- 1 (a) The elements of Period 3 form different oxides when reacted with oxygen.
 - (i) State and explain the variation in bonding within the oxides across Period 3.

The bonding within the oxide changes from **<u>ionic to covalent</u>** across the Period. [1]

Large difference in electronegativity between metallic atoms (e.g. Na/Mg/Al) and

oxygen results in the transfer of electrons and hence formation of ionic bonds.

Small difference in electronegativity between non-metallic atoms (e.g. Si/P/S) and

oxygen results in sharing of electrons and hence formation of covalent bonds. [1] [2]

Markers' Comments

 Many candidates misinterpreted the question and gave the structures (or even the acid-base nature) of the Period 3 oxides instead of the bonding. Even so, the structures of the oxides were also incorrect e.g. giant metallic structure for the metallic oxides or simple molecular structure for Al₂O₃. This is a book work question and candidates are advised to revise and distinguish accurately between the different types of structures and chemical bonding.

• Many candidates were also unable to explain why the type of bonding changes across the Period.

Compounds **A** and **B** are oxides of Period 3 elements which exist in the solid state at room temperature.

When excess water is added to a sample of **A**, the solid dissolves completely and an acidic solution is obtained.

However, when excess water is added to **B**, the solid remains insoluble and a neutral solution is obtained.

(ii) Identify compound **A**.

P4O10 [1]
Markers' Comments
SO3 is a colourless liquid that fumes in air at r.t.p. and hence is not accepted as the identity of compound A.
Many candidates struggled to give the correct formula of phosphorus (V) oxide e.g. PO4, or suggested the identity of the element rather than the compound (oxide).

(iii) Suggest two possible identities of compound **B** and describe how the identity of compound **B** can be confirmed using the acid-base behaviour of Period 3 oxides.

Include all relevant observations and an equation in your answer.

Possible identities of B: <u>aluminium oxide / AI_2O_3 and silicon dioxide / SiO_2 </u>. [1] <u>Add HC/(aq)</u> (or H₂SO₄(aq)) to a sample of compound B. If it is <u>soluble / dissolves</u> in HC/(aq), B is <u>AI₂O₃</u>. If it is <u>insoluble</u>, B is <u>SiO₂</u>. [1] for test, observation $AI_2O_3 + 6HCI \rightarrow 2A/CI_3 + 3H_2O$ OR $AI_2O_3 + 3H_2SO_4 \rightarrow AI_2(SO_4)_3 + 3H_2O$ [1] for equation OR <u>Add NaOH(aq)</u> to a sample of compound B. If it is <u>soluble / dissolves in NaOH(aq)</u>, B is <u>AI₂O₃</u>. If it is <u>insoluble</u>, B is <u>SiO₂</u> [1] for test,

observation; $Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2NaAl(OH)_4$ [1] for equation



• It should be noted that SiO₂ is an acidic oxide, but it can only react with hot and concentrated NaOH.

(b) (i) Complete the variation in the melting points of Period 3 oxides.



- (ii) Explain the variation in melting points from Na_2O to Al_2O_3 .
 - Ionic charge: Mg²⁺ > Na⁺ and Ionic radius: Mg²⁺ < Na⁺

Lattice energy (L.E.) $\propto \left| \frac{q_+ \cdot q_-}{r_+ r_-} \right|$, L.E. magnitude / ionic bond strength: MgO > Na₂O [1]

Energy required to break ionic bond: MgO > Na₂O, hence melting point: MgO > Na₂O

• <u>Charge density $\left(\frac{q_{+}}{r}\right)$: $Al^{3+} > Mg^{2+}$, Al^{3+} polarises O^{2-} electron cloud to a larger extent.</u>

<u>Al₂O₃ has partial covalent character</u>, hence melting point: Al₂O₃ < MgO [1] [2]

Markers' Comments

- For candidates who revised their Chemical Bonding and Periodic Table concepts thoroughly, they generally did well for this part.
- However, a sizeable number of candidates were still unable to explain the variation in melting points accurately, reflecting some gaps in conceptual understanding. One common error was stating that Mg²⁺ has a higher charge density than Na⁺ and hence MgO has a higher magnitude of lattice energy. They then used the same charge density reasoning to explain why Al₂O₃ has a partial covalent character and hence has weaker ionic bonds as compared to MgO, failing to see that they are contradicting themselves.
- It was concerning to see a sizeable number of candidates going on to address the melting point trends from SiO₂ to SO₃ when the question did not even ask for it. From several parts of Question 1, it is clear that these candidates need to work and improve on their question reading.
- (c) Sodium azide, NaN₃, is commonly used in car airbags to produce nitrogen gas upon collisions.
 - (i) Draw a 'dot-and-cross' diagram for the azide ion, N_3^- , showing all of the outer shell electrons.



Markers' Comments

- Common errors were not ensuring that each N atom had just 8 electrons around it. Many candidates had 10 or 12 electrons around the central N atom. N cannot expand octet structure due to lack of energetically accessible and vacant 3d orbitals.
- The additional electron from the negative charge should not go to the central N atom as the central atom is generally the least electronegative and hence will be least likely to accept the additional electron. Even though they are all N atoms in this case, but we will still follow the rule.
 - (ii) State and explain, with reference to the Valence Shell Electron Pair Repulsion theory, the shape and bond angle around the central atom of N_3^{-} .

