

EUNOIA JUNIOR COLLEGE JC2 Preliminary Examination 2022 General Certificate of Education Advanced Level Higher 2

CANDIDATE NAME					
CIVICS GROUP	2	1	-	INDEX NUMBER	
CHEMIST	RY			 	9729/03

Paper 3 Free Response

9729/03 21 September 2022 2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, civics group and registration number on all the work you hand in.

Write in dark blue or black pen.

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

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

Answer **all** questions in the spaces provided on the Question Paper. If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

Section A Answer all questions.	For Examiner's Use		
Section B	Section A		
Answer one question.	1	/ 20	
A Data Booklet is provided. The use of an approved scientific calculator is expected, where	2	/ 20	
appropriate.	3	/ 20	
At the end of the examination, fasten all your work securely together.	Section B		
or part question.	4	/ 20	
	5	/ 20	
	Total	/ 80	

This document consists of **32** printed pages.

Section A

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

- **1 (a)** Elements in Period 3 of the Periodic Table form chlorides and oxides with varying properties.
 - (i) Equal amounts of MgCl₂ and PCl₅ dissolve in equal volumes of water to form solutions with pH 6.5 and 1.0 respectively. Construct two equations to account for the different pH values.
 - (i) $[Mg(H_2O)_6]^{2+} \rightleftharpoons [Mg(OH)(H_2O)_5]^+ + H^+$ PC $l_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$

Comments:

Many students forgot that the hydrolysis of the hydrated magnesium ion is a reversible reaction since it is only partial hydrolysis.

- (ii) Explain why the first ionisation energies of aluminium and sulfur are lower than the element before it. [2]
- (ii) The first I.E. of Al is lower than that of Mg since the electron is removed from the higher energy 3p orbital of Al, hence less energy is required.
 The first I.E. of S is lower than that of P since the electron removed comes from a fully-filled 3p orbital, where the paired electrons experience inter-electronic repulsion, hence less energy is required.

Comments:

Many students stated that the p orbital of Al is higher in energy than the s orbital, without stating the principal quantum number. This makes it ambiguous, because it is only true if it is 3p vs 3s. If it was 2p vs 3s, then the 3s would be of higher energy. Thus, it is important to specify the principal quantum shell. Some students thought that the valence shell of Al and Mg contains 2p and 2s orbitals.

- (iii) Element L is an element in Period 3. L forms a chloride with a simple molecular structure but an oxide with a giant molecular structure. Identify element L and construct an equation for the reaction of its chloride with NaOH(aq).
- (iii) Element L is <u>silicon</u>. SiC l_4 + 4NaOH \rightarrow SiO₂ + 2H₂O + 4NaClor SiC l_4 + 4NaOH \rightarrow Si(OH)₄ + 4NaClor SiC l_4 + 6NaOH \rightarrow Na₂SiO₃ + 3H₂O + 4NaCl

Comments:

This was very badly attempted. One of the most common errors for this question was seeing HCI appear in the products. There is no chemical reaction known to mankind where adding a strong aqueous base, such as NaOH, will result in the formation of a strong aqueous acid, such as HCI. If this could happen, then none of us would be able to perform strong acid-strong base titrations.

Some students did not read the question and constructed reactions of $SiCl_4$ with water. Some students thought that the formula for the chloride of Si is $SiCl_2$ / $SiCl_3$.

The most common error was that students thought the identity of L was aluminium. This shows that many students did not read the question FULLY. It is stated in the question that the chloride of L has a simple molecular structure (which is true for both aluminium and silicon), but an oxide with a GIANT MOLECULAR STRUCTURE! AI_2O_3 is an ionic compound! Only SiO₂ has a giant molecular structure!

(b) 4-(butan-2-yl)phenol is an important intermediate in organic synthesis. It must be handled carefully as it is corrosive to the eyes and skin.



4-(butan-2-yl)phenol

4-(butan-2-yl)phenol can be synthesised by heating phenol and butan-2-ol in the presence of acid. The mechanism of this synthesis is thought to proceed via an acid-catalysed Friedel-Crafts alkylation, where butan-2-ol is first protonated by H^+ , before forming a carbocation.



(i) Draw the structure of the carbocation formed from intermediate X. [1]

Many students do not seem to understand what a carbocation is. As the selfexplanatory name suggests, it must carry a positive charge on a CARBON!

- (ii) Hence, describe the mechanism for the formation of 4-(butan-2-yl)phenol from the carbocation in (b)(i) and phenol.[3]
- (ii) Electrophilic substitution



Many did not write down the name of the mechanism.

The arenium ion was poorly drawn by many students. In the arenium ion, there is one sp^3 carbon atom and five sp^2 carbon atoms in the ring. The delocalisation of pi electrons must be drawn from the first sp^2 carbon atom to the last sp^2 carbon atom. It cannot be any less or any more than that. The positive charge must also sit within this region of delocalisation. Many students drew the positive charge protruding from the region of delocalisation.

Many students also missed out the regeneration of $\mathrm{H}^{\scriptscriptstyle +}$ in the final step of the mechanism.

- (iii) Describe a simple chemical test that could distinguish between butan-2-ol and 4-(butan-2-yl)phenol. [2]
- (iii) Add NaOH(aq), followed by $I_2(aq)$ and heat. Butan-2-ol will give a yellow ppt of CHI₃, while 4-(butan-2-yl)phenol will not give yellow ppt.

Accept Br₂(aq)/r.t., neutral FeCl₃(aq)/r.t., PCl₅/r.t. K₂Cr₂O₇(aq)/heat. With correct observations, Reject KMnO₄(aq) as both give the same observations.

Comments:

Generally well done. Students are reminded to include the conditions such as room temperature if they are using $Br_2(aq)$ and neutral FeCl₃(aq). Students are reminded to state the observations for BOTH compounds, not just the positive test observations when the distinguishing test is conducted on both. For the negative test observations, students are expected to state the 'opposite' of the positive test observations for instance: No violet complex observed for butan-2-ol when using neutral FeCl₃(aq)/r.t. Students were penalised for stating phrases like 'no observations', 'no reaction', 'no visible change' etc.

(iv) Compounds M and N are two minor products in the reaction.



Briefly explain why each of them is the minor product.

