CJC	Catholic Junior College JC2 Preliminary Examination Higher 2
CANDIDATE NAME	
CLASS	2T

CHEMISTRY Paper 2 Structured Questions

Candidates answer on the Question Paper. Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class 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. The use of an approved scientific calculation is expected, where appropriate.

For Examiner's Use		
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	Q1	/13
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Paper 2	Q4	/14
raper z	Q5	/10
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Paper 4		55
OVERALL		
(100%)		
GRADE		
	For Ex Paper 1 Paper 2 Paper 3 Paper 4 OVERALL (100%) GRADE	For Examiner's UsePaper 1Q1Q2Q3Q3Q4Q5Q6Paper 30Paper 40OVERALL (100%)0GRADE0

This document consists of **20** printed pages.

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2 hours

28 August 2023

- **1** (a) Nitrogen and phosphorus are elements of Group 15 in the Periodic Table.
 - (i) Explain why phosphorus has a larger atomic radius than nitrogen.

P has a larger atomic radius than N as although P has a <u>greater nuclear charge</u>, it has one more principal quantum shell and hence the outermost (valence)

electrons are further from the nucleus and experience greater shielding effect

due to inner electron shells. <u>Nuclear attraction</u> on the valence electrons is <u>lower</u>, hence the atomic radius of P is larger.

.....[2]

Most candidates were able to identify that increase in shielding effect was the dominant factor. Common mistakes were omitting the discussion on nuclear charge, failure to conclude the effect on attraction of the valence electrons to the nucleus or omitting key words (like nuclear charge, shielding effect).

(ii) Nitrogen exists naturally as gaseous diatomic N≡N molecules whereas phosphorus is a solid and exists as P₄ molecules comprising P-P single bonds.

Suggest why phosphorus does **not** occur naturally as $P \equiv P$ molecules.

Phosphorus is a relatively big atom with diffused (3p) orbitals, side-on overlap of its p orbitals to form π bonds is much less effective than head-on overlap to form sigma bond.

_____.[1]

Few candidates managed to recognise that side-on overlap of the diffused p orbitals would be less effective. Many candidates skipped this part.

- (b) Nitrate, NO_{3}^{-} , and phosphate, PO_{4}^{3-} , are oxoanions of nitrogen and phosphorous respectively.
 - (i) Draw dot–and–cross diagrams to show the bonding in NO_3^- and PO_4^{3-} ions. Hence, suggest the shape of each of these ions. [4]

ion	NO ₃ ⁻	PO4 ³⁻
dot-and-cross diagram	$\begin{bmatrix} & & & \\ & $	$\begin{bmatrix} 0 \\ X \\$
shape	trigonal planar	tetrahedral

Few candidates managed to get the correct dot-and-cross diagram for nitrate. It is important to note that N is in period 2 and hence cannot expand its octet. Other common mistakes include not differentiating the extra electrons with a different symbol, omitting the overall charge, omitting lone pairs of electrons on surrounding atoms, drawing numerous dative bonds from the same atom.

Most candidates managed to identify the correct shape. Candidates are reminded on the need to ensure their diagrams are well-spaced.

(ii) The 2s and 2p orbitals of nitrogen atoms can hybridise in the same way as the 2s and 2p orbitals of carbon atoms.

With reference to your answer in (b)(i), state the hybridisation state of nitrogen in NO_3^- . sp²

Many candidates were able to apply hybridisation of C to N here, where 3 σ bonds and 1 π bond indicates sp² hybridisation (based on the correct dotand-cross diagram). Candidates should ensure they write the number 2 as a superscript.

(iii) Table 1.1 shows the bond lengths of two nitrogen–oxygen bonds.

Table	1	.1
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bond	N–O	N=O
bond length (pm)	136	115

The experimental bond length of each nitrogen–oxygen bond in the nitrate ion, NO_3^- , is 128 pm.

With reference to your answers in (b)(i) and (b)(ii), explain this observed bond length in NO_3^- .

The continuous overlap of p orbitals between the N and O atoms allow the lone

Few candidates provided a good explanation. Candidates should deduce from the dot-and-cross diagram that the O atoms that are single bonded with N have a lone pair which can overlap with the <u>unhybridised p orbital</u> in N/ p orbital of the N=O bond, hence all the nitrogen-oxygen bonds have partial double bond character/ resonance structure.