There are **2 bond pairs and 0 lone pair** around the central **N atom**. **[1] allow ECF**

To minimise repulsion and maximise stability, the shape around the central N atom is

[1]

linear. As there are equal bond pair-bond pair repulsions, the bond angle is 180°.

Markers' Comments		
•	It has been repeatedly emphasised that regardless of the bond order (single, double, or triple bond), it is regarded as ONE bond pair. However, there are candidates still making the same mistake till this point.	. [2]
•	Given that there are zero lone pairs, it is unnecessary to mention about lone pair-lone pair and lone pair- bond pair repulsions.	

When a car is involved in a collision, sensors send an electric signal to the container inside the airbag where the sodium azide is stored. This triggers the decomposition of sodium azide and inflates the airbag with nitrogen gas to nearly its full volume in a very short period to protect the driver, after which the airbag slowly deflates. The typical volume of a fully inflated airbag is 60 dm³.

The decomposition of sodium azide is shown in reaction 1.

reaction 1
$$2NaN_3(s) \rightarrow 2Na(s) + 3N_2(g)$$

As the sodium metal by-product of reaction 1 is highly reactive, airbag manufacturers mix sodium azide with potassium nitrate to remove the sodium by-product as shown in reaction 2.

reaction 2 $2KNO_3(s) + 10Na(s) \rightarrow 5Na_2O(s) + K_2O(s) + N_2(g)$

This also produces additional nitrogen gas which contributes to the airbag.

(iii) Given that an airbag contains 100 g of sodium azide, calculate the volume of nitrogen gas that can be produced at room temperature and pressure.

Amount of NaN₃ =
$$\frac{100}{23.0 + 3(14.0)}$$
 = **1.5385 mol [1]**

N₂ from reaction 1: 2NaN₃ = $3N_2 \Rightarrow NaN_3 = \frac{3}{2}N_2$

Amount of N₂ produced from reaction 1 = 1.5385 $\times \frac{3}{2}$ = **2.3077 mol**

N₂ from reaction 2: 10NaN₃ = 10Na = N₂
$$\Rightarrow$$
 NaN₃ = Na = $\frac{1}{10}$ N₂

Amount of N₂ produced from reaction $2 = \frac{1.5385}{10} = 0.15385$ mol

Total amount of N_2 produced from reaction 1 & 2 = 2.3077 + 0.15385 = 2.4615 mol [1]

At r.t.p., molar volume of gas = 24.0 dm³ mol⁻¹ **Volume of N**₂ produced at r.t.p. = 2.4615 × **24.0** = 59.1 dm^3 (to 3 s.f.) [1] OR pV = nRT2.4615 × 9.21×202 At r.t.p., temperature = 20 °C (293 K),

Volume of N₂ produced at r.t.p. = $\frac{2.4615 \times 8.31 \times 293}{101\ 325}$ = $\underline{0.0591\ m^3}$ or $\underline{59.1\ dm^3}$ (to 3 s.f.) [1]

[3]

Markers' Comments

- Candidates who read the question carefully and extracted relevant information were generally able to score for this part of the question.
- The common error was calculating the volume of N₂ from just one of the reactions without realising that reactions 1 and 2 both produce N₂.



- 2 Wastewater comprises of various organic matter and is treated to remove all harmful contaminants before being discharged into water bodies.
 - (a) Tonalide is an organic compound commonly found in sewage sludge produced by wastewater treatment plants.

In an experiment, a sample of tonalide was combusted underneath a container containing 170 g of water. It was found that the temperature of the water increased by 55 °C after 0.050 mol of tonalide had been combusted.

(i) Calculate the enthalpy change of combustion of tonalide, ΔH_c , in kJ mol⁻¹. Assume the container absorbed negligible heat from the combustion.

```
Heat absorbed by water = mc\Delta T
=170 × 4.18 × 55
= 39083 J [1]
\Delta H_c = -\frac{39083}{0.0500}
= - 78166 J mol<sup>-1</sup>
= <u>- 782 kJ mol<sup>-1</sup> (3 s.f.)</u> [1] with negative sign
Markers' Comments
```

• Some candidates quoted the wrong value for specific heat capacity of water, c. This value should be taken from the Data Booklet since it was not specified in the question.

[2]

(ii) The literature value for enthalpy change of combustion of tonalide is -865 kJ mol⁻¹. Compare this value to the one you have calculated in (a)(i) and suggest a reason for the discrepancy.

 ΔH_c in (i) is <u>less exothermic</u> than the literature (actual) value because <u>heat was lost to</u> <u>the surroundings</u>. [1]

Markers' Comments Many candidates did not answer the first part of the question, which was to compare the literature value with their answer in (c)(i). When comparing enthalpy change *with negative values*, candidates are reminded to use terms like more/ less exothermic or larger/ smaller in magnitude. Ambiguous terms (e.g., lesser, smaller, greater, larger) would not be accepted.