[2]

(iv) Compound M, <u>the 3-isomer</u>, is a minor product as the phenolic OH group is a <u>2,4-</u> <u>directing group</u>.

Compound **N**, the 2-isomer, is a minor product due to <u>steric hindrance</u> between the phenolic OH group and the incoming carbocation.

Comments:

Generally well done. Candidates are reminded that Compound M is the position 3 isomer, not 3-directing group. Many candidates are penalised for omitting that M <u>is the 3-isomer</u>. This is because merely stating that the pre-existing side chain –OH is 2,4 directing does not adequately explain why M is minor product.

Candidates were also penalised for merely stating inter electronic repulsion without further elaboration when attempting to explain why N is minor product.

products as required by the question. Several candidates were penalised for

misinterpreting the question to be asking why N is formed but not M.

KMnO₄(aq), **U** is formed.

(c) Compound R, C₁₀H₁₄O, is a constitutional isomer of 4-(butan-2-yl)phenol. When R is heated strongly with acidified K₂Cr₂O₇(aq), S (C₁₀H₁₂O) is formed. S gives an orange precipitate with 2,4-DNPH. When R is heated strongly with concentrated sulfuric acid, T (C₁₀H₁₂) is formed, which decolourises Br₂(aq). When T is heated with acidified



Deduce the structures of **R**, **S**, and **T** and explain the reactions involved.

[6]

- R is a <u>2° alcohol</u> as it undergoes <u>oxidation</u> by reacting with hot acidified K₂Cr₂O₇ to form a ketone.
- S reacts with 2,4-DNPH via a <u>condensation</u> reaction to give an orange ppt, it is a <u>ketone</u>.
- **R** reacts with concentrated sulfuric acid via an <u>elimination</u> of H₂O to form an <u>alkene</u>.
- **R** is an alkene that undergoes <u>electrophilic addition</u> with Br₂(aq).
- U is formed via oxidation. T must contain two alkyl chains bonded to positions 1 and 2 of the benzene ring.



Comments:

Generally well done. There is considerable improvement from Mid Year Examination structural elucidation question in terms of the attempts to link type of reactions and functional groups involved in the reactions as stated in the question. Responses for identifying type of reaction as dehydration instead of elimination and merely stating reaction with 2,4-DNPH as oxidation or positive carbonyl test were not accepted. Candidates were reminded to refer to their list of reaction types covered in 'Introduction to Organic Chemistry' for acceptable types of reactions, hence terms such as dehydration is not accepted.

Common mistakes revolve around the wrong structures where there are total of 11 carbon atoms or cycloalkene/di-alkene in T which differ from the given molecular formula stated in the question stem. Candidates are therefore reminded to check on the molecular formula of the structures that they have elucidated as well as whether the structures that they have come up with comply with the given reactions. Candidates were often penalised for giving only 1 and not 2 alkyl side chains in the structures.

[Total: 20]



This reaction occurs via a three-step mechanism.

- Step 1 The base removes an H^+ ion to form a methoxide anion, CH_3O^- .
- Step 2 The methoxide anion undergoes nucleophilic addition with the carbonyl group generating an anionic intermediate.
- Step 3 The anionic intermediate abstracts a proton from a H₂O molecule.
- (a) (i) Draw the mechanism for steps 2 and 3. In your answer, you should show all relevant charges, dipoles, and lone pairs; and show the movement of electrons by curly arrows.



Comments:

Generally badly done with a lot of careless mistakes. Common mistakes are missing dipoles, missing arrows and missing lone pairs of electrons. Students using pencils the lone pairs are usually not clearly shown.

In Step 3 many students were penalised for not balancing the equation leaving out :OH

- (ii) A student suggests using NaOH to generate the methoxide ion. Suggest why this is not feasible. Hence, state a Period 3 element that is able to generate the methoxide needed for this reaction.
- (ii) Methoxide is <u>a stronger base than OH</u> as <u>methoxide is less stable than OH</u>. ./ Methanol is a <u>weaker acid than H₂O</u>, hence, methoxide is <u>less likely to form</u> compared to OH⁻.

Sodium/Na metal.

Comments:

Generally badly attempted. Erroneous response like using NaOH to react with alcohol to produce methoxide ion. Students were not able to make use of methoxide is less stable than OH⁻ because of electron donating methyl group intensifies the -ve charge destabilising the ion. Hence methoxide is a stronger base than OH⁻.

Students also suggest all elements in Period 3 (except Na) to react with methanol to produce methoxide ion.

- (iii) Suggest a simple chemical test to differentiate between ethanal and methanol. State the observations and write a balanced equation for the positive reaction. [2]
- (iii) Tollens' reagent, heat.
 Silver mirror/Grey ppt formed with ethanal.
 2[Ag(NH₃)₂]⁺ + CH₃CHO + 3OH⁻ → CH₃CO₂⁻ + 2Ag(s) + 4NH₃ + 2H₂O

Note: Can use 2,4-DNPH, r.t. or Fehling's reagent, heat or PC1₅, r.t., I₂, NaOH, heat.

Comments:

Generally badly done: A lot of difficulties stating observations and writing balanced equations. So many students unable to give correct reagents and conditions for reaction to carry out the distinguishing tests. Many students could not give correct structure for reagent 2,4-DNPH. Many were confused with the correct observations for using Tollens reagents and Fehlings solutions.

Aldehydes that have acidic α -hydrogens react with themselves when mixed with a dilute aqueous acid or base. The resulting compounds, β -hydroxy aldehydes, are referred to as aldol compounds.



- (b) (i) State the functional groups that are present in aldol compound **B**. Hence, state the nucleophile that is generated from ethanal for the given aldol reaction. [2]
 - (i) Secondary alcohol and aldehyde.

-CH₂CHO

Comments:

Very badly done: Majority of the students did not state alcohols as secondary. Many students give alkane, alkyl, hydroxyl as functional groups.

Students sadly forgot that nucleophiles are negatively charged or having a lone pair of electrons. Many students give +vely charged species and some even +ve and -ve charges together.

