

## TAMPINES MERIDIAN JUNIOR COLLEGE JC2 PRELIMINARY EXAMINATION

CANDIDATE NAME

## **SUGGESTED ANSWERS**

**CIVICS GROUP** 

## H2 CHEMISTRY

Paper 2 Structured Questions

9729/02

15 September 2022 2 hours

Candidates answer on the Question Paper.

Additional materials: Data Booklet

## **READ THESE INSTRUCTIONS FIRST**

Write your name and civics group in the spaces at the top of this page.Write in dark blue or black pen.You may use an HB pencil for any diagrams and graphs.Do not use paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.

A Data Booklet is provided.

The number of marks is given in brackets [ ] at the end of each question or part question.

Examiner's Use					
Paper 1	MCQ	/ 30			
	Q1	/ 15			
	Q2	/ 14			
Paper 2	Q3	/ 16			
	Q4	/ 15			
	Q5	/ 15			
		/ 75			
Paper 3		/ 80			
Paper 4		/ 55			
Total		/ 100			
Grade					

This document consists of 25 printed pages.

Answer **all** questions in the space provided.

- 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 **ionic to covalent** across the Period.

Large difference in electronegativity between metallic atoms (e.g. Na/Mg/A*l*) 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. [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.

(ii) Identify compound A.

P<sub>4</sub>O<sub>10</sub> [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.

Possible identities of <b>B</b> : aluminium oxide / Al <sub>2</sub> O <sub>3</sub> and silicon dioxide / SiO <sub>2</sub> .
<u>Add HC/(aq)</u> (or $H_2SO_4(aq)$ ) to a sample of compound <b>B</b> . If it is <u>soluble / dissolves</u> in
HCl(aq), B is <u>Al<sub>2</sub>O</u> <sub>3</sub> . If it is <u>insoluble</u> , B is <u>SiO</u> <sub>2</sub> .
$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O \ OR \ Al_2O_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2O$
OR Add NaOH(aq) to a sample of compound B.
If it is <b>soluble / dissolves in NaOH(aq)</b> , <b>B</b> is <u>Al<sub>2</sub>O</u> 3. If it is <b>insoluble</b> , <b>B</b> is <u>SiO</u> 2
$Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2NaAl(OH)_4$
[3]

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



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

• <u>Ionic charge: Mg<sup>2+</sup> > Na<sup>+</sup> and Ionic radius: Mg<sup>2+</sup> < Na<sup>+</sup></u> Lattice energy (L.E.)  $\propto \left| \frac{q_{+}\cdot q_{-}}{r_{+}+r_{2}} \right|$ , <u>L.E. magnitude / ionic bond strength: MgO > Na<sub>2</sub>O</u> Energy required to break ionic bond: MgO > Na<sub>2</sub>O, hence melting point: MgO > Na<sub>2</sub>O • <u>Charge density  $\left( \frac{q_{+}}{r_{+}} \right)$ : Al<sup>3+</sup> > Mg<sup>2+</sup>, Al<sup>3+</sup> polarises O<sup>2-</sup> electron cloud to a larger extent. <u>Al<sub>2</sub>O<sub>3</sub> has partial covalent character</u>, hence melting point: Al<sub>2</sub>O<sub>3</sub> < MgO [2]</u>



- (c) Sodium azide, NaN<sub>3</sub>, 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  $N_3^{-}$ .

There are <u>2 bond pairs and 0 lone pair</u> around the central N atom. allow ECF To minimise repulsion and maximise stability, the shape around the central N atom is <u>linear</u>. As there are equal bond pair-bond pair repulsions, the bond angle is <u>180°</u>. allow ECF



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 dm<sup>3</sup>.

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  $NaN_3 = \frac{100}{65.0} = 1.5385 \text{ mol}$ 

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N<sub>2</sub> from reaction 1: 2NaN<sub>3</sub> =  $3N_2 \Rightarrow NaN_3 = \frac{3}{2}N_2$ 

Amount of N<sub>2</sub> produced from reaction  $1 = 1.5385 \times \frac{3}{2} = 2.3077$  mol

N<sub>2</sub> from reaction 2:  $10NaN_3 \equiv 10Na \equiv N_2 \Rightarrow NaN_3 \equiv Na \equiv \frac{1}{10}N_2$ Amount of N<sub>2</sub> 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

Volume of N<sub>2</sub> produced at r.t.p. =  $2.4615 \times 24 = 59.1 \text{ dm}^3$  (to 3 s.f.) *OR*  pV = nRTVolume of N<sub>2</sub> produced at r.t.p. =  $\frac{2.4615 \times 8.31 \times 293}{101325}$ =  $0.0591 \text{ m}^3$  or  $59.1 \text{ dm}^3$  (to 3 s.f.) [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,  $\Delta H_c$ , in kJ mol<sup>-1</sup>. Assume the container absorbed negligible heat from the combustion.