(b) Tonalide has molecular formula $C_x H_y O$.

0.3 dm³ of gaseous tonalide was combusted in excess oxygen in an enclosed vessel at 400 °C. The gas mixture obtained at the end of combustion was then treated by:

- passing it through a dehydrating agent, resulting in a volume contraction of 3.9 dm³; followed by
- bubbling the remaining gas mixture through aqueous sodium hydroxide, with a further contraction of 5.4 dm³.

Determine the values of *x* and *y* in the molecular formula of tonalide. Show your working clearly.

Complete combustion of $C_x H_y O(g)$ will form $H_2 O(g)$ and $CO_2(g)$ at 400°C.

Volume of $C_x H_y O(g) = 0.3 \text{ dm}^3$ (*limiting reagent*)

Volume of $H_2O(g) = 3.9 \text{ dm}^3$ (from dehydration contraction)

Volume of $CO_2(g) = 5.4 \text{ dm}^3$ (from contraction upon passing through NaOH(aq) that absorbed the acidic CO_2 gas)

Given that temperature and pressure is kept constant,

by Avogadro's Law, volume ratio = mole ratio

Since $C_x H_y O \equiv x CO_2$ and

$$\Rightarrow \frac{\text{Volume of CO}_2}{\text{Volume of C}_x\text{H}_y\text{O}} = \frac{\text{Amount of CO}_2}{\text{Amount of C}_x\text{H}_y\text{O}} = \frac{x}{1}$$
$$\Rightarrow \frac{5.4}{0.3} = \frac{x}{1} \qquad \therefore x = \underline{18} \qquad [1]$$

Since
$$C_x H_y O \equiv \frac{y}{2} H_2 O$$
 and

$$\Rightarrow \frac{\text{Volume of H}_2\text{O}}{\text{Volume of C}_x\text{H}_y\text{O}} = \frac{\text{Amount of H}_2\text{O}}{\text{Amount of C}_x\text{H}_y\text{O}} = \frac{y}{2}$$
$$\Rightarrow \frac{3.9}{0.3} = \frac{y}{2} \qquad \therefore y = \underline{26} \qquad [1]$$

Molecular formula of tonalide is thus C₁₈H₂₆O

Markers' Comments

- As all the gases are measured at the same temperature and pressure, volume ratio \equiv mole ratio.
- As such, attempts should <u>not</u> be made to calculate the amount of the gas (by dividing the volume over 24 dm³ mol⁻¹ or 22.7 dm³ mol⁻¹) because the reaction did not occur at r.t.p (20 °C) nor s.t.p (0 °C).
- Attempt to compare volume ratio of CO₂ and H₂O directly is <u>not</u> accepted because this approach is used for finding empirical formula of tonalide.

[2]

(c) Ammonia is also another contaminant commonly found in agricultural wastewater. It is harmful to the aquatic ecosystems if present in significant quantity.

When ammonia is completely combusted, it produces nitrogen gas and water only.

- (i) Define, with aid of an equation, the standard enthalpy change of combustion of ammonia, NH₃(g).
 Standard enthalpy change of combustion of ammonia is the <u>energy released</u> when
 <u>1 mol of ammonia</u> is completely <u>burnt in excess oxygen</u> under <u>standard conditions</u>
 of 298 K and 1 bar. [1] NH₃(g) + ³/₄O₂(g) → ¹/₂N₂(g) + ³/₂H₂O(I) [1] with state symbols [2]
 - Markers' Comments
 Candidates are highly encouraged to do their book work properly. Common mistakes include

 missing key words (i.e., energy *released*, burn in *excess* oxygen)
 missing state symbols for equation (take note that H₂O is a liquid at standard condition)
 - missing state symbols for equation (take note that n₂O is a liquid at standard
 - balancing equation with <u>1 mol</u> of NH₃
- (ii) Using appropriate data from the *Data Booklet*, calculate the enthalpy change of combustion of ammonia.

$$\underset{H}{\stackrel{N}{\longrightarrow}}_{H} (g) + \frac{3}{4} \xrightarrow{O} (g) \longrightarrow \frac{1}{2} \xrightarrow{N} (g) + \frac{3}{2} \xrightarrow{O}_{H} (g)$$

(*BE of Reactants – BE of Products*) *BERP* $\Delta H_{\rm r} = \Sigma BE(\text{bonds broken}) - \Sigma BE(\text{bonds formed})$ = $[3 \times BE(N-H) + \frac{3}{4} \times BE(O=O)] - [\frac{1}{2} \times BE(N=N) + \frac{3}{2} \times 2 \times BE(O-H)]$ = $[3(390) + \frac{3}{4}(496)] - [\frac{1}{2}(944) + 3(460)]$ [1] for correct BE values quoted = -310 kJ mol^{-1} [1]

Markers' Comments

• Some candidates struggled with quoting the correct bond energy as the wrong bonds are quoted. Some candidates also failed to account for the correct number of bonds broken / formed.

[2]

2022 H2 Chem Prelim P2 (Ans)

(iii) With the advancement in combustion technology, ammonia has been studied as a potential source for clean energy. Presently however, oxides of nitrogen are often produced as by-products of the reaction.