(ii) Hence, draw the skeletal structure of the aldol compound formed when the α -hydrogens of propanal undergoes the above reaction. [1]

OH **(ii)**

Yellow ppt formed.







peroxybutanoic acid

A mixture containing 3-oxobutanoic acid and peroxybutanoic acid was titrated using the double-indicator method. 25.0 cm³ of the solution required 13.50 cm³ of 0.250 mol dm⁻³ sodium hydroxide to decolourise the first indicator. A few drops of the second indicator was added and the titration continued until the indicator changed colour. The total volume of sodium hydroxide needed for the titration was 35.00 cm³.

- (c) (i) The smaller the pK_a value, the stronger is the acid. Explain why 3-oxobutanoic acid is a stronger acid than peroxybutanoic acid.
 [1]
 - (i) The conjugate base of 3-oxobutanoic acid is more stabilised because the negative charge on the -CO₂⁻ can delocalised into the C=O forming two equivalent resonance structures while the conjugate base of peroxybutanoic acid cannot.

Comments:

It is surprising that many candidates did not do well for this basic question on comparing acidity. Many candidates missed out key phrases such as 'formed two equivalent resonance structures', and did not get the credit.

- (ii) Hence, calculate the concentrations of 3-oxobutanoic acid and peroxybutanoic acid. [2]
- (ii) Since 3-oxobutanoic acid is a stronger acid, it will be neutralised first. Vol. of NaOH for 3-oxobutanoic acid = 13.50 cm³ Vol. of NaOH for peroxybutanoic acid = 35.00 - 13.50 = 21.50 cm³ Amount of NaOH needed for 3-oxobutanoic acid = $\frac{13.50}{1000} \times 0.250$ = 3.375 × 10⁻³ mol Amount of NaOH needed for peroxybutanoic acid = $\frac{21.50}{1000} \times 0.250$ = 5.375 × 10⁻³ mol [3-oxobutanoic acid] = $\frac{3.375 \times 10^{-3}}{\frac{25.0}{1000}}$ = 0.135 mol dm⁻³ [peroxybutanoic acid] = $\frac{5.375 \times 10^{-3}}{\frac{25.0}{1000}}$ = 0.215 mol dm⁻³

There is a large group of candidates who swooped the concentrations of the two acids, and this shows a lack of understanding of the pK_a values of the acids. The lower the pK_a value, the higher the K_a value of the acid, and the stronger the acid is.

- (iii) During the course of titration, the pH remains relatively constant around pH 3.6 at the mid-point of the first titration. Explain why this is so. [1]
- (iii) pH 3.6 is the pK_a of 3-oxobutanoic acid, which is the **point of** <u>maximum buffering</u> <u>capacity</u>. Hence, pH is relatively constant because of the buffering effect of the solution.

Comments: Generally well done!

(iv) Calculate the concentration of the peroxybutanoate ions (CH₃CH₂CH₂CO₃⁻) at the mid-point of the first titration.

(iv)	At mid-point of the 1 st titration, pH = p K_a of 3-oxobutanoic acid = 3.6 [H ⁺] = 10 ^{-3.6} = 2.51 × 10 ⁻⁴ mol dm ⁻³						
	Total vol. of solution = $25.0 + \frac{13.50}{2} = 31.75 \text{ cm}^3$						
	New [peroxybutano	ic acid] = 0.2°	$15 \text{ x} \frac{25.0}{31.75} = 0.169 \text{ mol dm}^{-3}$				
	CH	I ₃ CH ₂ CH ₂ CC	$0_3 H \rightleftharpoons CH_3 CH_2 CH_2 CO_3^- +$	H+			
	Initial/mol dm ⁻³	0.169	0	_			
	Change/mol dm ⁻³	- <i>x</i>	+ <i>x</i>	+ <i>x</i>			
	Eqm/mol dm ⁻³	0.169 – <i>x</i>	x	2.51×10 ⁻⁴			
		≈ 0.169					
	K - 10-8.2 - [peroxybu	utanoate][H ⁺] _ [peroxybutanoate](2.51×10 ⁻⁴) -63	10~10-9			

 $K_{a} = 10^{-8.2} = \frac{[peroxybutanoate][H^{-}]}{[peroxybutanoic acid]} = \frac{[peroxybutanoate](2.51\times10^{-7})}{0.169} = 6.310\times10^{-5}$ $\Rightarrow [peroxybutanoate] = 4.26\times10^{-6} \text{ mol dm}^{-3}$

Comments:

Only a small group of candidates got this right. Many did not realise that question asked for $[CH_3CH_2CH_2CO_3^-]$, and calculated $[CH_3COCH_2CO_2^-]$ instead. Those who are aware missed out the calculation on the new $[CH_3CH_2CH_2CO_3H]$ at the mid-point of the first titration, and wrongly used the $[CH_3CH_2CH_2CO_3H]$ in c(ii).

Chlorine-containing compounds **C** and **D** can be obtained from compound **B** and 3-oxobutanoic acid, respectively.



Unlike chlorobenzene which does not reacts with sodium hydroxide, compound D reacts with NaOH much more readily than compound C.

- (d) (i) State the reagents and conditions for the conversion 3-oxobutanoic acid to compound D. [1]
 - (i) PCl_5 at r.t./PCl₃ with heat/SOCl₂ with heat

Comments: Generally well done!

- (ii) Explain why the rate of reaction with sodium hydroxide differs between chlorobenzene, compound **C**, and compound **D**. [3]
- (ii) For chlorobenzene, the Cl atom cannot be substituted because the <u>lone pair of electrons on Cl delocalises into the benzene ring</u>, creating a <u>partial double bond characteristics</u>. Hence, more difficult to break.
 The carbonyl carbon of CH₃COCH₂COCl (compound D) is <u>more electron-deficient</u> due to the <u>electron-withdrawing O and Cl atoms</u>. In addition, the carbonyl carbon is <u>trigonal planar</u>, hence, less steric effect as compared to the tetrahedral carbon of the halogenoalkane in compound C.