Common mistakes:

-Some candidates misread the question and simply explained the difference in N–O and N=O bond lengths

-Some stated that 128 pm is the average of single and double bond lengths but did not explain <u>why</u> the average could be taken

-Some stated that hybrid orbitals with partial s or p character will form bonds with partial double bond character, which is completely incorrect

- 4
- (c) A nuclear reaction is a reaction in which there is a change to an atomic nucleus.

A scientist attempts to produce ${}^{32}_{15}$ P synthetically using a nuclear reaction where a neutron collides with an isotope **E** of another element as shown in the equation below (n represents a neutron).

isotope E + $^{1}_{0}n \rightarrow ^{32}_{15}P$ + $^{3}_{1}H$

Identify isotope E, showing clearly its mass number.

16[°]S

A majority of candidates were able to deduce the correct proton and mass number, and hence identify isotope E as ${}^{34}_{16}$ S. Common mistakes:

-Some candidates did not <u>identify</u> E, or wrote P, although proton number 16 indicates sulfur.

-Some candidates were unclear about what mass number represents, and hence added the numbers wrongly, or gave a mass number with a decimal eg. 34.0 or 32.1, but mass number should be a whole number as it is the total number of neutrons and protons in the nucleus of a particular atom/isotope, while relative atomic mass (A_r) is the <u>average</u> mass of one atom of the <u>element</u> (considering relative abundance of all isotopes existing in nature), and is expressed as a decimal.

(d) Another type of nuclear reaction is radioactive decay, which occurs spontaneously in elements with an unstable atomic nucleus.

Uranium–234 is used in nuclear power generation, and emits a constant stream of α particles, which are equivalent to Helium–4 nuclei.

lodine–131 is used in treatment for thyroid cancer. On decaying, it emits β particles, which can be considered as electrons.

A small amount of Uranium–234 and Iodine–131 are separately placed in an ionisation chamber to emit a constant stream of radiation, and the emitted particles are passed through an electric field.

(i) On the diagram below, sketch the deflection path for the emitted particles in an electric field.

You may label the emitted particles as α particles and β particles respectively.

	Emitted particles from ²³⁴ U and ¹³¹ I		β particles $θ_1 > θ_2$ α particles
Ionisation Chamber			
		-	

[1]

A good number of candidates were able to draw the diagram correctly. Common mistakes:
-Some candidates showed the path of the particles hitting the plates, but the path should
leave the electric field in order to be detected.
-Some candidates did not show clearly that the β particles are deflected to a greater
extent than the α particles, ie $\theta_1 > \theta_2$. (if candidate drew the path hitting the plate, the β
particles should hit earlier)
-Some candidates did not recognise that <u>Helium-4 nuclei</u> consist of 2 protons and 2
neutrons, and no electrons.
-Some candidates showed deflection starting only in the middle of the electric field, but
it should start upon entering the field.
-Some candidates did not read instructions and labelled the paths wrongly, eg. as ¹³¹ I and ²³⁴ I.

(ii) A deflection of +16° was observed when a beam of α particles was passed through an electric field.

In another experiment, a beam of doubly charged **X** particles was passed through the electric field under the same experimental conditions. The angle of deflection was found to be -4° .

Suggest the identity of ion **X**. Show your working.

Angle of deflection = $k(\frac{q}{m})$

 $16^{\circ} = k(\frac{2}{4}), k = 32$

 $-4^{\circ} = (32 \times \frac{-2}{m})$ (opposite charge from α particles since angle of deflection is in opposite direction)

 \Rightarrow m = mass number = 16

 \Rightarrow X is O²⁻

[2]

This question was poorly attempted. Common mistakes: -Some candidates could not recall the basic relationship: angle of deflection = k (charge/mass) -Some candidates did not recognise that Helium-4 nuclei would have a charge of +2, or that mass is 4 -Some candidates thought that "doubly charged X particles" meant that the charge was double of the helium-4 nuclei -Some candidates calculated that mass is 16, but could not identify the correct element, or simply stated "oxygen" instead of the exact ion, O²⁻

[Total: 12]

2 (a) Sulfanilamide is an antibiotic used to treat streptococcal infections.



sulfanilamide

(i) Explain why sulfanilamide is soluble in dilute HC*l*.

Sulfanilamide will react with dilute HCI to form an ionic salt. It can form ion-dipole attractions between the ions and water, and release sufficient energy to compensate for the energy required to overcome the electrostatic forces of attraction between the ions, and intermolecular hydrogen bonds between water molecules.