Suggest one advantage and one disadvantage of using ammonia as a fuel.

Advantage Any one of the following (or other feasible advantage) [1]

- It does not generate greenhouse gases (such as CO₂) that contributes to global warming.
- It is widely available.

Disadvantage Any one of the following (or other feasible disadvantage) [1]

- It generates nitrogen oxide during combustion that causes air pollution (or acid rain).
- It is <u>difficult to burn</u> (or <u>does not readily ignite</u>).
 Markers' Comments

 Many candidates did not recognise that oxides of nitrogen would be produce alongside with N₂ and H₂O. Hence, ammonia is <u>not</u> a source for clean energy. This is further proven when oxides of nitrogen are identified as pollutants (causing harm to human and environment).
- (iv) The process of nitrification is often used to convert ammonia into a less toxic nitrate.

$$NH_3(aq) + 2O_2(g) \rightarrow NO_3^-(aq) + H^+(aq) + H_2O(I) \Delta H_1$$

Using the information below, construct a suitable energy cycle to determine the enthalpy change of nitrification reaction, ΔH_r .

$$\begin{aligned} \mathsf{NH}_3(\mathsf{aq}) + \mathsf{O}_2(\mathsf{g}) + \mathsf{H}_2(\mathsf{g}) &\rightarrow \mathsf{NH}_2\mathsf{OH}(\mathsf{aq}) + \mathsf{H}_2\mathsf{O}(\mathsf{l}) & \Delta \mathcal{H}_1 = -284 \text{ kJ mol}^{-1} \\ \mathsf{NH}_2\mathsf{OH}(\mathsf{aq}) + \mathsf{H}_2\mathsf{O}(\mathsf{l}) + \frac{1}{2}\mathsf{O}_2(\mathsf{g}) &\rightarrow \mathsf{NO}_3^-(\mathsf{aq}) + 2\mathsf{H}_2(\mathsf{g}) + \mathsf{H}^+(\mathsf{aq}) & \Delta \mathcal{H}_2 = +1653 \text{ kJ mol}^{-1} \\ 2\mathsf{H}_2\mathsf{O}(\mathsf{l}) &\rightarrow 2\mathsf{H}_2(\mathsf{g}) + \mathsf{O}_2(\mathsf{g}) & \Delta \mathcal{H}_3 = +572 \text{ kJ mol}^{-1} \\ \mathsf{H}_2(\mathsf{g}) + \mathsf{NH}_3(\mathsf{aq}) + 2\mathsf{O}_2(\mathsf{g}) & \Delta \mathcal{H}_r & \mathsf{NO}_3^-(\mathsf{aq}) + \mathsf{H}^+(\mathsf{aq}) + \mathsf{H}_2\mathsf{O}(\mathsf{l}) + \mathsf{H}_2(\mathsf{g}) \\ \Delta \mathcal{H}_1 & \bigvee & \mathsf{NH}_2\mathsf{OH}(\mathsf{aq}) + \mathsf{H}_2\mathsf{O}(\mathsf{l}) + \mathsf{O}_2(\mathsf{g}) & \mathcal{I}_2 \\ \Delta \mathcal{H}_2 & \bigvee & \mathsf{I}_2 \\ \mathsf{NO}_3^-(\mathsf{aq}) + 2\mathsf{H}_2(\mathsf{g}) + \mathsf{H}^+(\mathsf{aq}) + \frac{1}{2}\mathsf{O}_2(\mathsf{g}) \\ \end{aligned}$$

$$\begin{aligned} \mathsf{I1} \text{ for partial cycle (incorporating either \Delta \mathsf{H}_1 \text{ or } \frac{1}{2} \Delta \mathsf{H}_3) \\ \mathsf{I2} \text{ for correct cycle (ignore state symbols)} \\ \mathsf{By Hess Law}, & \Delta \mathcal{H}_r + \frac{1}{2} \Delta \mathcal{H}_3 = \Delta \mathcal{H}_1 + \Delta \mathcal{H}_2 \\ \mathsf{OR} & \Delta \mathcal{H}_r &= \Delta \mathcal{H}_1 + \Delta \mathcal{H}_2 - \frac{1}{2} \Delta \mathcal{H}_3 \\ &= -284 + 1653 - \frac{1}{2} \text{ (572)} \\ &= \pm 1083 \text{ kJ mol}^{-1} \text{ OR} \\ &\pm 1080 \text{ kJ mol}^{-1} [\mathsf{1}] \\ \end{aligned}$$

3 (a) Halogenoalkanes are important intermediates in organic chemistry. Fig. 3.1 shows the conversion of an alcohol to nitrogen-containing compounds, **F** and **G**, involving a halogenoalkane.





(i) Draw the **displayed** formula of **C**.



(ii) Draw the structures of **D** and **E**.



(iii) State the reagents and conditions for steps II and III.

step II	alcoholic KCN, heat [1]					
step III	dilute HC <i>I</i> , heat [1]					
	[2]					
 Markers' Con Many candid reminded to Candidates of score any magnetic 	International American Strategy and Strategy					

(iv) Describe and explain how the basicity of G would compare to that of F.

