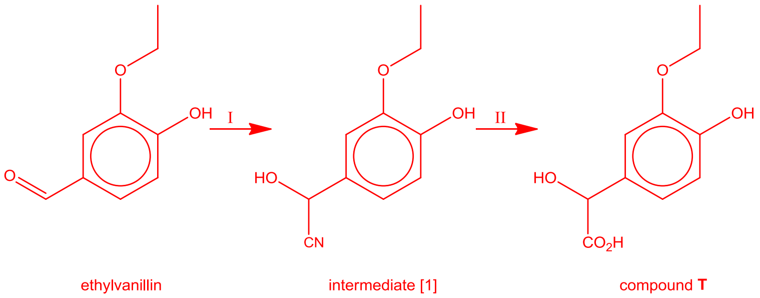


Assume that the ether functional group (R–O–R') is inert.

(i) Explain the purpose of adding NaOH in step **I**. [1]
To deprotonate the phenol functional group 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]



Step I: HCN, trace amount of KCN / NaCN, 10-20 °C
Step II: dilute HC*l* / H_2SO_4, heat

[Total: 20]

END OF PAPER