.....[2]

This question was poorly attempted. Many candidates are able to recognise that the phenylamine will react with HCl to form ammonium salt. However, the question is asking about solubility. Many candidates failed to identify the correct solute-solvent interaction which is the ion-dipole attraction between the ammonium ion and water molecules.

Take note that dilute HC*l* is used here, so water is in large excess and is the solvent here. Many candidates failed to identify the correct solute-solute interaction (ionic bonds between the ammonium ions) and the correct solvent-solvent interaction (intermolecular hydrogen bonds between water molecules).

(ii) In sulfanilamide, the carbon atoms are sp² hybridised. Draw a labelled diagram to show the orbitals overlapping between any two carbon atoms in sulfanilamide.

side-on overlap between unhybridised p orbital (to form pi bond)



head-on overlap between sp^2 hybrid orbitals (to form sigma bond)

This question was poorly attempted. Question asked for 'a' labelled diagram. Only 1 diagram should be drawn to show the sp² hybrid orbitals and p orbitals are perpendicular from each other. The lobes of sp² should include one big and one small lobe, they should not be equal in size. The sp² orbitals should overlap. The drawings of p orbitals should not overlap with each other. Many candidates also did not label the orbitals or indicate the type of overlap (head-on or side-on). (iii) A 0.3 g sample containing sulfanilamide (M_r of 172.1) was dissolved and diluted to 100 cm³. A 20 cm³ aliquot was used to react with 1.33 x 10⁻³ mol Br₂ (which was in excess) to form **Y**.



KI was then added to react with any remaining unreacted Br_2 . The liberated iodine was subsequently titrated with 15.70 cm³ of 0.1 mol dm⁻³ sodium thiosulfate as shown in the equations below.

Br₂ + 2I⁻ → 2Br⁻ + I₂ I₂ + 2S₂O₃²⁻ → 2S₄O₆²⁻ + 2I⁻

Calculate the percentage by mass of sulfanilamide in the sample.

Amount of sodium thiosulfate = $\frac{15.70}{1000}$ x 0.1 = 1.57 x 10⁻³ mol

 $2S_2O_3^{2-} \equiv I_2 \equiv Br_2$

Amount of Br₂ (excess unreacted) = $\frac{1.57 \times 10^{-3}}{2}$ = 7.85 x 10⁻⁴ mol

Amount of Br_2 (reacted with sulfanilamide) = 1.33x 10⁻³ - 7.85 x 10⁻⁴ = 5.45 x 10⁻⁴ mol

Amount of sulfanilamide = $\frac{5.45 \times 10^{-4}}{2}$ = 2.725x 10⁻⁴ mol

Mass of sulfanilamide = $2.725 \times 10^{-4} \times 172.1 \times \frac{100}{20} = 0.234 \text{ g}$

% mass in sample = $\frac{0.234}{0.3}$ x 100 = 78.2%

[4]

This question was quite well done. Common mistakes include not calculating the amount of Br_2 (reacted with sulfanilamide) and mass of sulfanilamide in 100cm³ solution.

(b) (i) Describe the reaction of SO₃ with water. Include the approximate pH value of any resulting solution, and write an equation for any reaction that occurs.

SO₃ reacts vigorously with water (pH \approx 2 or 1).

 $\textbf{SO}_3 \textbf{+} \textbf{H}_2\textbf{O} \rightarrow \textbf{H}_2\textbf{SO}_4$

Mark was lost when candidates did not describe how vigorous the reaction was.

Th	is question was well done.
(iii)	Explain why sulfur has a lower first ionisation energy than phosphorus.
	S has a lower first IE than P as less energy is required to remove a paired
	3p electron in S than an unpaired 3p electron in P due to inter-electronic
	repulsion.

[Total: 12]

3 Wine contains varying concentrations of different acids, and the amount of acids is influenced by factors such as climate and the fermentation process of grapes that make the wine. The principal acid present in grapes is tartaric acid, which gives wine the tart taste.



- (a) In an experiment to determine the tartaric acid content of a 750 cm³ bottle of white wine, a titration was carried out and 17.60 cm³ of 0.01 mol dm⁻³ NaOH was found to react with 25.0 cm³ of diluted white wine. The original white wine was ten times more concentrated.
 - (i) Write an equation for the reaction that has taken place.



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This question was surprisingly not well attempted.
Common mistakes:
Some candidates wrongly showed reaction between NaOH with ROH groups.
Some candidates did not balance the equation correctly and either did not

- Some candidates did not balance the equation correctly and either did r include H_2O or erroneously included H_2 or O_2 as products formed.

