Suggested Answers

TAMPINES MERIDIAN JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION

CANDIDATE NAME

CIVICS GROUP

H2 CHEMISTRY **9729/02**

Paper 2 Structured Questions **16 September 2021**

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

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

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**
Paper 2	**Q1**	**/ 12**
	Q2	**/ 13**
	Q3	**/ 17**
	Q4	**/ 17**
	Q5	**/ 16**
		/ 75
Paper 3		**/ 80**
Paper 4		**/ 55**
Total		**/ 100**
Grade		

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

1 Despite having a common element, the Period 3 chlorides (NaC*l* to PCl_5) have a large variation in their chemistry.

(a) Describe and explain the variation in bonding of the Period 3 chlorides from NaC*l* to PCl_5.

- Changes **from ionic bonding** in NaC*l* and MgCl_2 **to covalent bonding** in AlCl_3, SiCl_4 and PCl_5.
- This is due the **large electronegativity difference** between the elements for NaC*l* and MgCl_2, causing the **complete transfer of electrons to form cations and anions** .
- As for the other three, the **small electronegativity difference** does not lead to transfer of electrons, and the atoms instead **share valence electrons**

[3]

(b) Different reactions occur when MgCl_2 and PCl_5 are added separately to water. Write equation(s) for the reactions that occur and state the expected pH in each case.

	equation(s)	pH
MgCl_2	• $MgCl_2(s) + 6H_2O(l) \rightarrow [Mg(H_2O)_6]^{2+}(aq) + 2\,Cl^-(aq)$ • $[Mg(H_2O)_6]^{2+}(aq) \rightleftharpoons [Mg(H_2O)_5(OH)]^+(aq) + H^+(aq)$	5–6.5
PCl_5	• $PCl_5(s) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 5HCl\,(aq)$ **OR** • $PCl_5(s) + H_2O(l) \rightarrow POCl_3(aq) + 2HCl\,(aq)$	1–2

[3]

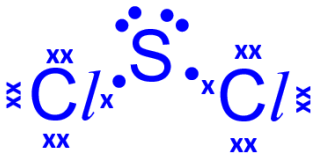
(c) The melting point of NaC*l* is 801 °C and that of MgCl_2 is 715 °C. Suggest an explanation for the lower than expected melting point for MgCl_2.

1 Mg^{2+} has **high charge density** *(as compared to Na^+)* and **polarises Cl^- anion electron cloud** to some extent ,

2 resulting in some **covalent character** in the **ionic bonding**, weakening the electrostatic forces of attraction between Mg^{2+} and Cl^- ions.

[2]

(d) **(i)** Draw a dot-and-cross diagram of the SCl_2 molecule. With reference to the Valence Shell Electron Pair Repulsion theory, state and explain the shape and bond angle.



- **2 bond pairs, 2 lone pairs** around central S atom,
- Shape is **Bent**
- **Lone pair-lone pair repulsion is stronger than bond pair-lone pair repulsion, stronger than bond pair-bond pair repulsion**
- **105°** (can accept 103° – 105.5°)

[3]

(ii) OCl_2 molecule has a similar shape as SCl_2 but a larger bond angle. Suggest why the bond angle in OCl_2 is larger than that in SCl_2.

- **O is more electronegative than S, draws in the bond pairs more strongly. Bond pairs repel** each other **more.**

[1]

[Total: 12]

2 Cadmium metal and its compounds have many uses, ranging from standard cells, batteries to semiconductors. It is one of the main components used in the Weston standard cell. The simplified Weston standard cell is shown in Fig. 2.1.

The anode of this cell is cadmium while the cathode is made up of mercury with a layer of mercurous sulfate, Hg_2SO_4, deposited on top. The electrolyte is a solution of cadmium sulfate.

a(iii)