Comments:

- Generally not well attempted
- Candidates mistook the rate of reaction of the 3 compounds with NaOH as acidbase reaction, and tried to compare the acidity of the 3 compounds instead
- Majority of the cohort missed out the explanation on comparing steric effect of nucleophilic substitution on compound D vs compound C (carbonyl carbon in D is trigonal planar, and α carbon in halogenoalkane in C is tetrahedral)
- Common misconception: Quite a large group of students wrongly thought that the p orbital of C1 overlaps with C=O in compound D, imparting partial double bond character in C-C1, and makes the bond stronger and more difficult to cleave. In actual fact, the electron withdrawing effect of the 2 electronegative atoms, O and C1, on the carbonyl carbon in compound D far outweighs the electron donating effect of the p orbital of C1.
 - (iii) Describe a simple chemical test to distinguish between compound **C** and compound **D**. [1]
 - (iii) <u>H₂O at r.t.</u>: <u>White fumes of HCl(g)</u> for CH₃COCH₂COCl <u>AgNO₃(aq) at r.t.</u>: <u>White ppt of AgCl(g)</u> for CH₃COCH₂COCl

(Can also use Tollens', Fehling's, $KMnO_4/H_2SO_4/heat$, $K_2Cr_2O_7/H_2SO_4/heat$ for the aldehyde; I_2 , NaOH, heat for methylketone functional group)

Comments:

- Generally well done
- Many candidates missed out the conditions, such as room temperature or heat. Both reagents and conditions must be included for simple chemical test, and/ or distinguishing test.

[Total: 20]

3 Ozonolysis is a reaction where the unsaturated bonds of alkenes are cleaved with ozone, followed by adding excess Zn, to form carbonyl compounds.



If Zn is replaced by excess acidified H_2O_2 , a carboxylic acid (R_1CO_2H) is obtained instead of the aldehyde (R_1CHO).

- (a) (i) State the role of Zn in the ozonolysis process. [1]
 - (i) Zn is acting as a <u>reducing agent</u>.

Comments:

This part is not well attempted by candidates. Many students wrongly identified the role of Zn as either the catalyst or an oxidising agent. While there is no change in the oxidation states of carbon atoms from the cyclic intermediate to the products (aldehyde and ketone), oxygen is reduced (cyclic intermediate is a peroxide, with oxidation number of oxygen being -1). Hence, Zn is the reducing agent. A tip to recognise the role of Zn would be to know the nature of the metal, where it has a greater tendency to lose electrons and act as a reducing agent (itself oxidised) than to gain electrons.

(ii) Draw the skeletal formula of the product that is formed when compound **X** undergoes ozonolysis in the presence of excess Zn.



compound X

NH

[1]

Comments:

(ii)

Generally well-attempted, most students can identify the structure of the product that is formed. The most common mistake that students made when drawing the skeletal structure is to include the C–H bond at the aldehyde functional group.

- (iii) Suggest a simple chemical test to check that the ozonolysis process of compoundX is completed. State the observations. [2]
- (iii) Br_2/CCl_4 , r.t. or $Br_2(aq)$, r.t. Orange-red Br_2 in CCl_4 or Orange Br_2 decolourised.

- A lot of students gave chemical tests for the functional groups present in the products formed from ozonolysis (tests for aldehydes, ketones, and carboxylic acids). But these tests will not be able to check that the ozonolysis process is complete as once the first trace of the products are formed, positive test results will be observed constantly. - Another group of students were able to give the correct test for C=C but did not provide the correct colour for the reagents used. Students are reminded that the Data Booklet provides the colours for $Br_2(aq)$ and Br_2 in CCL and should use them when stating the observations for these tests.

- (iv) State the oxidation states of the carbon in C=O in both the aldehyde (R1CHO) and the carboxylic acid (R1CO2H).
- (iv) Aldehyde carbonyl carbon oxidation state is +1. Carboxylic acid carbonyl carbon oxidation state is +3.

Comments:

Generally well-attempted by most students. Students are reminded to take note of the presentation of oxidation numbers. The correct presentation is "+1" and not "1+".

- (v) Construct the oxidation half-equation for the conversion of R₁CHO to R₁CO₂H in an acidic medium. Hence, with reference to the *Data Booklet*, write the overall redox equation between R₁CHO and acidified H₂O₂.
- (v) $R_1CHO + H_2O \rightarrow R_1CO_2H + 2H^+ + 2e^ H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ $R_1CHO + H_2O_2 \rightarrow R_1CO_2H + H_2O$

Comments:

- There is a significant improvement of crafting redox equations from MYEs by the cohort. Keep up the good work! Students who are still unable to write the redox equations accurately are strongly encouraged to revise for this topic.

- A common mistake made in this part by students is to use "[O]" as they write the oxidation half equation. For organic chemistry, "[O]" is used to represent the oxidising agent when writing the <u>overall</u> chemical equation, and <u>not</u> the half equation.

(b) When compound X reacts with Br₂ in CCl₄, it forms a bicyclic compound Y as shown below.



- (i) Compound X exhibits stereoisomerism. State the type of stereoisomerism and draw the pair of stereoisomers.
 [2]
- (i) cis-trans isomerism



- Most students were able to identify that the type of stereoisomerism exhibited by Compound X was cis-trans isomerism and could draw the correct cis-isomer.

- Many students struggled with drawing the trans-isomer – with many drawings showing non-cyclic structures or having the wrong number of carbons in the cyclic ring. Sensible structures were awarded credit.

 (ii) Describe the mechanism for the formation of the bicyclic compound Y formed in the above reaction. [2]



Comments:

- Students are reminded to be mindful and exercise great care when drawing organic mechanisms – where arrows should clearly start from an electron source (i.e. bonds or lone pairs of electrons) and the arrow head should be pointed towards an atom (and not towards the charges of the atoms).

- Other common mistakes observed:

- Missing labels of "slow" / "fast" steps.
- For the 2nd step, many students drew mechanisms that showed the lone pair of electrons on Br⁻ ion attacking the positively charged carbon in the intermediate and forming a second C–Br bond. This is followed by a nucleophilic substitution mechanism, which showed one of the C–Br bond breaking and the lone pair of electrons on N attacking as the nucleophile. Given the proximity of the lone pair of electrons on N to the positively charged carbon in the intermediate, it is more likely that the lone pair of electrons on N will directly attack in the 2nd step of the electrophilic addition mechanism.

- A tip for students: Since the final product is already given in this question, students do not need to know how the cyclisation happens during the reaction. Students just need to draw the electrophilic addition mechanism correctly and draw the final product from the question paper. (Though it is still good that students can visualise the cyclisation!) Do analyse the question carefully and make good use of the information given in the question.