(ii) Calculate the total mass of tartaric acid present in the original 750 cm³ bottle of white wine.

Amt NaOH reacted with 25.0 cm³ dilute wine = $(17.60/1000) \times 0.01 = 1.76 \times 10^{-4}$ mol Amt tartaric acid in 25.0 cm³ dilute wine = $(1.76 \times 10^{-4}) / 2 = 8.80 \times 10^{-5}$ mol M_r tartaric acid = 150.1 Mass tartaric acid in 25.0 cm³ dilute wine = $(8.80 \times 10^{-5}) \times 150.1 = 1.30 \times 10^{-2}$ g Mass tartaric acid in 25.0 cm³ original wine = $(1.30 \times 10^{-2}) \times 10 = 1.30 \times 10^{-1}$ g Mass tartaric acid in 750 cm³ original wine = $(1.30 \times 10^{-1}) \times (750/25) = 3.90$ g

[2]

This question clearly highlighted candidate's mole concept understanding and ability to analyse the data provided in the question in a sequential manner.

common mistakes:

- Many candidates neglect to include the original white wine was ten times more concentrated in their final calculation.

- Many candidates did not calculate the M_r of tartaric acid correctly (M_r 150)

(iii) Tartaric acid is a muscle toxin and in high doses causes paralysis and death. The median lethal dose is about 7.5 grams tartaric acid per kg mass for a human. Based on your answer in (a)(ii), deduce whether a 70 kg human might die from an overdose of tartaric acid after drinking 5 bottles of white wine.

Lethal dose of tartaric acid for 70 kg human = $70 \times 7.5 = 525$ g Mass of tartaric acid in 5 bottles of white wine = $5 \times 3.9 = 19.5$ g Hence, 70 kg human will not die from tartaric acid overdose after drinking 5 bottles white wine.

[1]

This question was generally well attempted, although there were some candidates who did not make a final deduction or conclusion after their calculation and hance were not awarded the mark. (b) Tartaric acid can be synthesised from fumaric acid, which occurs widely in nature, in a 3-step synthetic route as shown.



In part (iv), candidates should not mention reflux or distillation setup for simple chemical tests which normally involve small samples using test tube apparatus. The inability to mention the correct colour of bromine in various solvents was surprising given the information being available in Data Booklet.

(c) Tartaric acid can also be prepared from maleic acid, C₄H₄O₄, by reacting with hydrogen peroxide in the presence of a catalyst as shown below.



Name the type of reaction occurring in step 2.

Hydrolysis [1]

Only a small number of candidates were able to deduce hydrolysis reaction occuring in step 2.

- (d) Maleic acid and fumaric acid are stereoisomers with different physical properties. Maleic acid is less soluble in water compared to fumaric acid.
 - (i) Draw the skeletal formula of maleic acid, clearly displaying the stereoisomerism it exhibits.



[1]

(ii) Suggest a reason why maleic acid is less soluble in water in comparison with fumaric acid.

Intra-molecular hydrogen bonding occurs in maleic acid, which reduce the extent of inter-molecular hydrogen bonding between maleic acid molecules with water molecules, hence less soluble in water.

.....[1]

[Total: 14]

A significant number of candidates were unable to attempt this part correctly. In part (i), some candidates drew both the cis and trans isomers without clearly indicating which is maleic acid (cis) and hence were not given credit. In part (ii), many were unable to recognize the presence of intra-molecular hydrogen bonding occurring within each maleic acid molecule and wrongly attributed to pd-pd or polarity of the molecule in their attempt to explain the difference in solubilities. 4 (a) When air is passed through an aqueous solution containing CoCl₂, H₂NCH₂CH₂NH₂ and HCl, a green complex cation X with formula [Co(H₂NCH₂CH₂NH₂)₂Cl₂]⁺ is produced. Evaporation of X at 90°C produces a red complex cation Y with the same formula as X. X has no dipole moment, whereas Y does. Complex cations Y and Z rotate plane-polarised light in opposite directions but with equal magnitude.

The structure of complex cation **X** is given below:



(i) In the boxes below, suggest the structural formulae of complex cations Y and Z. [2]



This question was poorly attempted with many candidates changing the formula of the cation despite the question stating that cations Y and Z have the same formula. Common mistakes include drawing the wedge and dashed lines wrongly for an octahedral shape and forgetting to draw $-CH_2CH_2$ - chain. Candidates should start with the information given in the question, that cation Y has a net dipole moment and draw two CI ligands adjacent to each other. This can be followed by drawing Z as a mirror image of Y, as it is given in the question that Z is the enantiomer of Y.