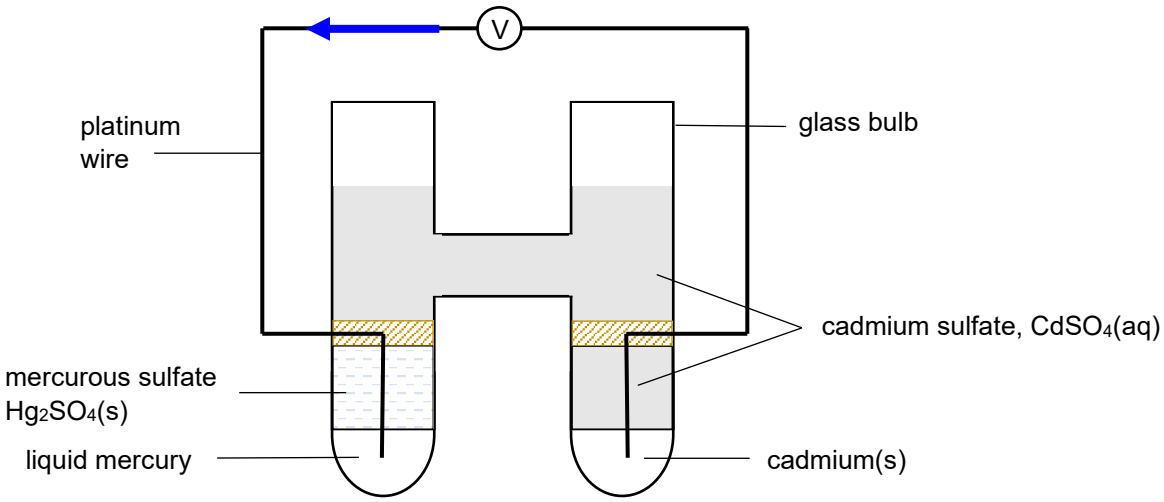


Fig. 2.1

At the cathode, both liquid mercury and sulfate ions are produced from mercurous sulfate. The equation for the reaction taking place at the anode is given below.

$$\text{Anode: } Cd \rightarrow Cd^{2+} + 2e^-$$

(a) (i) State the type of reaction that takes place at the Hg_2SO_4/Hg electrode and write the half-equation for the reaction occurring at this electrode.

Type of reaction: .. **Reduction** .....

Half-equation: .. $Hg_2SO_4(s) + 2e^- \rightarrow 2Hg(l) + SO_4^{2-}(aq)$ ..... [2]

(ii) Hence, write the overall equation for the cell reaction.

$Hg_2SO_4 + Cd \rightarrow 2Hg + SO_4^{2-} + Cd^{2+}$

.....[1]

(iii) Draw on Fig. 2.1 the direction of electron flow when the reaction in **(a)(ii)** is occurring.

[1]

(b) The cell is capable of producing an e.m.f of 1.018 V.

(i) Given that the $E^{\ominus}$ for Cd^{2+}/Cd is −0.403 V, calculate the $E^{\ominus}$ value for the cathode half-cell.

$E^{\ominus}_{Cell} = E^{\ominus}_{red} - E^{\ominus}_{oxid}$

$1.018 = E^{\ominus}_{red} - (-0.403\ V)$

$E^{\ominus}_{red} = +0.615\ V$

[1]

(ii) Suggest and explain what happens to the standard cell potential $E^{\ominus}_{cell}$ when

- solid $Cd(NO_3)_2$ is added to the electrolyte.

$Cd^{2+} + 2e^- \rightleftharpoons Cd$ -------- (1)

- Addition of Cd^{2+} ions will cause $[Cd^{2+}]$ to increase.
- By Le Chatelier's Principle, the **equilibrium position will shift right to decrease $[Cd^{2+}]$** with eqm shown
- Since $E^{\ominus}_{cell} = E^{\ominus}_{red} - E^{\ominus}_{oxid}$, **$E^{\ominus}_{ox}$ will become more positive/ less negative**
- **Hence, $E^{\ominus}_{cell}$ becomes less positive (or decreases).**

[2]

- the mass of cadmium electrode is increased.

$Cd^{2+} + 2e^- \rightleftharpoons Cd$ -------- (1)

- Increase the mass will **not affect the equilibrium position** of equation 1.
- **No change** to **$E^{\ominus}_{cell}$ value**

[1]

(iii) Calculate $\Delta G^{\ominus}$ for the Weston standard cell.

$\Delta G^{\ominus} = -nFE^{\ominus}$, where n = 2 electrons transferred

$= -2 \times 96500 \times (+1.018)$

$= -196\ 474\ J\ mol^{-1}$

$= \mathbf{-196\ kJ\ mol^{-1}}$

[2]

(iv) The standard enthalpy change for the same reaction in the Weston standard cell is −194.6 kJ mol^{-1} at 298 K. Calculate $\Delta S^{\ominus}$ for the reaction.