G (amide) is less basic than F (amine). [1]

For G, the lone electron pair on N atom is delocalised with the adjacent C=O,

reducing the electron density on the N atom. Hence, N atom is less available to

accept a proton OR form a dative bond with H⁺. [1]

Markers' Comments

- The basicity of nitrogen-containing compound is an important concept. Many candidates were unable to provide a clear explanation and did not use exact key phrases. Candidates are expected to do their bookwork well.
- (b) The hydrolysis of 2-bromo-2-methylpropane takes place as follows.

 $(CH_3)_3CBr$ + $H_2O \rightarrow (CH_3)_3COH$ + H^+ + Br^-

An experiment to investigate the kinetics of the reaction was carried out. The results were consistent with the reaction being overall first order.

- (i) Suggest a suitable experimental technique for studying the rate of this reaction.
 <u>Titrating</u> reaction sample with NaOH (aq) [1], accept other logical answers
 [1]
- (ii) Write the rate equation for the reaction and state the units of the rate constant.

rate equation rate = k[(CH ₃) ₃ CBr]	
units of rate constant	[1] for both
	[1]

(iii) Draw the structure of the intermediate formed in the reaction.



[1]

Markers' Comments

- Many candidates failed to realise that 'reaction being overall first order' meant that order of reaction w.r.t. halogenoalkane (reactant) is 1 (and hence zero w.r.t. to water). Hence the mechanism is S_N1 and intermediate is carbocation.
- A large percentage of the cohort is unable to write the correct rate equation and units for the overall first order reaction. Common mistakes were to omit "rate =" and to write rate equation in terms of [product].

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- (c) Carbocations frequently undergo structural changes, called rearrangements, to form more stable ions.
 - (i) Explain why a tertiary carbocation is more stable than a secondary carbocation.



Fig. 3.2 shows two types of carbocation rearrangements: a hydride shift and a methyl shift.





Once rearranged, the resultant carbocation will react further to form a final product (rearranged substitution product) which has a different alkyl skeleton from the starting compound.

An example of a reaction with rearrangement is the S_N1 reaction of 2-bromo-3-methylbutane in boiling ethanol as shown in Fig. 3.3.



Fig. 3.3

(ii) Complete the four-step mechanism involving a hydride shift for the formation of 2-ethoxy-2-methylbutane (rearranged substitution product) as shown in Fig. 3.3.

Include all the necessary charges, dipoles, lone pairs and curly arrows.

Step 1: Ionisation of 2-bromo-3-methylbutane gives a carbocation.



2-bromo-3-methylbutane

[1]





Step 3: CH₃CH₂OH attacks the rearranged carbocation.



Step 4: Deprotonation gives 2-ethoxy-2-methylbutane.



	,
Markers' Comments	3]
 Many candidates did not include dipoles (δ+ and δ−) across the C−Br bond or Br[−] in Step 1. 	
 Step 3 and step 4 proved challenging for students. 	
• Candidates are reminded to write balanced equations in their answers and to start the curly arrows at t	he
bond or lone pair of electrons.	

(d) When 1-bromo-2,2-dimethylpropane is boiled in ethanol, it gives only a rearranged substitution product, **H**, as shown in Fig. 3.4.



```
Fig. 3.4
```

(i) Suggest why (CH₃)₃CCH₂OCH₂CH₃ is not formed.

1° carbocation is unstable and will not be formed. [1] OR 1° carbocation formed will immediately undergo methyl shift to form the more stable 3° carbocation. [1] or (simultaneous shifting of CH₃ and leaving of bromine occurs)

(ii) Suggest the structure of the rearranged substitution product H.



- 4 Methanoic acid, HCOOH, is the simplest carboxylic acid. It occurs naturally in the stings of certain ants.
 - (a) When an ant bites, it injects a solution containing 58% by volume of methanoic acid. A typical ant may inject around 6.0×10^{-3} cm³ of this solution.
 - (i) When an ant bites a person, it typically injects 80% of its methanoic acid and keeps the rest as reserve.

Calculate the volume of pure methanoic acid found in an ant.

Volume of methanoic acid = $6.0 \times 10^{-3} \times 0.58 \times \frac{100}{100}$

= 4.35 × 10⁻³ cm³ [1]



(iii) **K** and **L** are constitutional isomers of **J** (HCOOCH₂CH₃). Table 4.1 shows some information about the isomers.

isomer boiling point / ° C		reaction with Na ₂ CO ₃ (s) at r.t.p.			
J	54.0	no effervescence			
K 57.1		no effervescence			
L 141.2		gas evolved gave white ppt with limewater			

Table 4.1

Use the information in Table 4.1 to suggest the structural formulae of K and L and explain why L has a higher boiling point than J or K.

K CH₃COOCH₃ OR CH₃OCOCH₃

[1] for both structures

L CH₃CH₂COOH (do not accept alcohols)

<u>More energy</u> is required to overcome strong <u>hydrogen bonding</u> between L molecules than <u>permanent dipole-permanent dipole attractions/ instantaneous</u> [2]

dipole-induced dipole between J or K molecules. [1]

Markers' Comments

- Candidates need to deduce that L is carboxylic acid from the reaction with Na₂CO₃ and K and L are isomers of J (same molecular formula. K and J are esters and will not react with Na₂CO₃.
- Errors include not indicating the type of intermolecular forces of attraction to account for the lower boiling point for J and K (they do not have hydrogen bonding) or indicating wrongly the type of attraction for L.