(ii) Suggest the isomeric relationship between complex cations Y and Z.



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(b) (i) When $NH_3(aq)$ is added to a sample of $[Cu(H_2O)_6]^{2+}(aq)$, a pale blue precipitate is produced, which dissolved in excess ammonia to produce a dark blue solution.

Complete the equation for the formation of the pale blue precipitate. Include state symbols.

 $[Cu(H_2O)_6]^{2+}(aq) + \underbrace{2...NH_3(aq)}_{Or} \rightarrow \underbrace{Cu(H_2O)_4(OH)_2(s) + 2NH_4^+(aq)}_{Or \ Cu(OH)_2(s) + 2NH_4^+(aq) + 4H_2O(l)}$ [1]

This question was poorly answered with many candidates not even knowing that the blue precipitate is simply Cu(OH)₂. There were many attempts to form other complexes. Candidates should also note that precipitates should be an overall neutral compound.

(ii) The dark blue solution can also be prepared by adding copper metal to an alkaline solution of oxygen dissolved in aqueous ammonia. With reference to the *Data Booklet*, write a balanced equation for this reaction and calculate the E°_{cell} of this reaction.

[Cu(NH ₃) ₄] ²⁺ + 2e ⁻ ⇒ Cu + 4NH ₃	–0.05V
O ₂ + 2H ₂ O + + 4e ⁻ ⇔ 4OH ⁻	+ 0.40V
$E_{\text{cell}} = +0.40 - (-0.05) = +0.45 \text{V} >$	0
Reaction is feasible	
$2Cu + O_2 + 2H_2O + 8NH_3 \rightarrow 4O$	H ⁻ + 2 [Cu(NH₃)₄] ²⁺
	[2]

This part was poorly answered. The main difficulty was picking out the correct half-equations from the data booklet.

(iii) Explain why so many transition metal complexes are coloured.

In the presence of ligands, the partially filled \checkmark d orbitals split into 2 energy levels with a small energy gap. In the presence of visible light, a d electron in a d orbital of lower energy absorbs energy from visible light region and is promoted to the higher energy d* orbital \checkmark via d-d* electronic transition. The complementary colour \checkmark is observed.

.....[3]

This question was well-answered by students who prepared well. Common mistakes were to misuse orbitals and subshells. Some students also describe excitation of d orbitals instead of electrons.

(c) Transition metal compounds are frequently coloured. Some data about chromium compounds are given in the table below.

salt	colour	K _{sp} value at 25°C
BaCrO ₄	yellow	1.2 x 10 ⁻¹⁰
Ag ₂ CrO ₄	red	1.1 x 10 ⁻¹²

(i) Write an expression for K_{sp} of Ag₂CrO₄, stating its units.

 $K_{sp} = [Ag^+]^2 [CrO_4^{2-}]$ units: mol³ dm⁻⁹

Well-answered. A small number of candidates could not recognise the chromate (VI) ion, $CrO_4^{2^-}$.

(ii) Calculate the solubility of Ag_2CrO_4 in g dm⁻³.

[2]