$\Delta G^{\ominus}$ $= \Delta H^{\ominus} - T\Delta S^{\ominus}$

-196 $= -194.6 - 298\Delta S^{\ominus}$

$\Delta S^{\ominus}$ $= + 4.70 \times 10^{-3}$ kJ mol^{-1} K^{-1}

$=$ **+ 4.70 J mol^{-1} K^{-1}**

[1]

(v) By considering the entropy and enthalpy changes during the reaction, comment qualitatively on the feasibility of the reaction with varying temperature.

[Calculation is **not** required for this question.]

ΔH is negative and ΔS is positive

When **ΔH < 0 and Δ*S* > *0*** then **$-T\Delta S < 0$,**
Reaction is spontaneous at all temperatures

[1]

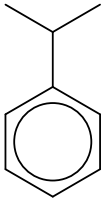
(c) Suggest one hazard associated with the use of this standard cell.

Disposal of heavy metal such as cadmium and mercury will be an **environmental/ ecosystem concern**. OR **Cadmium and mercury are toxic** OR has **harmful effects on human**

[1]

[Total: 13]

3 Cumene is a constituent of crude oil and coal tar. It is also used as a starting material to make other chemicals.

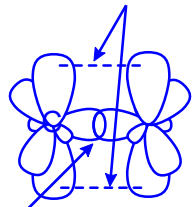


cumene

(a) State the type of hybridisation of the carbon atoms in the benzene ring of cumene. Draw a labelled diagram to show the orbitals overlap that form both σ and π bonds between a pair of carbon atoms in the ring.

Type of hybridisation: **sp^2**

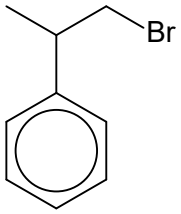
π bond from side-on overlap of p orbitals of each C atom



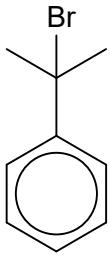
σ bond from head-on overlap of sp_2 orbitals of each C atom

[2]

(b) When cumene is reacted with bromine in the presence of ultraviolet light, a mixture of products may be obtained. This mixture includes compounds **A** and **B** with molecular formula $C_9H_{11}Br$.



A



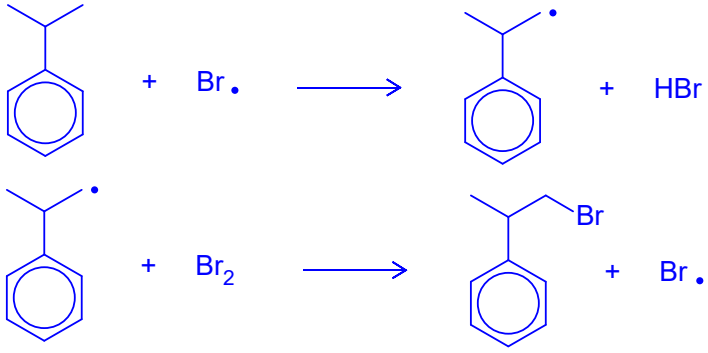
B

(i) Name and outline the mechanism of the reaction between cumene and bromine that forms compound **A**.

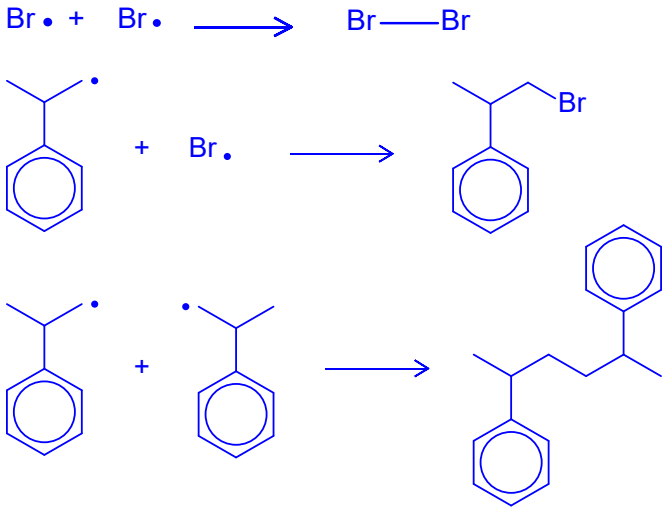
Free radical substitution

Initiation

Propagation



Termination



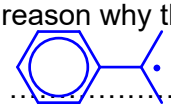
[4]

(ii) Suggest what is the ratio of compound **A** to compound **B** in the mixture.