Ozone undergoes decomposition as shown below.

step 1
$$O_3 \xrightarrow[k_1]{k_1} O_2 + O$$

step 2 $O_3 + O \xrightarrow{k_2} 2O_2$

Step 1 reaches dynamic equilibrium producing a constant concentration of O radicals.

Chlorofluorocarbon (CFC) is known to destroy stratospheric ozone through the production of the Cl radical. The Cl radical can react with the O atom through the following mechanism.

$$Cl + O \rightarrow ClO$$
$$ClO + O \rightarrow Cl + O_2$$

- (c) (i) Explain the term *dynamic equilibrium*.
 - (i) It refers to a <u>reversible process</u> at equilibrium in which the <u>rate of the forward</u> <u>reaction equals to the rate of backward reaction</u> and are non-zero and the <u>concentrations of the reactants and products are constant.</u>

Comments:

Many students did not get full credit for this part because they missed out a critical part of the definition.

(ii) Write down the equilibrium constant for step 1 with units. Hence, express the equilibrium constant in terms of the rate constants, k_1 and k_{-1} . [2]

(ii)
$$K_c = \frac{[O_2][O]}{[O_3]} \text{ mol dm}^{-3}$$

forward rate = backward rate

$$k_{1}[O_{3}] = k_{-1}[O_{2}][O]$$
$$K_{c} = \frac{[O_{2}][O]}{[O_{3}]} = \frac{k_{1}}{k_{-1}}$$

Comments:

- Most students were able to write out the correct K_c expression.

- Several students did not read the question requirements carefully and did not include the units for the equilibrium constant. Many students did not understand the second part of the question and could not express the equilibrium constant using the rate constants given. Some students were confused between equilibrium constant, K_{c} , and the rate constants k_1 and k_{-1} .

- A handful of students wrote the K_p expression instead of K_c expression and went on to express K_p using the rate constants given. This is inaccurate. The rate equation is an experimentally determined mathematical equation between the reaction rate and the <u>concentration</u> of reactants at a particular temperature. By extension, rate constants are expressed in terms of concentration terms and not partial pressure terms.

[1]

Therefore, for a reaction: $aA(g) + bB(g) \Rightarrow cC(g) + dD(g)$

$$[\text{ideal gas}] = \frac{n}{V} = \frac{p}{RT}$$
$$\mathcal{K}_{c} = \frac{\left(\frac{p_{C}}{RT}\right)^{c} \left(\frac{p_{D}}{RT}\right)^{d}}{\left(\frac{p_{A}}{RT}\right)^{a} \left(\frac{p_{B}}{RT}\right)^{b}}$$
$$= \frac{\left(p_{C}\right)^{c} \left(p_{D}\right)^{d}}{\left(p_{A}\right)^{a} \left(p_{B}\right)^{b}} (RT)^{a+b-c-d}$$
$$\Rightarrow \mathcal{K}_{c} = \mathcal{K}_{p} (RT)^{a+b-c-d}$$

Hence, students are not awarded credit if they expressed K_p in terms of the rate constants.

- (iii) Explain the role of the Cl radical in the decomposition of stratospheric ozone. [1]
- (iii) The Cl radical is acting as a homogeneous <u>catalyst</u> as it is <u>regenerated</u>.

Comments:

Many students did not get full credit as they did not explain how C*l* is a catalyst as it is regenerated in the second step of the mechanism.

- (iv) Hence, explain how the Cl radical affects the reaction in step 1. [2]
- (iv) The C*l* radical reacts with the O radical, as such, <u>[O] decreases</u>. The <u>position of</u> <u>equilibrium shifts right</u> to <u>increase the [O]</u>. Hence, the <u>rate of O₃</u> <u>decomposition increases</u>.

Comments:

The action of Cl as a catalyst in the decomposition of ozone is rather special. It catalyses the formation of O_2 from the O radicals and not the breakdown of O_3 directly. As such, to describe how the Cl radical affects the reaction in step 1, students should mention that it decreases the concentration of O radicals by reacting with it, and thus the position of equilibrium shifts to the right to increase the concentration of O radicals.

- (v) Suggest whether step 1 is exothermic or endothermic. Hence, suggest how an increase in temperature would affect the position of equilibrium for step 1. [2]
- (v) The reaction is <u>endothermic</u> as in involves <u>bond breaking</u>. An increase in temperature would cause the <u>position of equilibrium to shift right</u> to <u>absorb</u> excess <u>heat</u>.

Comments:

Many students missed out full credit for this part as the answers provided were not specific enough.

- Firstly, students should explain and provide a reason for why the reaction is endothermic. In the decomposition of O_3 , there is <u>only</u> bond breaking, where the O–O bond breaks to form O_2 and O radical. Hence, the reaction is endothermic.

- Secondly, students should also clearly explain <u>why</u> the endothermic reaction is favoured when temperature increases, this is because the endothermic reaction helps to <u>absorb the excess heat</u>.

- (vi) Explain why step 1 is spontaneous at high temperatures.
- (vi) Since ΔH is positive and ΔS is positive, from $\Delta G = \Delta H T\Delta S$, ΔG is negative at high temperatures. high temperatures. Hence, reaction is spontaneous at high temperatures.

Generally well-attempted by students. Students are reminded to take note of their phrasing when explaining such questions. "Entropy is positive" does not adequately express the meaning of ΔS being positive. The correct phrase should be entropy <u>change</u> is positive OR entropy <u>increases</u>.

[Total: 20]

[1]

Section B

Answer **one** question from this section.

4 Fluorine is the most reactive of all elements. It forms compounds, under appropriate conditions, with every other element except He, Ar and Ne, frequently combining directly and with such vigour that the reaction becomes explosive.

One reason for the great reactivity of F_2 compared to the rest of the halogens can be related to the weak F–F bond.

In fact, F_2 is the only halogen which reacts directly with the noble gases, notably xenon, to give binary fluorides, such as XeF₂, XeF₄ and XeF₆.

- (a) (i) Unlike the other halogens, fluorine almost exclusively assumes an oxidation state of −1 in its compounds. Explain why this is so.
 - (i) Fluorine is the <u>most electronegative</u> element and hence will assume a <u>negative</u> oxidation state.
 Fluorine is <u>short of one electron</u> from the octet and is <u>not able to expand its</u> <u>octet</u> due to the unavailability of energetically accessible vacant orbitals.