[1

Let the solubility be x mol dm⁻³.

```
1.1 x 10^{-12} = 4x^3
x = 6.50 \times 10^{-5} mol dm<sup>-3</sup>
Solubility of Ag<sub>2</sub>CrO<sub>4</sub> in <u>g dm<sup>-3</sup></u> = 6.50 x 10^{-5} \times 332 = 0.0216
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Generally well-answered. A number of candidates did not covert to gdm^{-3} and lost a mark.
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(iii) State the expected observations when 50 cm³ of 2.0 x 10⁻⁴ mol dm⁻³ of K₂CrO₄ solution is mixed with 50 cm³ of a mixture containing 8.0 x 10⁻⁵ mol dm⁻³ AgNO₃ solution and 8.0 x 10⁻⁵ mol dm⁻³ of Ba(NO₃)₂. Justify your answer with relevant calculations.

Ionic product of Ag₂CrO₄

$$= \left(\frac{8.0 \times 10^{-5}}{2}\right)^{2} \left(\frac{2.0 \times 10^{-4}}{2}\right)$$

= 1.60 x 10⁻¹³ < K_{sp} (Ag₂CrO₄)
lonic product of BaCrO₄
$$= \left(\frac{8.0 \times 10^{-5}}{2}\right) \left(\frac{2.0 \times 10^{-4}}{2}\right)$$

= 4.00 x 10⁻⁹ > K_{sp} (BaCrO₄)

yellow ppt of BaCrO₄

[2] [Total: 14]

Many candidates did not know that they had to calculate ionic product and compare it to K_{sp} . Some forgot to calculate the new concentrations after the change in volume. Some candidates did the calculations correctly but did not state the colour of the precipitate. Candidates are reminded to use information given in the question.

5 Alkali metals, such as lithium, are good reducing agents and can reduce the carbon-halogen bonds of alkyl halides to give organolithium compounds.

The carbon-lithium covalent bond in organolithium compounds is polarised $\begin{array}{c} \delta - \delta + \\ C-Li. \end{array}$ Organolithium compounds act as sources of negatively charged carbon, i.e. carbanions, and are useful reagents in organic synthesis involving carbon-carbon bond formation. They react with carbonyl compounds to give lithium alkoxides, which form alcohols on treatment with dilute acid. This sequence is known as the organolithium reaction.

$$\text{R-X} + 2\text{Li} \rightarrow \text{R-Li} + \text{LiX}$$



(R is alkyl; R' and R" are either alkyl or H)

For example, propan-1-ol can be synthesised from 1-bromoethane and methanal.

$$\label{eq:ch_3CH_2Br} \begin{array}{l} \rightarrow CH_3CH_2Li\\ CH_3CH_2Li + CH_2O \rightarrow CH_3CH_2CH_2OLi\\ CH_3CH_2CH_2OLi + H^+ \rightarrow CH_3CH_2CH_2OH + Li^+ \end{array}$$

- (a) Deduce the structures of a suitable bromoalkane, RBr, and a suitable carbonyl compound, R'R"CO, to synthesise each of the following alcohols.
 - (i) $CH_3CH(OH)CH_2CH_3$

CH₃CH₂Br & CH₃CHO OR CH₃Br & CH₃CH₂CHO

& CH₃Br

[2]

[2]

Some candidates gave HBr and $CH_3COCH_2CH_3$ as one of the answers for (a)(i). HBr is an acid and not a bromoalkene, thus no credit was awarded. Candidates need to be able to analyse and evaluate information so as to identify patterns, report trends and conclusions, and draw inferences as listed in the syallbus requirements.

(b) Compound U can be synthesised by the following route involving an intramolecular organolithium reaction.

T gives a silver mirror when boiled with Tollens' reagent. **T** also gives a cream precipitate when heated with ethanolic silver nitrate.



(i) State the reagents and conditions for step 1.

K₂Cr₂O₇(aq), H₂SO₄(aq), heat with immediate distillation

.....[1]

Some candidates used KMnO₄, dilute H_2SO_4 , heat to oxidise S to T. However, the clue given in the question stated that an aldehyde is formed in T. (T gives silver mirror when boiled with Tollen's reagent, and there was no carboxylic acid formed as seen in the molecular formula.) Thus, a milder oxidising agent such as $K_2Cr_2O_7(aq)$, dilute H_2SO_4 must be used instead of a strong oxidising agent. In addition, candidates who stated the correct reagents, but mentioned only "heat" was not given credit as aldehydes can only be obtained through distillation during the synthesis process. In addition, state symbols are necessary when question asks for reagents and conditions.

(ii) Draw the structures of **S** and **T**.



[2]

Only a handful of candidates managed to get the reagents to the intramolecular cyclisation reaction correct based on the clues given in the question.