6:1

.....[1]

(iii) In reality, compound **B** is formed in a higher proportion than compound **A**. Suggest a reason why this may be so.



intermediate radical formed is **more stable** (due to resonance effect where radical delocalises into the ring / due to more electron-donating alkyl groups)

.....[1]

(iv) State the isomeric relationship between compounds **A** and **B**.

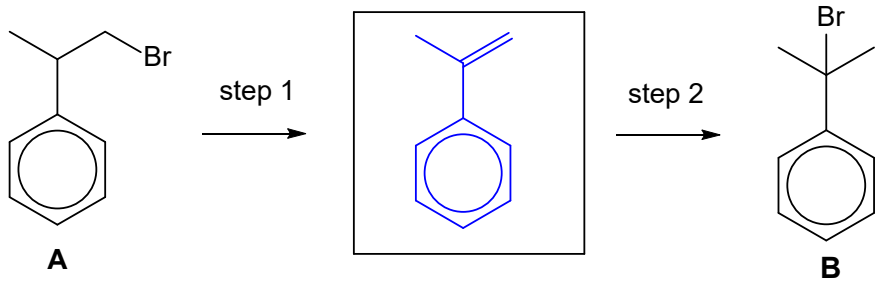
Constitutional isomerism (Structural / Positional isomerism)

.....[1]

(c) Compound **A** can be converted into compounds **B** and **C** as shown below in two steps.

State the reagents and conditions for each of the steps. Show the structure of the intermediate organic compound in each case.

(i)



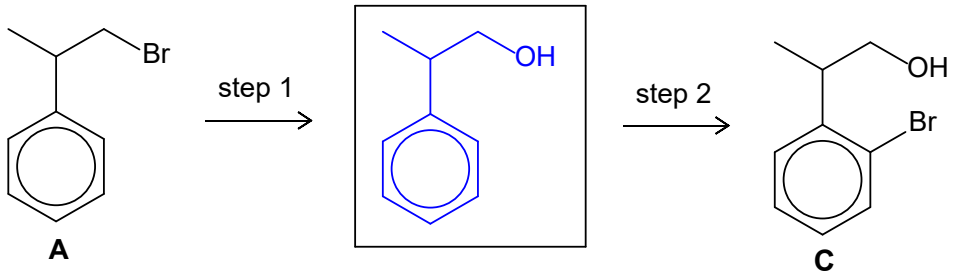
Reagents and conditions

step 1 **alcoholic NaOH**, **heat**

step 2 **HBr (g)** / **HBr in CCl_4**

[3]

(ii)



Reagents and conditions

step 1 **aqueous NaOH**, **heat**

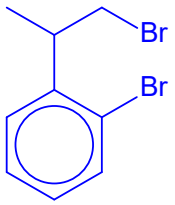
step 2 **Br_2 (g)**, **AlBr_3** (/ $FeBr_3$ / Fe) catalyst, (heat)

[3]

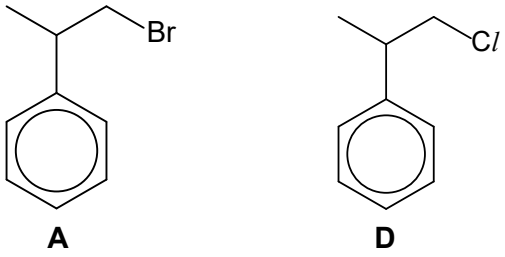
OR

step 1: **Br_2 (g)**, **AlBr_3** (/ $FeBr_3$ / Fe) catalyst, (heat)

step 2: **aqueous NaOH**, **heat**



(iii) Compound **D** shown below is an analogue of compound **A**.



A **D**

Both compounds **A** and **D** can undergo nucleophilic substitution to form alcohols.

Deduce, with a reason, whether compound **D** would react more or less readily than compound **A**.

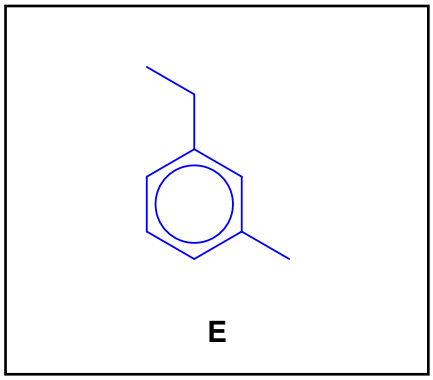
C–C*l* bond energy is **stronger** than that of **C–Br** and thus **less easily broken**,

hence compound **D** would react **less readily**. [1]

(d) Compound **E** (C_9H_{12}) is an isomer of cumene.

