Answer all questions in the space provided.

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

.....[2]

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.

Identify compound **A**. (ii)

......[1]

(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.

.....[3]

1



(ii) Explain the variation in melting points from Na_2O to Al_2O_3 .





- (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.

[1]

(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^- .



2022 H2 Chem Prelim P2 (QP)

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.

[3] [Total: 15]

- 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.

(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.

......[1]



(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.



[2]

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, $NH_3(g)$.

.....[2]

(ii) Using appropriate data from the *Data Booklet*, calculate the enthalpy change of combustion of ammonia.

[2]

(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.

(iv) The process of nitrification is often used to convert ammonia into a less toxic nitrate.

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

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

$$\begin{aligned} \mathsf{NH}_{3}(\mathsf{aq}) + \mathsf{O}_{2}(\mathsf{g}) + \mathsf{H}_{2}(\mathsf{g}) &\to \mathsf{NH}_{2}\mathsf{OH}(\mathsf{aq}) + \mathsf{H}_{2}\mathsf{O}(\mathsf{I}) & \Delta H_{1} = -284 \text{ kJ mol}^{-1} \\ \mathsf{NH}_{2}\mathsf{OH}(\mathsf{aq}) + \mathsf{H}_{2}\mathsf{O}(\mathsf{I}) + \frac{1}{2}\mathsf{O}_{2}(\mathsf{g}) &\to \mathsf{NO}_{3}^{-}(\mathsf{aq}) + 2\mathsf{H}_{2}(\mathsf{g}) + \mathsf{H}^{+}(\mathsf{aq}) & \Delta H_{2} = +1653 \text{ kJ mol}^{-1} \\ 2\mathsf{H}_{2}\mathsf{O}(\mathsf{I}) &\to 2\mathsf{H}_{2}(\mathsf{g}) + \mathsf{O}_{2}(\mathsf{g}) & \Delta H_{3} = +572 \text{ kJ mol}^{-1} \end{aligned}$$

[3]

[Total: 14]



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	 	 	 	 	 	 	
step III	 	 	 	 	 	 	

[2]

[1]

10

2022 H2 Chem Prelim P2 (QP)

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

(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.

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



[1]

- Carbocations frequently undergo structural changes, called rearrangements, to form more (c) 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.



Fig. 3.2

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.





Tampines Meridian Junior College

(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



Step 3: CH₃CH₂OH attacks the rearranged carbocation.

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



2-ethoxy-2-methylbutane

[3]

(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.





(i) Suggest why $(CH_3)_3CCH_2OCH_2CH_3$ is not formed.

.....[1]

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



[1] [Total: 16]

2022 JC2 Preliminary Examination H2 Chemistry

- 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.

[1]

(ii) Suggest a method whereby ant stings can be treated. Explain your answer.

.....[1]

(b) One industrial method of producing methanoic acid is a 2-step reaction, via the carbonylation of ethanol, as shown below.

step 1:
$$CH_3CH_2OH + CO \xrightarrow{CH_3CH_2O^*Na^+}_{high pressure}$$
 $HCOOCH_2CH_3$
step 2: $HCOOCH_2CH_3 + H_2O \xrightarrow{heat}$ $HCOOH + CH_3CH_2OH$

Tampines Meridian Junior College

(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
К	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.

κ:....

L :

......[2]



2022 JC2 Preliminary Examination H2 Chemistry

- (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 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*.

.....[1]

(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 (•).





[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.

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

......[1]

(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.

[1]

[Turn over

(iv) Show that ΔG° at 298 K for the equation you have written in (d)(ii) is -284 kJ mol⁻¹.

(v)	[1] Based on the setup in Fig. 4.2, suggest a reason to explain why the actual E^{e}_{cell} value measured in a DFAFC may be lower than +1.47 V.
	[2]

[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.

т.	614	. 6	4
Та	ble	e 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.

......[1]

(ii) Using the information in Fig. 5.1 and Table 5.1, suggest which indicators could best be used to determine the end-points of the successive titrations for M and N.
 Indicator for M
 Indicator for N
 [1]
 (iii) Give a reason for your choice of indicators in (a)(ii).



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

omino opid	glutamic acid	proline		
	NH ₂ CO ₂ H	NH		
isoelectric point	3.1	6.5		

Table 5.2

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*.

......[1]

(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.

positive end	negative end

(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.

.....[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.

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

[*M*^r of Na⁺A⁻ is 204.1]



[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)]⁻.
- (ii) [Fe(edds)]⁻ and [Fe(edta)]⁻ have different colours.

Explain why the two complexes differ in colour.

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

Table 5.3

complex	K _{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.

.....[1]

(iv) When an excess of edta⁴-(aq) is added to [Fe(edds)]⁻, the following equilibrium is established.

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

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

[1]

[Total: 15]