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(c) *Tautomers* are isomers of organic compounds which are readily interconverted. Ethanal and ethenol are tautomers, and they rapidly equilibrate as shown.



- (i) State what the K_c value indicates about the position of equilibrium and identify the major species in the mixture.
 - *K*_c value is <u>much smaller than 1</u> and indicates that the position of equilibrium lies largely to the <u>left</u>. Major species in the mixture is <u>ethanal</u>.

.....[1]

This question was well attempted. Most candidates were able to identify that the position of the equilibrium lies largely to the left due to the small K_c value, and thus correctly identify the major species to be ethanal. Common mistakes include stating that since K_c value is positive, therefore p.o.e lies to the right and the major species is ethanol.

(ii) Ethanal has an acidic hydrogen on its α -carbon. In the presence of strong bases, the hydrogen on its α -carbon is abstracted to form a resonance-stabilised enolate anion as shown below:



two resonance structures of the enolate anion

Resonance structures differ only in the position of their electrons.

Complete the diagram above by drawing in curly arrows to show movement of electrons to form the second resonance structure. [1]



two resonance structures of the enolate anion

This question was well attempted. Most candidates were able to show clearly the movement of electrons from the lone pair of electrons to the C-C bond, and the arrow from the C=O to the O atom.

(iii) Another pair of tautomers is shown below. Draw a fully labelled diagram to show why 4-hydroxy-3-penten-2-one is the dominant form at equilibrium.



2,4-pentanedione (15%)

4-hydroxy-3-penten-2-one (85%)

Intramolecular H-bonding δ+

The enol form of 4-hydroxy-3-penten-2-one at equilibrium is not only stabilized by electron delocalisation, but also by intramolecular H-bonding of the acidic hydrogen between the two oxygen atoms.

[1] [Total: 10]

This question was poorly attempted. Most candidates were unable to apply the concept that the presence of intramolecular hydrogen bonding can increase stability of anions and/or molecules. Due to the increase in stability, p.o.e. lies largely to the right, and percentage of 4-hydroxy-3-penten-2-one at eqm is 85%.

6 Tin metal, Sn, and its salts have many uses in daily life. The commonly used tin salts include tin(II) chloride, SnC*l*₂, and tin(IV) oxide, SnO₂.

19

Tin(IV) oxide, SnO₂, has long been used as a white colorant in ceramic glazes for earthenware and wall tiles. Synthetic tin(IV) oxide, SnO₂, is produced by burning tin metal, Sn, in air.

(a) Define the term standard enthalpy change of formation of SnO₂.

It refers to the enthalpy change of reaction when 1 mole of SnO₂ is formed from <u>solid tin and oxygen gas</u> (OR: from its constituent elements, <u>tin and oxygen in their most stable physical states</u>) under [1 <u>standard conditions of 298 K and 1 bar.</u>

Many candidates did not score here. There was obviously little effort put into memorizing definitions.

Common errors include:

- Instead of stating 'enthalpy change', many went on to state 'energy absorbed/released or energy required to form 1 mole of substance, without making reference to 1 mole of SnO₂ too'
- Note that there is still a difference between enthalpy change and energy change hence it is <u>not right to replace enthalpy change with energy change</u> in the definition.
- There are some candidates who could not list out the standard conditions of 298 K (or 25 °C) and 1 bar; often it was mixed up with standard temperature and pressure of 273 K and 1 bar.

Tin(IV) oxide is also formed when anhydrous tin(IV) chloride, $SnCl_4$, fumes in humid air as shown in the equation below:

 $SnCl_4(s) + 2H_2O(l) \rightarrow SnO_2(s) + 4HCl(g)$ $\Delta H^{\circ} = -463 \text{ kJ mol}^{-1}$

(b) Use the enthalpy change of reaction given above and the relevant standard enthalpy change of formation data from Table 6.1 to calculate the standard enthalpy change of the following conversion:

$HCl(g) \rightarrow HCl(aq)$	$\Delta H^{o} = x k$	J mol ⁻¹		
Table 6.1				
compound	ΔH_{f}^{Θ} / kJ mol ⁻¹			
SnO ₂ (s)	-578			
$H_2O(l)$	-286			
SnCl ₄ (s)	-510			
HC <i>l</i> (aq)	-167			