When compound **E** is treated with hot acidified $KMnO_4$, the organic product formed is benzene-1,3-dicarboxylic acid.

Draw the structure of compound **E**.



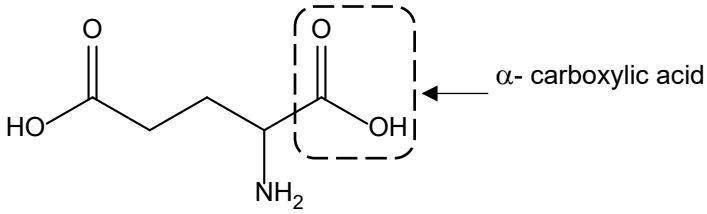
E

[1]

[Total: 17]

4 Amino acids are the building blocks of proteins which are vital for physiological functions.

Glutamic acid is an amino acid found in soy beans. The distinctive salty taste of soy sauce is due to salts of glutamic acid formed during fermentation in the production process.



glutamic acid

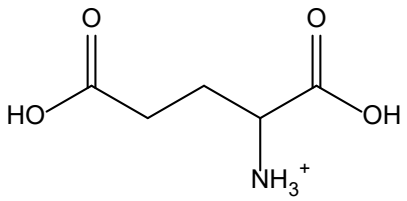
There are three pK_a values associated with glutamic acid: 2.19, 4.25 and 9.67, with the α-carboxylic acid having the lowest pK_a value.

(a) State and explain the relative acidity of the two carboxylic acid functional groups in glutamic acid.

The α-carboxylic acid is **closer to the electron-withdrawing –NH_2 group**. .....

This **stabilises the corresponding conjugate base/anion** to a greater extent, resulting in **greater tendency to dissociate/lose H^+**. Thus the **α-carboxylic acid is a stronger acid**. .....[2]

(b) At low pH, glutamic acid exists in its fully protonated form as shown.



When 0.100 mol dm^{-3} of glutamic acid in its fully protonated form is titrated with aqueous NaOH, the following curve is obtained.

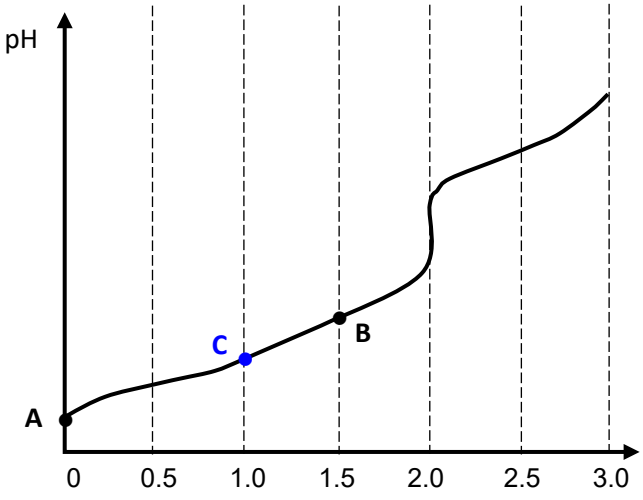


Fig. 4.1

(i) Calculate a value for the pH at point **A** in Fig. 4.1.

In this case, you may assume that the fully protonated form of glutamic acid behaves as a weak monobasic acid.

Give your answer to 1 decimal place.

Assuming that the acid is a weak acid such that $[acid]_{eqm} \approx [acid]_{initial}$