- (c) In the presence of hydroxyl radicals (•OH), methanoic acid can decompose into carbon dioxide and water. The mechanism of this reaction is thought to involve three steps:
 - step I: Hydroxyl radical radicals are generated from H₂O₂ through photocatalysis via homolytic fission.
 - step II: The hydroxyl radical abstracts a hydrogen from a methanoic acid to form an intermediate and water.
 - step III: Another hydroxyl radical abstracts a hydrogen from the intermediate and forms carbon dioxide gas and water.
 - (i) Explain what is meant by the term *homolytic fission*.

It is the breaking of a covalent bond between 2 atoms such that each atom retains

only one of the shared electrons resulting in the formation of free radicals. [1]

Markers' Comments
Candidates need to define homolytic – equal sharing or distribution of electrons/ each atom only retains one of the shared electrons.

- Candidates need to define fission breaking of a covalent bond.
- (ii) Complete Fig. 4.1 to suggest the mechanism for steps I to III.

Show the structural formulae of the intermediates, the movement of unpaired electron by using curly arrow (\frown) and indicate any unpaired electron with a dot (•).





[1] for step 1 intermediate and curly arrows [1] for step 2 intermediate and curly arrows

[2]

(d) Methanoic acid has, in recent years, gained attention as a potential fuel for generating electricity. The Direct Formic Acid Fuel Cell (DFAFC) has been developed and is used to power vehicles, including buses. Fig. 4.2 shows the setup of a DFAFC.



In the DFAFC, methanoic acid is oxidised at the anode while oxygen is reduced at the cathode. The E_{cell}^{e} value for the cell is +1.47 V.

(i) Write an equation for the reaction occurring at the anode.

Anode: $HCOOH \rightarrow CO_2 + 2H^+ + 2e^-$ [1] [1]

(ii) Hence or otherwise, construct a balanced equation for the reduction of oxygen by one mole of methanoic acid.

```
HCOOH + \frac{1}{2}O_2 \rightarrow CO_2 + H<sub>2</sub>O [1], do not award if HCOOH is not of 1 mole [1]
```

Markers' Comments

- Common errors include not emphasizing only ONE mole of methanoic acid and not realising the balanced equation is formed through the 2 half-equations.
 Reduction: O₂(g) + 4H+(aq) + 4e⁻ → 2H₂O
 Oxidation: HCOOH □ → CO₂ + 2H+ + 2e⁻
- (iii) Using appropriate data from the *Data Booklet*, determine a value for the standard electrode potential, E° , of the CO₂(g)/HCOOH(aq) half-cell.

<u>L</u>______

 $E^{\mathfrak{p}}_{cell} = E^{\mathfrak{p}}_{red} - E^{\mathfrak{p}}_{oxd} \qquad (E^{\mathfrak{p}}_{cell} = +1.47 \text{ V}, E^{\mathfrak{p}}_{red} = E^{\mathfrak{p}}_{O_2/H_2O} = +1.23 \text{ V}, E^{\mathfrak{p}}_{oxd} = E^{\mathfrak{p}}_{CO_2/HCOOH})$ 1.47 = 1.23 - $E^{\mathfrak{p}}_{CO_2/HCOOH}$ $E^{\mathfrak{p}}_{CO_2/HCOOH} = -0.24 \text{ V} [1]$ (iv) Show that ΔG° at 298 K for the equation you have written in (d)(ii) is -284 kJ mol⁻¹.

 $\Delta G^{\circ} = - nFE^{\circ}$ = <u>-2 × 9.65 × 10⁵ × (+1.47)</u> [1] = -2.84 × 10⁵ J mol⁻¹ = -284 kJ mol⁻¹ (shown)

[1]
 (v) Based on the setup in Fig. 4.2, suggest a reason to explain why the actual E[⊕]_{cell} value measured in a DFAFC may be lower than +1.47 V.

```
O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l) --- (1)
The <u>pressure of the O<sub>2</sub> in the air supplied may not be at 1 bar</u> [1]. By Le Chatelier's
Principle, the <u>equilibrium position</u> of (1) <u>shifts left</u> to <u>increase the pressure of O<sub>2</sub></u>,
hence <u>E<sub>red</sub> is less positive</u> [1] and E<sub>cell</sub> becomes lower than expected. [2]
```

Markers' Comments

- Candidates need to be careful to consider the correct reference in determining the effects to E_{red} or E_{oxid.}
- A significant number of candidates explained using the oxidation half-equation not realising that the equation
 was swapped around when considering the redox potentials (E_{oxid}).

Oxidation: HCOOH $\square \rightarrow CO_2 + 2H + 2e^ CO_2 + 2H^+ + 2e^- \rightleftharpoons HCOOH (E_{oxid}) \square$ $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O (E_{red}) \square$

 [H⁺] factor was not accepted as a reason because the changes to [H⁺] for E_{oxid} and E_{red} will counterbalance, negating any changes.