Comments:

- Generally not well-attempted.
 - Candidates generally did not realise that there are two features to explain:
 - Why is the oxidation state negative, which has to do with fluorine being the most electronegative element.
 - Why is the oxidation state 1, which as to do with fluorine being one electron short of the octet configuration and its inability to expand its octet.
 - (ii) Suggest a reason for the weak F–F bond.

[1]

(ii) Due to the <u>small size of the fluorine atom</u> / <u>short length of the F–F bond</u>, there is significant <u>inter-electronic repulsion</u> between the <u>lone pairs of</u> <u>electrons</u> on the two F atom, leading to the weak F–F bond.

- Generally not well-attempted.
- A number of candidates mentioned vaguely that there will be inter-electronic repulsion between the electron cloud of the two fluorine atoms due to the small size. However, the electron cloud can also refer to the shared electron pair, besides the lone pairs, which is not clear.

- (iii) By quoting suitable data from the *Data Booklet* and considering the weak F–F bond, suggest another factor which explains why only F₂ reacts with xenon vigorously, but not the other halogens.
- (iii) The F−F bond is very weak at 158 kJ mol⁻¹ coupled with the small covalent radius of the fluorine atom at <u>0.072 nm</u>, implies that the <u>Xe−F bond</u> formed is the shortest and <u>strongest</u>, hence the reaction between Xe and F₂ is expected to the <u>most exothermic</u>.

- Generally not well-attempted.
- Many candidates still quoted data for the bond energy of the X–X bond despite the question asking for *another factor* besides the weak F–F bond.
- Many candidates quoted electrode potential. However, in this case, the reaction is not in aqueous medium and does not involve the formation of F⁻. The bonding in XeF_x are covalent Xe–F bonds, and so student should be looking at the strength of the Xe–F bond instead.
- Some candidates quoted ionic radius rather than the covalent radius. Note that the "atomic" radius given in the *Data Booklet* for fluorine is the *single covalent* radius, and not the radius of an isolated atom.
- Some candidates who quoted correctly the single covalent radius of fluorine did to follow up on the strength of the Xe–F bond, but talked about steric hindrance and repulsion instead. However, Xe is a very large central atom. So the size of the peripheral halogen atom is not that important, especially XeX₂ which is linear.

Fluorine derives its name from the early use of fluorspar (CaF_2) as a flux (Latin *fluor*, flowing). However, all attempts to isolate the element were foiled by the extreme reactivity of free fluorine.

Success was finally achieved on 26 June 1886 by H. Moissan who electrolysed a cooled solution of potassium bifluoride, KHF₂, in anhydrous liquid HF, using platinum-iridium electrodes sealed into a platinum U-tube sealed with fluorspar caps.

- (b) KHF_2 is an ionic compound containing the HF_2^- ion.
 - (i) Draw the dot-and-cross diagram of the HF_2^- ion.

[1]



- Very badly attempted.
- Many students drew a structure with F–F bond, which will only work for HF₂⁺, if the F forms a dative bond with H⁺. There is no way a F–F molecule can form a dative bond with H⁻ to give HF₂⁻!
- Since students drew F–H–F, with 2 bond pairs around the H, without realising that H only have one 1s orbital and so is not able to form 2 σ bonds.

- (ii) Using your answer to (b)(i), suggest why only fluorine forms a stable HX₂⁻ ion, while that of the rest of the halogens are unstable.
- (ii) Only F⁻ is able to form <u>strong hydrogen bonds</u> with the H of the H–F molecule, while the <u>ion-dipole interactions</u> for the rest of the HX₂⁻ ions are <u>much weaker</u>.

- Very badly attempted.
- Since candidates are not able to draw the correct structure of HF₂⁻ with a hydrogen bond, they are not able to compare the difference with the other halogens.
 - (iii) Define the term *lattice energy*.

[1]

(iii) Lattice energy is the energy released when <u>one mole</u> of a crystalline <u>ionic solid</u> is formed from its <u>constituent gaseous ions</u>, all under <u>standard state</u>.

Comments:

- Generally well-attempted. The "standard state" was not marked for.
- Common errors are
 - Energy needed/required instead of energy released
 - Missing out the "one mole"
 - Missing out the "solid"
 - (iv) Use the data in Table 4.1, together with data from the *Data Booklet*, to calculate a value for the lattice energy of potassium bifluoride, KHF₂(s). Show your working.

	value / kJ mol ⁻¹
electron affinity of fluorine, $F(g) + e^- \rightarrow F^-(g)$	-328
enthalpy change for the reaction, HF(g) + $F^{-}(g) \rightarrow HF_2^{-}(g)$	-240
standard enthalpy change of atomisation of K(s)	+89
standard enthalpy change of formation of KHF ₂ (s)	-928

[4]



L.E.(KHF₂(s)) = +240+328+562-418-158-218-89-928 = -681 kJ mol⁻¹

- Generally not well-attempted.
- The most common error pertains to the H–F formed:
 - Using a value of +562 kJ mol⁻¹ for the formation of HF(g) from H and F(g), forgetting that bond energy is for the cleavage of the H–F bond.
 - Assuming that HF is formed from H⁺ and F⁻ while using the bond energy of 562 kJ mol⁻¹ from the *Data Booklet*, forgetting that the bond energy in the *Data Booklets* are homolytic bond energy [H–F(g) → H(g) + F(g)) and not heterolytic bond energy [H–F(g) → H⁺(g) + F⁻(g)].
 - (v) Compare the magnitude of the lattice energy of KHF₂ to that of KF. Explain the difference. [1]
 - (v) HF_2^- and F^- have the <u>same charge</u>, but <u> HF_2^- has a larger ionic radius than</u>

<u>F</u>. Based on |L.E.| $\propto \left| \frac{q_+ \times q_-}{r_+ + r_-} \right|$, the two compounds differ in *r*₋.

Hence, the magnitude of the lattice energy of KHF₂ is smaller than that of KF.

- Generally well-attempted.
- However, candidates are reminded to try to answer the question asked. Many candidates used "less exothermic" lattice energy for KHF₂, although the question asked for the *magnitude* of the lattice energy. Although they are the same, it is advisable to follow what the question ask for.