$[H^+] = \sqrt{10^{-2.19} \times 0.100}$

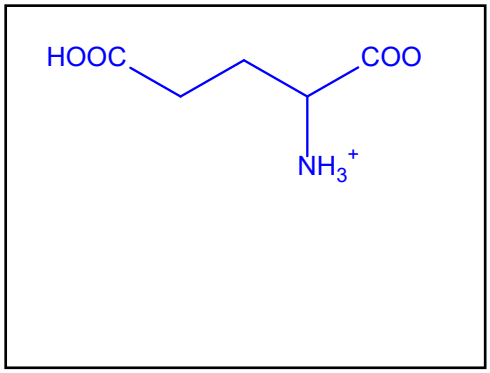
$= 0.02541 mol\ dm^{-3}$

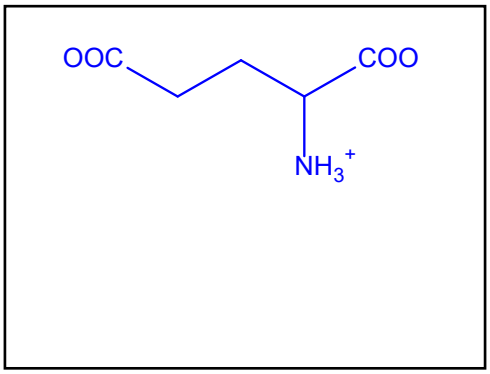
pH = –lg 0.02541 = **1.6**

[2]

(ii) There are two predominant species present in equal amounts at point **B** in Fig. 4.1.

Draw the structures of these two species and state the pH of the solution at this point.





pH of solution = **4.25**

[3]

(iii) The isoelectric point of an amino acid refers to the pH at which the amino acid has no overall charge. On the graph in Fig. 4.1, indicate a point **C** which corresponds to the isoelectric point of glutamic acid.

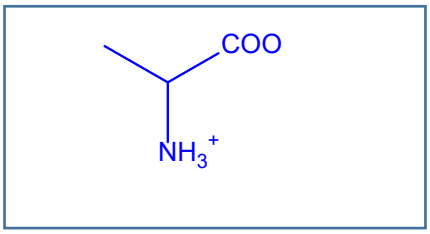
[1]

(c) Some properties of the amino acid alanine and 3-aminobutan-1-ol are given in Table 4.2.

Table 4.2

	M_r	solubility in water	melting point/ °C
$CH_3CH(NH_2)CO_2H$ alanine	89	soluble	300
$CH_3CH(NH_2)CH_2CH_2OH$ 3-aminobutan-1-ol	89	soluble	–1

(i) Despite having a similar molecular mass, alanine and 3-aminobutan-1-ol have very different melting points. Draw the structure of alanine which accounts for the difference in the melting points.



[1]

(ii) A 0.100 mol dm^{-3} aqueous solution of 3-aminobutan-1-ol has a pH of about 11.

Explain each of the following observations, with the aid of a relevant equation showing the chemistry of the resultant species.

[Calculation is **not** required for this question.]

I When the aqueous solution of 3-aminobutan-1-ol is mixed with an equal volume of 0.100 mol dm^{-3} HC*l*, the pH of the resultant solution was below 7.

The resultant **salt/conjugate acid** undergoes **hydrolysis** to give an acidic solution.

$CH_3CH(NH_3^+)CH_2CH_2OH + H_2O \rightleftharpoons CH_3CH(NH_2)CH_2CH_2OH + H_3O^+$

II When the aqueous solution of 3-aminobutan-1-ol is mixed with an equal volume of 0.050 mol dm^{-3} HC*l*, the resultant solution was able to resist pH changes upon addition of a small amount of NaOH.

The resultant solution contains a **buffer** (alkaline buffer) which is able to remove the added OH^-, thereby maintaining $[H^+]$ and hence the pH.

$CH_3CH(NH_3^+)CH_2CH_2OH + OH^- \rightarrow CH_3CH(NH_2)CH_2CH_2OH + H_2O$

[4]

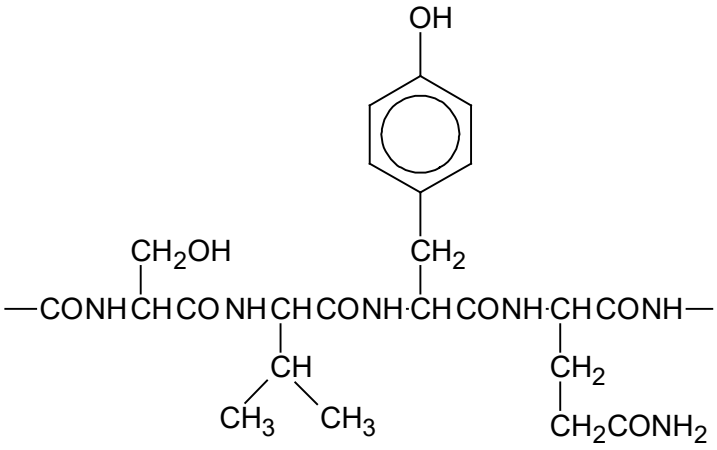
(iii) Give one example of a buffer system in blood.