[Total: 15]



5 (a) Ethylenediamine has the structural formula NH₂CH₂CH₂NH₂.

When an aqueous solution of ethylenediamine is titrated with HC*l*(aq), two successive acidbase reactions take place.

A 0.10 mol dm⁻³ solution of ethylenediamine has a pH of 11.5. When 30 cm³ of 0.10 mol dm⁻³ HC*l*(aq) is added to 10 cm³ of a 0.10 mol dm⁻³ solution of ethylenediamine, the final pH is 1.6.

Fig. 5.1 shows the pH changes that occur during this addition of HCl(aq).





Table 5.1 shows some indicators used in acid-base titrations.

Table	5.1
-------	-----

indicator		colour in				
indicator	prirange	acid	end-point	base		
malachite green	0.2 – 1.8	yellow	green	blue-green		
methyl orange	3.2 - 4.4	red	orange	yellow		
bromocresol green	3.8 – 5.4	yellow	green	blue		
bromothymol blue	6.0 - 7.6	yellow	green	blue		
phenol red	6.4 - 8.0	yellow	orange	red		
phenolphthalein	8.2 – 10.0	colourless	pale pink	pink		
alizarin yellow	10.1 – 13.0	yellow	orange	red		

(i) Write equations for the two acid-base reactions when ethylenediamine is titrated with HCl.

$NH_2CH_2CH_2NH_2 + HCl \rightarrow NH_2CH_2CH_2NH_3^+Cl^-$	[1] for both, accept		
$NH_2CH_2CH_2NH_3^+Cl^- + HCl \to Cl^- + NH_3CH_2CH_2NH_3^+Cl^-$	ionic eqns; ignore +/- on organic salt [1]		
 Markers' Comments Many candidates were surprisingly unable to recognise the successive a the amines (a base) with HCl (acid) to form the salt, and the next neutral 	cid-base reactions between one of isation with the other amine group.		

over the equivalence point in the titration. [1]	٢1	1
	Ľ	1

OR pH of equivalence point is within the pH range of the indicator

Markers' Comments While many candidates were awarded credit for this part, many answers showed a poor conceptual grasp of the operation of an indicator in terms of its pH range lying within the region of rapid pH change over the equivalence point. Candidates should also note that equivalence point and equivalence pH does not necessarily equate to endpoint of a titration when using the terms.

(b) Glutamic acid and proline are naturally occurring amino acids shown in Table 5.2.

Table 5.2

	glutamic acid	proline		
amino acid	NH ₂ CO ₂ H	CO ₂ H		
isoelectric point	3.1	6.5		

The isoelectric point of an amino acid is the pH at which it exists as a zwitterion.

(i) Explain what is meant by the term *zwitterion*.

It is an <u>electrically neutral dipolar ion [1]</u> (arising from internal acid-base reaction

between the acidic carboxylic acid group and basic amine group of the amino acid) [1]

Markers' Comments

• Answers which were vague in terms of highlighting that the ion is electrically neutral (arising from a positive and negative charge – ie. dipolar) were not awarded credit.

(ii) A mixture of amino acids may be separated using electrophoresis. A typical practical set up is shown in Fig. 5.2.



A mixture containing glutamic acid and proline was analysed by electrophoresis using a buffer solution at pH 4.0.

Suggest the structures of the amino acid species at the positive and negative ends of the filter paper strip after the electrophoresis was carried out for a period of time.



with the isoelectric point which indicates the presence of a zwitterion, candidates were required to infer the species of the two amino acids in the buffer solution and decide which species would be attracted to the positive / negative end of the strip based on the overall net charge.

(c) The weak acid ACES, C₄H₁₀N₂O₄S, together with its sodium salt, C₄H₉N₂O₄SNa, can be used to make a buffer solution for electrophoresis experiments.

You may use HA and Na⁺A⁻ to represent ACES and its sodium salt.

(i) Write an ionic equation to show how the buffer solution maintains a fairly constant pH when a small amount of acid is added to it.

$$A^{-} + H^{+} \rightarrow HA \quad [1] \qquad [1]$$

A buffer solution is prepared by the following steps.

_ _ _

- 3.50 g of Na⁺A⁻ is dissolved in 100 cm³ of distilled water. •
- 50.0 cm³ of 0.200 mol dm⁻³ dilute HC*l* is added to the solution.
- The resulting mixture is transferred to a 250.0 cm³ volumetric flask, and the solution made • up to the mark.

The p*K*_a of HA is 6.88 at 298 K.