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Heat absorbed by water = mc\Delta T
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=170 × 4.18 × 55
= 39083 J
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\Delta H_c = -\frac{39083}{0.0500}
= -78166 J mol<sup>-1</sup>
= <u>-782 kJ mol<sup>-1</sup> (3 s.f.)</u>
```

[2]

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

$\Delta H_{\rm c}$ in (i) is <u>less exothermic</u>	than the literature	(actual) va	alue because	neat was l	<u>ost to</u>
the current diago					
<u>the surroundings</u> .					[1]



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

0.3 dm<sup>3</sup> 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 dm<sup>3</sup>; followed by
- bubbling the remaining gas mixture through aqueous sodium hydroxide, with a further contraction of 5.4 dm<sup>3</sup>.

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)

Since  $C_x H_y O \equiv x CO_2$  and

by Avogadro's Law, volume ratio = mole ratio

$$\Rightarrow \frac{\text{Volume of } CO_2}{\text{Volume of } C_xH_yO} = \frac{\text{Amount of } CO_2}{\text{Amount of } C_xH_yO} = \frac{x}{1}$$
$$\Rightarrow \frac{5.4}{0.3} = \frac{x}{1} \qquad \therefore x = \underline{18}$$

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

by Avogadro's Law, volume ratio = mole ratio

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

Molecular formula of tonalide is thus C18H26O

[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, NH<sub>3</sub>(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. NH<sub>3</sub>(g) + <sup>3</sup>/<sub>4</sub>O<sub>2</sub>(g) → <sup>1</sup>/<sub>2</sub>N<sub>2</sub>(g) + <sup>3</sup>/<sub>2</sub>H<sub>2</sub>O(l) [2]
- (ii) Using appropriate data from the *Data Booklet*, calculate the enthalpy change of combustion of ammonia.

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

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

[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.

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

- It does not generate greenhouse gases (such as CO<sub>2</sub>) that contributes to global warming.
- It is <u>widely available</u>.
   Disadvantage Any one of the following (or other feasible disadvantage)
- It generates nitrogen oxide during combustion that <u>causes air pollution</u> (or <u>acid rain</u>).
- It is <u>difficult to burn</u> (or <u>does not readily ignite</u>).

[2]

(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,  $\Delta H_r$ .

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



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(ignore state symbols)
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By Hess Law,  $\Delta H_r + \frac{1}{2} \Delta H_3 = \Delta H_1 + \Delta H_2$ OR  $\Delta H_r = \Delta H_1 + \Delta H_2 - \frac{1}{2} \Delta H_3$   $= -284 + 1653 - \frac{1}{2} (572)$  $= +1083 \text{ kJ mol}^{-1} (\text{or } +1080 \text{ kJ mol}^{-1})$ 

[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	alcoholic KCN, heat	
step III	dilute HC <i>I</i> , heat	
·		[2]

[1]

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

G (amide) is <u>less basic</u> than F (amine). For G, the <u>lone electron pair on N atom is delocalised with the adjacent C=O</u>, reducing the electron density on the N atom.

Hence, <u>N atom is less available to accept a proton OR form a dative bond with H</u><sup>+</sup>.....[2]

(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 reaction sample with NaOH (ag)</u>

   [1]
- (ii) Write the rate equation for the reaction and state the units of the rate constant.

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



[1]

[1]



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

3° carbocation has greater no. of electron-donating alkyl groups causing a greater extent of dispersal of the positive charge on the carbocation and hence greater stability compared to 2° carbocation. .....[1]

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



2<sup>o</sup> carbocation

3<sup>o</sup> carbocation (more stable)