Like ethanoic acid, its structural analogue trifluoroethanoic acid, CF₃CO₂H, is also a colourless liquid with a vinegar smell.

Trifluoroethanoic acid is prepared industrially by the electrofluorination of ethanoyl chloride, to give first trifluoroethanoyl fluoride, CF_3COF .

$$CH_{3}COCl + 4HF \rightarrow CF_{3}COF + 3H_{2} + HCl$$

- (c) (i) State and explain the relative acidity of CF_3CO_2H and CH_3CO_2H . [2]
 - (i) Due to presence of the three highly electronegative fluorine atoms, <u>CF₃</u>- is a powerful <u>electron withdrawing group</u>. It further <u>disperse</u> the <u>negative charge</u> of the CF₃CO₂⁻ conjugate base, making it <u>more stable</u> than the CH₃CO₂⁻ ion, rendering CF₃CO₂H is <u>more acidic</u> than CH₃CO₂H.

Comments:

- Generally well-attempted.
- Most students did not realise that both CF₃CO₂⁻ and CH₃CO₂⁻ are resonance stabilised, where the negative charge is dispersed over the two O atoms. What the CF₃ does is to further disperse the negative charge by drawing electron density away from the carboxylate group, -CO₂⁻.
 - (ii) Suggest the reagent and condition for the conversion of CF₃COF into CF₃CO₂H, and state the type of reaction involved.
 [2]
 - (ii) H₂O, r.t.

Nucleophilic substitution / Hydrolysis

Comments:

- Generally not well-attempted for the reagent, but type of reaction is wellattempted.
- Many candidates uses dilute acids or dilute alkaline which is not necessary. Water alone will do the trick.
 - (iii) Explain why the two carboxylic acids, CF₃CO₂H and CH₃CO₂H, cannot be distinguished by a simple chemical test.
 - (iii) This is because the <u>C-F bond is too strong to be cleaved</u> via nucleophilic substitution.

- Generally not well-attempted.
- Many candidates did not read the question carefully. The question already stated that the two are carboxylic acids, so it is obvious that they cannot be differentiated via the carboxyl group. The remaining difference is the CH₃-versus the CF₃- group where the focus should be on the C-F bond.

(iv) An older route to trifluoroethanoic acid commences from 1,1,2-trichloro-3,3,3trifluoroprop-1-ene.



1,1,2-trichloro-3,3,3-trifluoroprop-1-ene

Suggest the reagent and condition for the one-step conversion of 1,1,2-trichloro-3,3,3-trifluoroprop-1-ene into CF_3CO_2H , and suggest the identities of the likely byproducts. [2]

(iv) KMnO₄(aq), H₂SO₄(aq), heat HCl and CO₂

Comments:

- Generally the reagent and condition is well-attempted, although the by-products is not.
- Some students suggested KMnO₄(aq), NaOH(aq), heat for the reagent. However, they would need to acidify the mixture subsequently to isolate trifluoroethanoic acid. Some candidates wrote *acidified* KMnO₄. Candidates are reminded to specify the acid used.
- The oxidative cleavage of the C=C will give an acid chloride and COC l_2 (some sort of a diacid chloride). The acid chloride will hydrolyse in water to give trichloroethanoic acid and HC l, while COC l_2 + H₂O \rightarrow CO₂ + HC l. Candidates who gave H₂O as a by-product is ignored.

[Total: 20]

- **5** Copper is a transition element which use dates to prehistoric times. The metal, its compounds, and alloys have numerous applications in every sphere of life, making it one of the most important metals.
 - (a) Cross-coupling reactions are powerful tools for carbon-carbon bond formation and have been widely utilised in organic synthesis. These transformations are typically catalysed by palladium complexes. Recently, tremendous efforts have been invested in developing copper as an alternative, due to the high cost and low natural abundance of palladium.

Fig. 5.1 shows an example of the cross-coupling between 1-chloro-4-iodobenzene and boronic ester **1**, catalysed by copper(I) chloride in the presence of a neutral phosphorus-containing tridentate ligand, Xantphos.



Fig. 5.1

- (i) Define the term *tridentate ligand*.
- (i) A tridentate ligand is one which can form <u>3 dative bonds</u> to the <u>central metal</u> <u>ion/atom</u> in a complex.

[1]

Comments:

- Generally well-attempted.
- Candidates are reminded that a tridentate ligand can form 3 dative bonds simultaneously with the same central metal ion/atom.
 - (ii) CuC*l* and Xantphos form a tetrahedral complex in a 1:1 ratio. Draw the structure of the complex, showing its shape.

Use
$$P$$
 O P to represent Xantphos. [1]



Comments:

- Very badly attempted.
- Candidates are not able to draw 3-dimensional representation of a tetrahedral shape properly.
- A number of candidates got the charge of the complex wrong too, although it is given in the question that the ligand is neutral.
 - (iii) Copper(II) complexes are coloured, while copper(I) complexes, such as the complex between CuCl and Xantphos, are generally colourless. Explain. [3]
 - (iii) In the <u>presence of ligands</u>, the five 3d orbitals are <u>split into two groups of different energies</u>. An electron in the lower energy 3d orbital can <u>absorb energy from the visible light spectrum</u> and be promoted to the higher energy 3d orbital. The <u>colour complementary</u> to the colour of light absorbed will be seen. Cu(I) has a <u>3d¹⁰</u> configuration. There is <u>no vacancy in the higher energy 3d</u> <u>orbital</u> to promote the electrons in the lower energy 3d orbitals.

- Generally well-attempted.
- However, a number of candidates seems to suggest that the splitting of the dorbitals into two sets of different energy only takes place when the 3d subshell is incompletely filled. Candidates are reminded that splitting of the 3d subshell takes place in the presence of ligands, and this is independent of the occupancy of the 3d subshell.
- Candidates are also reminded that "does not have a partially filled 3d subshell" does not imply that the subshell is fully filled. It can be totally vacant too. Candidates are encouraged to be specific to state that Cu⁺ has a "fully filled 3d subshell".