Calculate the pH of the buffer solution formed at 298 K. Show your working. (ii)

[*M*⁺ of Na⁺A⁻ is 204.1]

	HC <i>l</i>	+	Na⁺A⁻	\rightarrow	HA	+	NaCl
Initial amount / mol	$0.200 \times \frac{50}{1000} = 0.01000$	<u>,</u>	3.50 204.1 = 0.01715	both [1]	0		0
Change in amount / mol	-0.01000		-0.01000		+0.01000		+0.01000
Final amount / mol	0		0.01715 – 0.0 = 0.007148 [01000 1]	0.01000		0.01000
$pH = pK_a + log(\frac{[Na^+A^-]}{[HA]})$ = 6.88 + log($\frac{0.007148 \div \frac{250}{1000}}{0.0100 \div \frac{250}{1000}}$) = 6.73 [1] OR K_a = 10^{-6.88} = 1.32 × 10^{-7} mol dm^{-3} [H^+] = (1.32 × 10^{-7}) × 0.01 / 0.0071(48) = 1.86 × 10^{-7} (1.8465 × 10^{-7}) mol dm^{-3} pH = -log(1.86 × 10^{-7}) = 6.73 [1]							
 Markers' Comments This calculation proved t HCl (strong acid) was lin would generate the resu salt and of the strong a amount or concentration 	o be challenging niting and would Itant buffer; con acid and applyin of the remainin	g for majo I react with mmon error ng it to th ng conjug	rity of candidates wh h the conjugate base ors included incorrect the buffer equation o ate base (salt) and t	no did not anal e to generate t ctly determinin r neglecting t he weak acid	yse the questio he weak acid; t g the concentra o determine th generated.	n carefi his mix ation of e resul	ully. ture the tant

• Some candidates did not made use of the Mr information of the salt provided but instead incorrectly determined the molar mass of the salt. _____

[3]

(d) Edds^{4–} and edta^{4–} are polydentate ligands which can be derived from ethylenediamine. These ligands form octahedral complexes with Fe³⁺(aq).



The formulae of the complexes are [Fe(edds)]⁻ and [Fe(edta)]⁻ respectively.

(i) On the diagram of edds⁴⁻, circle each atom that forms a bond to the Fe³⁺ ion in [Fe(edds)]⁻.

Markers' Comments

- Many candidates did not appreciate that for the octahedral complexes, the coordination number is 6, and thus with the given complex formula of [Fe(edds)]⁻, only 1 ligand of edds⁴⁻ is present and the ligand should be hexadentate.
- Common mistake was for candidates to neglect the understanding of the presence of a lone pair of electrons on N of the each of the amine segment that is able to contribute to the dative / coordinate bonding in the complex.
- (ii) [Fe(edds)]⁻ and [Fe(edta)]⁻ have different colours.

Explain why the two complexes differ in colour.

The two **ligands split the d orbitals to different extent** / **d-orbital splitting** occurs to different extent, resulting in the <u>d-d energy gap / ΔE being different</u> [1]. The complexes <u>absorb different wavelengths</u> of light from the visible spectrum for d-d transition [1],

hence different wavelengths of light not absorbed are observed.

	[2]
 Markers' Comments Some candidates did not explain why the complexes differed in colour, but instead provided the explanation account for colour of complexes. 	n to

2022 H2 Chem Prelim P2 (Ans)

(iii) Table 5.3 shows the values for the stability constants, K_{stab} , of both complexes for the equilibrium below when L(aq) representing the ligand edds^{4–}(aq) or edta^{4–}(aq) is added to Fe³⁺(aq).

equilibrium 1 $[Fe(H_2O)_6]^{3+}(aq) + L(aq) \rightleftharpoons [Fe(L)]^-(aq) + 6H_2O(I)$

complex	$K_{\rm stab}$ / mol ⁻¹ dm ³
[Fe(edds)] ⁻	3.98×10^{20}
[Fe(edta)] [_]	1.26×10^{25}

Predict which of the [Fe(edds)]⁻ and [Fe(edta)]⁻ complexes is more stable.

Explain your answer with reference to the K_{stab} value for each complex.

[Fe(edta)]⁻ is more stable due to its higher K_{stab} value. [1]

......[1]

Markers' Comments

- Candidates are advised to perform careful reading of the questions, as many misread the numerical value of *K*_{stab} and came to an incorrect conclusion.
- (iv) When an excess of edta⁴⁻(aq) is added to [Fe(edds)]⁻, the following equilibrium is established.

equilibrium 2 $[Fe(edds)]^{-}(aq) + edta^{4-}(aq) \rightleftharpoons [Fe(edta)]^{-}(aq) + edds^{4-}(aq)$

Using the K_{stab} values given in Table 5.3 in **(d)(iii)**, calculate the equilibrium constant, K_{c} , for equilibrium 2.

$$\begin{aligned} \mathcal{K}_{c} &= \frac{[[Fe(edta)]^{-}][edta^{+}]}{[[Fe(edds)]^{-}][edta^{+}]} \\ &= \frac{[[Fe(edta)]^{-}]}{[edta^{+}]} \times \frac{[edds^{+}]}{[[Fe(edds)]^{-}]} \\ &= \frac{\mathcal{K}_{stab}(edta^{+})}{\mathcal{K}_{stab}(edds^{+})} \\ &= \frac{1.26 \times 10^{25}}{3.98 \times 10^{20}} = \underline{3.17} \times \underline{10^{4}} \text{ (or } \underline{31700} \text{) [1] (3 s.f.)} \end{aligned}$$

[1]

[Total: 15]



Table 5.3