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<sub>N</sub>1 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





Step 3: CH<sub>3</sub>CH<sub>2</sub>OH attacks the rearranged carbocation.



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



(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° carbocation is unstable and will not be formed. *OR* 1° carbocation formed will immediately undergo methyl shift to form the more stable 3° carbocation. or other [1] reasonable answer (such as simultaneous shifting of CH<sub>3</sub> and leaving of bromine occurs)

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



[1]

[Total: 16]

- 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  $6.0 \times 10^{-3}$  cm<sup>3</sup> 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 =  $6.0 \times 10^{-3} \times 0.58 \times \frac{100}{100}$ 

- (ii) Suggest a method whereby ant stings can be treated. Explain your answer.
   Apply an <u>alkaline</u> solution to <u>neutralise</u> the methanoic acid.
   [1]
- (b) One industrial method of producing methanoic acid is a 2-step reaction, via the carbonylation of ethanol, as shown below.

CH<sub>3</sub>CH<sub>2</sub>O<sup>-</sup>Na<sup>+</sup>  $CH_3CH_2OH + CO$ HCOOCH<sub>2</sub>CH<sub>3</sub> step 1: **→** high pressure J step 2:  $HCOOCH_2CH_3 + H_2O$ HCOOH +  $CH_3CH_2OH$ heat J (i) Name the ester J, HCOOCH<sub>2</sub>CH<sub>3</sub>. ethyl methanoate (ii) Suggest the type of reaction for step 2.

Step 2: ......[1]

(iii) K and L are constitutional isomers of J (HCOOCH<sub>2</sub>CH<sub>3</sub>). Table 4.1 shows some information about the isomers.

isomer	boiling point / ° C	reaction with Na <sub>2</sub> CO <sub>3</sub> (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.

K : CH<sub>3</sub>COOCH<sub>3</sub> OR CH<sub>3</sub>OCOCH<sub>3</sub>

L CH<sub>3</sub>CH<sub>2</sub>COOH

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

- (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 H<sub>2</sub>O<sub>2</sub> 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 <u>the breaking of a covalent bond</u> between 2 atoms such that <u>each atom retains</u> <u>only one</u> of the shared <u>electrons</u> resulting in the formation of free radicals. [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 (•).





Fig. 4.1

[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.



Fig. 4.2

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]

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

 $HCOOH + \frac{1}{2}O_2 \rightarrow CO_2 + H_2O$ [1]

(iii) Using appropriate data from the *Data Booklet*, determine a value for the standard electrode potential,  $E^{\circ}$ , of the CO<sub>2</sub>(g)/HCOOH(aq) half-cell.

 $E^{\Theta}_{cell} = E^{\Theta}_{red} - E^{\Theta}_{oxd} \qquad (E^{\Theta}_{cell} = +1.47 \text{ V}, E^{\Theta}_{red} = E^{\Theta}_{O_2/H_2O} = +1.23 \text{ V}, E^{\Theta}_{oxd} = E^{\Theta}_{CO_2/HCOOH})$ 1.47 = 1.23 -  $E^{\Theta}_{CO_2/HCOOH}$  $E^{\Theta}_{CO_2/HCOOH} = -0.24 \text{ V}$ 

[1]

[1]

(iv) Show that  $\Delta G^{\circ}$  at 298 K for the equation you have written in (d)(ii) is -284 kJ mol<sup>-1</sup>.

 $\Delta G^{\circ} = - nFE^{\circ}$ = <u>-2 × 9.65 × 10<sup>5</sup> × (+1.47)</u> = -2.84 × 10<sup>5</sup> J mol<sup>-1</sup> = -284 kJ mol<sup>-1</sup> (shown) (v) Based on the setup in Fig. 4.2, suggest a reason to explain why the actual  $E^{\bullet}_{cell}$  value measured in a DFAFC may be lower than +1.47 V.

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

[Total: 15]



5 (a) Ethylenediamine has the structural formula NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>.

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

A 0.10 mol dm<sup>-3</sup> solution of ethylenediamine has a pH of 11.5. When 30 cm<sup>3</sup> of 0.10 mol dm<sup>-3</sup> HC*l*(aq) is added to 10 cm<sup>3</sup> of a 0.10 mol dm<sup>-3</sup> 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.

indiaatar			colour in	