- (iv) The copper(I) halides, CuCl, CuBr and CuI are white solids when pure. However, upon exposure to air, CuBr turns light green, while CuI becomes light brown in colour. Suggest separate reasons for the two colour changes. [2]
- (iv) The <u>Cu(I)</u> in CuBr is <u>oxidised to Cu(II)</u> by oxygen in air, resulting in the green colour observed.
 The <u>iodide</u> in CuI is <u>oxidised to I₂</u> by oxygen in air, resulting in the light brown colour observed.

- Generally badly attempted.
- Some candidates talked about the complexes having different colours, without reading the question carefully that CuX are white solids. The colours only arise when exposed to air, which suggest that some form of oxidation had taken place.
- I⁻ is a stronger reducing agent that Br⁻, so I⁻ is oxidised to I₂, hence giving the brown colour, while the Cu⁺ in CuBr is oxidised to Cu²⁺ hence giving the green colour.

The cross-coupling is interesting in that it involves the cleavage of a carbon-halogen bond in the halogenoarene.

- (v) Explain why the carbon-halogen bond in halogenoarenes are difficult to break. [2]
- (v) A <u>p orbital carrying a lone pair</u> of electrons on the halogen can <u>overlap with</u> <u>the p orbitals of the benzene ring</u>, resulting in <u>delocalisation of the lone pair</u> <u>of electrons into the benzene ring</u>, imparting <u>partial double bond character</u> to the C-X bond, making it stronger and more difficult to break.

Comments:

- Generally well-attempted.
- Some candidates missed out on the overlap of the p orbital on the halogen with the p orbitals / π electron cloud of the benzene ring.
 - (vi) There are two different carbon-halogen bonds in 1-chloro-4-iodobenzene. By quoting suitable data from the *Data Booklet*, suggest why the reaction took place as shown in Fig. 5.1.
 - (vi) Bond energy of C–Cl bond is <u>340 kJ mol⁻¹</u> and that of C–I is <u>240 kJ mol⁻¹</u>. Since the C–Cl bond is much <u>stronger</u> than the C–I bond, it is the <u>C–I bond which</u> <u>cleave preferentially</u> in the cross-coupling.

- Generally very well-attempted.
- Some candidates missed out on the overlap of the p orbital on the halogen with the p orbitals / π electron cloud of the benzene ring.

(b) Soft, highly malleable, conductive, corrosion-resistant, and most importantly economical, copper is a perfect choice for many applications. While copper is great, the material is not suitable for applications where strength is desired. For such cases, copper electroplating can be an ideal solution. The outer layer will deliver the same properties that the application requires while the core provide the strength or any other mechanical properties that is needed.

For copper electroplating, an electrolytic cell is used where the metal core is made the cathode, while the anode is a copper rod.

- (i) Suggest an electrolyte to use for the copper electroplating cell. [1]
- (i) copper(II) sulfate

Comments:

- Generally very well-attempted.
- However, candidates who gave Cu²⁺(aq) without a specific anion are not awarded the mark.

[2]

(ii) Draw a labelled diagram of the cell for copper electroplating.



- Generally well-attempted.
- However, a number of candidates drew separate containers for the cathode and anode, forgetting that the Cu²⁺ produced at the anode is used to plate the metal core at the cathode. So the electrolyte must be common to both electrodes.
 - (iii) The copper rod used does not need to be of high purity, it can contain impurities such as silver and iron. Explain. [2]
 - (iii) If the copper rod contains metals with <u>more positive electrode potentials</u>, for example, Ag and Au, these <u>will not be oxidised</u> and hence will not be deposited on the metal core.
 If the copper rod contains metals with <u>(more) negative electrode potentials</u>, for example, Fe and Zn, these although will be oxidised and goes into solution as ions, but <u>will not be discharged at the cathode</u> due to their negative electrode potentials.

- Generally, not well-attempted.
- A few candidates uses the reactivity series or electrochemical series. Candidates are advised to use electrode potential instead for discussion.
- Some candidates chose E^{\ominus} (Fe³⁺ |Fe²⁺) = +0.77 V instead without realising that
 - the iron present in the iron rod is in the form of iron metal. So they concluded wrongly that Cu is the only metal that is oxidised at the anode.

The same setup can be used to determine an accurate value for the Avogadro constant as well. However, in this case, the copper anode needs to be of very high purity (> 99.99% Cu). In one such experiment, when a current of 3.0 A is passed through the cell for 32 minutes, the mass of the cathode is found to increase by 1.896 g.

 (iv) Calculate the amount of electrons, in moles, required to deposit the observed mass of copper at the cathode.

(iv)
$$n_{Cu} = \frac{1.896}{63.5} = 0.02986 \text{ mol}$$

Since $Cu^{2+} + 2e^- \rightarrow Cu$, $n_{e^-} = 2n_{Cu} = 2 \times 0.02986 = 0.0597 \text{ mol}$

Comments:

- Generally very well-attempted.
 - (v) Using your answer to (b)(iv), calculate a value for the Faraday's constant, F, the charge of one mole of electrons.

(v)
$$Q = I \times t = 3.0 \times 32 \times 60 = 5760 \text{ C}$$

 $F = \frac{Q}{n_{c^{-}}} = \frac{5760}{0.05972} = 96450 \approx 96500 \text{ C mol}^{-1}$

Comments:

- Generally very well-attempted.
 - However, many candidates did not give the units or gave a wrong unit.

(vi) Calculate, using your answer to (b)(v), a value for the Avogadro constant, L. [1]

(vi)
$$L = \frac{F}{\text{electronic charge, } e} = \frac{96450}{1.60 \times 10^{-19}} = \frac{6.03 \times 10^{23} \text{ mol}^{-1}}{10^{-19}}$$

Comments:

- Generally well-attempted.
- However, many candidates did not give the units.

(vii) Explain why the copper anode must be of very high purity. [1]

(vii) If the copper rod contains other <u>metals which can be oxidised to a different</u> <u>oxidation state (from +2)</u>, it will <u>consume different amount of electrons</u> to be oxidised (*i.e.* $n_{e^-} \neq 2n_{Cu}$).

- Badly attempted.
- Candidates did not realise that if the impurity in the copper rod can be oxidised to M²⁺, due to the Cu²⁺ in the electrolyte, Cu will still be deposited at the cathode, and there will be no difference.
- The problem arise if the impurity oxidises to M⁺ or M³⁺, then the amount of electrons required will not be twice the amount of Cu deposited on the cathode.

[Total: 20]