```
By Hess' Law,

-463 = +510 + 2(286) - 578 + 4(-167) - 4x

4x = +463 + 510 + 2(286) - 578 + 4(-167)

x = +74.8 \text{ kJ m}^{29/02/CJC} JC2 Preliminary Examination 2023
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Marks were often lost due to missing/wrong details in the energy cycles drawn. Presentation of working steps could have been clearer too. <u>Common errors include</u>:

- missing out multiplying $\triangle H_f$ (H₂O(I)) by 2 and/or $\triangle H_f$ (HCl(aq)) by 4
- missing out sign of x in the conversion of HCl (aq) $\rightarrow HCl$ (g)
- missing out + sign in the final answer for x
- missing state symbols in the energy cycles
- when formula $\Delta H_r = \sum \Delta H_f(products) \sum \Delta H_f(reactants)$ was used, presentation of working steps were often unclear, leaving marker to interpret candidates' intentions.
- (c) Tin(II) chloride solution, $SnCl_2(aq)$, acidified with small amount of hydrochloric acid, is used for tinplating of steel, during the production of tin cans. An electric potential is applied, and tin metal is formed at the cathode via electrolysis.
 - (i) Write the half-equation for the reaction that occurs at the cathode during electrolysis of tin(II) chloride.

Sn²⁺ + 2e⁻ → Sn

```
.....[1]
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While most candidates could score here, it was observed quite a handful of candidates wrongly represented tin as Ti or Tn instead of Sn as given in the question above.

Another common error involved the use of reversible arrows (\Rightarrow)instead of single arrow (\rightarrow) in the above reduction equation. Candidates need to learn to read and interpret question carefully.

(ii) In an experiment, a current of 2.50 A was passed through a tin(II) chloride solution for 2 hours.

Tin produced at the cathode is isolated and cleansed. It has a mass of 9.11g.

Calculate the mass of tin that would be deposited at the cathode, assuming that the process is 100% efficient. Hence, calculate the percentage efficiency of this electrolysis process.

Total charge, Q = I x t = 2.50 x 2 x 60 x 60 = $\frac{18\ 000\ C}{}$ Total amount of electrons transferred = $\frac{18000}{96500}$ = $\frac{0.1865\ mol}{96500}$ = $\frac{0.1865\ mol}{96500}$ = $\frac{0.1865\ mol}{96500}$ = $\frac{0.1865\ mol}{2}$ Since Sn = 2e⁻ Total amount of Sn deposited = $\frac{0.1865}{2}$ = $\frac{0.09325\ mol}{2}$ Expected mass of deposited Sn = 0.09325×118.7 = $\frac{11.07\ q}{}$

% efficiency = $\frac{9.11}{11.07}$ × 100% = $\underline{82.3}$ % The electrolysis process is $\underline{82.3\%}$ efficient. This is a typical electrolysis calculation question but a significant number of candidates either left it blank or could only score 1 mark by calculating total charge, Q (i.e. could only apply the formula Q = It). Some candidates forgot to convert time into seconds resulting in wrong value of Q. BOD was given for missing units, but no credit was given for wrong units. <u>Other common errors include</u>:

- Not dividing the amount of electrons by 2 to calculate amount of Sn deposited.
- Wrongly equating Q to-nF E°_{cell} (note it should be $\Delta G^{\circ} = -nFE^{\circ}_{cell}$)

(d)

Tin can form various compounds with organic molecules. Such tin-based organometallic compounds consist of Sn–C covalent bonds and often exhibit *cis-trans* isomerism, where the ligands around the Sn atom can be arranged in different spatial orientations.

Consider a series of tin(IV) organometallic compounds with the general formula SnX_2Y_2 , where X and Y are monodentate ligands. You may assume a square planar geometry around the tin atom.

In the *cis*-isomer, two similar ligands are positioned next to each other whereas in the *trans*-isomer, two similar ligands are positioned directly opposite each other.

(i) Draw the structural formula and label clearly the *cis* and *trans* isomers of a tin(IV) compound when $X = CH_3$ and $Y = OCH_2CH_3$.



This was supposed to be a simple application question, but many wrong answers given reflected a lack of careful reading and understanding of the question posed.

Common errors include:

- Including a charge in the isomers drawn (despite question stating organic <u>molecules</u> are formed).
- Drawing the isomers in terms of X and Y instead of the given ligands in the question.
- Missing out the dotted lines in the square planar structures or drawing solid lines instead (Note: solid lines denote covalent bonds)
- Wrongly drawing Sn-C bonds formed between the OCH₂CH₃ ligands and central Sn ion (instead of the correct Sn-O bonds)
- Not drawing Sn-C bonds clearly between -CH₃ ligands and central Sn ion.
- Drawing CH₃CH₂O ligand in the reverse direction as H₃CH₂CO despite being reminded before not to do so.

[2]

(ii) Suggest, with a reason, whether the *cis* or *trans* isomers are more stable.

<u>Trans isomers are more stable</u> than cis isomers because the <u>bulky</u> <u>ligands are further apart</u> from each other.

.....[1]

[Total: 12]

While many students could suggest the correct answer (trans isomers are more stable), not many could attribute it to correct reason of lower steric hindrance due to further proximity of the bulky ligands. Most often, the wrong reason given for the higher stability of trans isomers was "the lack of net dipole moment" or "trans isomers are non-polar".