Indicator	pn range	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 HC*l*.  $NH_2CH_2CH_2NH_2 + HCl \rightarrow NH_2CH_2CH_2NH_3^+Cl^ NH_2CH_2CH_2NH_3^+Cl^- + HCl \rightarrow Cl^- ^+NH_3CH_2CH_2NH_3^+Cl^-$ [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	phenolphthalein
Indicator for N.	bromocresol green OR methyl orange
	[1]

(iii) Give a reason for your choice of indicators in (a)(ii).

The	<mark>рН</mark>	transi	tion	range	of th	e indicator	lies	within	the	region	of	rapid	рH	chang	<u>e</u>
<u>over</u>	<u>the</u>	e equiv	<u>aler</u>	nce po	i <mark>nt</mark> in t	he titration									[1]

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



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

	glutamic acid	proline
amino acid	NH <sub>2</sub> CO <sub>2</sub> H	CO <sub>2</sub> H
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*.

It is an electrically neutral dipolar ion (arising from internal acid-base reaction between

the acidic carboxylic acid group and basic amine group of the amino acid) [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.



[2]

You may use HA and Na<sup>+</sup>A<sup>-</sup> 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.

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

A buffer solution is prepared by the following steps.

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

The p*K*<sub>a</sub> of HA is 6.88 at 298 K.

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

[*M*<sup>r</sup> of Na<sup>+</sup>A<sup>-</sup> is 204.1]

Initial amount of C<sub>4</sub>H<sub>9</sub>N<sub>2</sub>O<sub>4</sub>SNa (Na<sup>+</sup>A<sup>-</sup>) =  $\frac{3.50}{204.1}$  = 0.01715 mol

Amount of HC*l* added =  $0.200 \times \frac{50}{1000} = 0.0100 \text{ mol}$  (*limiting*)

 $NaA + HCl \rightarrow NaH + NaCl \Rightarrow HCl \equiv Na^+A^-_{reacted}$ 

Final amount of C<sub>4</sub>H<sub>9</sub>N<sub>2</sub>O<sub>4</sub>SNa (Na<sup>+</sup>A<sup>-</sup>) (unreacted excess) = 0.01715 - 0.0100= 0.007148 mol

Amount of ACES (HA) formed = **0.0100 mol** 

$$pH = pK_{a} + \log\left(\frac{[Na^{+}A^{-}]}{[HA]}\right)$$
$$= 6.88 + \log\left(\frac{0.007148 \div \frac{250}{1000}}{0.0100 \div \frac{250}{1000}}\right)$$
$$= 6.73$$

$$\begin{split} & OR \\ & \mathcal{K}_{a} = 10^{-6.88} = 1.32 \times 10^{-7} \text{ mol } dm^{-3} \\ & [H^+] = (1.32 \times 10^{-7}) \times 0.01 \ / \ 0.0071(48) \\ & = \textbf{1.86} \times \textbf{10}^{-7} \ (1.8465 \times 10^{-7}) \ \text{mol } dm^{-3} \\ & \text{pH} = -\text{log}(1.86 \times 10^{-7}) = \textbf{6.73} \end{split}$$



[3]

(d) Edds<sup>4–</sup> and edta<sup>4–</sup> are polydentate ligands which can be derived from ethylenediamine. These ligands form octahedral complexes with Fe<sup>3+</sup>(aq).



The formulae of the complexes are [Fe(edds)]<sup>-</sup> and [Fe(edta)]<sup>-</sup> respectively.

- (i) On the diagram of edds<sup>4-</sup>, circle each atom that forms a bond to the Fe<sup>3+</sup> ion in [Fe(edds)]<sup>-</sup>.
- (ii) [Fe(edds)]<sup>-</sup> and [Fe(edta)]<sup>-</sup> 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 /  $\Delta E$  being different</u>. The complexes <u>absorb different wavelengths</u> of light from the visible spectrum for d-d transition, hence different wavelengths of light not absorbed are observed. [2]

(iii) Table 5.3 shows the values for the stability constants,  $K_{\text{stab}}$ , of both complexes for the equilibrium below when L(aq) representing the ligand edds<sup>4–</sup>(aq) or edta<sup>4–</sup>(aq) is added to Fe<sup>3+</sup>(aq).

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

Table 5.3

complex	K <sub>stab</sub> / mol <sup>−1</sup> dm <sup>3</sup>
[Fe(edds)]⁻	$3.98 \times 10^{20}$
[Fe(edta)]⁻	1.26 × 10 <sup>25</sup>

Predict which of the [Fe(edds)]<sup>-</sup> and [Fe(edta)]<sup>-</sup> complexes is more stable.

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

[Fe(edta)]<sup>-</sup> is more stable due to its higher K<sub>stab</sub> value.

......[1]



(iv) When an excess of edta<sup>4</sup>-(aq) is added to [Fe(edds)]<sup>-</sup>, 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.

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

[1]

[Total: 15]