H_2CO_3/HCO_3^- in blood

.....[1]

(d) Protein chains contain a large number of amino acids bonded by peptide or amide bonds. The sequence of amino acids forms the primary structure of proteins.

The hormone insulin is an example of a protein. A part of the insulin molecule is shown below.



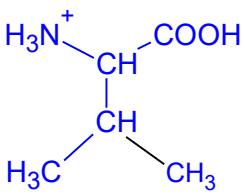
(i) What reagents and conditions could you use to hydrolyse the protein chain into its constituent amino acids?

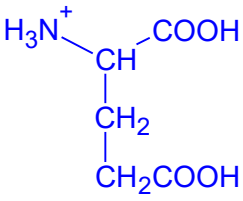
HC*l*(aq) or H_2SO_4(aq) or NaOH(aq) with prolonged heating or heat under reflux

.....[1]

(ii) Draw the structural formula for **two** amino acids with the longest non-aromatic side chains that would be produced by hydrolysing this segment of the protein chain using the conditions you have given in **(d)(i)**.

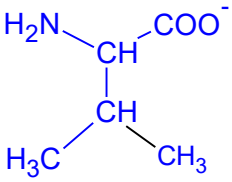
acidic hydrolysis

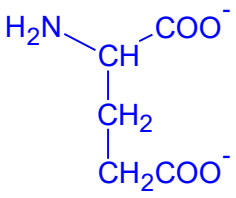




basic hydrolysis

OR





[2]

[Total: 17]

5 Ultraviolet-visible spectroscopy is a method to analyse concentrations of chemical compounds that can absorb a wavelength of light from the ultraviolet and visible region of the electromagnetic spectrum.

The simplified diagram below shows how the concentration of a sample can be measured using ultraviolet-visible spectroscopy.

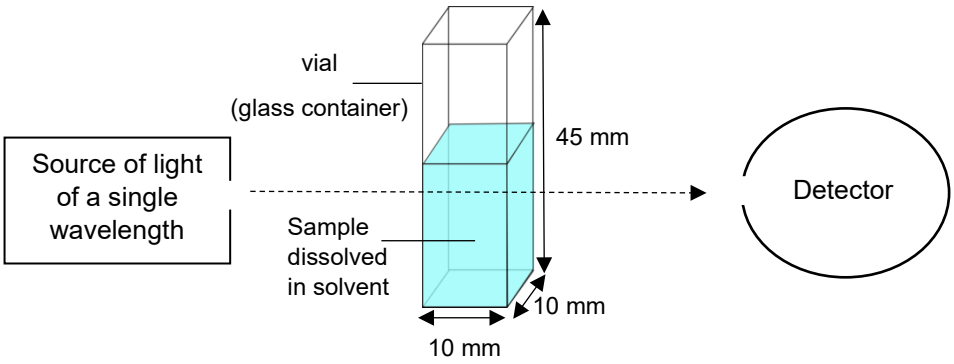


Fig 5.1

The dissolved sample is placed into the vial in which light of a single wavelength will emit from the source and pass though the sample. The distance which the light travels through the sample is known as the path length. Eventually, the detector detects the remaining intensity of light and measures the absorbance.

Beer-Lambert's Law states that for a dilute solution, the absorbance, A, of the analyte is proportional to its concentration.

$$A = \varepsilon c l$$

where ε is a constant measured in $M^{-1}cm^{-1}$ (1 M = 1 mol dm^{-3}),

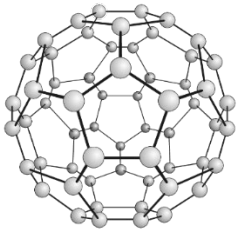
c is the concentration in mol dm^{-3},

l is the path length in centimeter, cm.

(a) With reference to Fig. 5.1, suggest a value of the path length in cm.

Path length: ..... 1 ..... cm [1]

Buckminsterfullerene, C_{60}, is a molecule with 60 carbon atoms arranged in a spherical structure.



buckminsterfullerene, C_{60}

(b) To prepare the sample of C_{60} for analysis, 10 cm^3 of concentrated C_{60} was diluted to 200 cm^3 with a suitable solvent. The diluted C_{60} is then analysed using ultraviolet-visible spectroscopy at a specific wavelength and the absorbance value is found to be 0.96.

The value of ε is 1.75 x 10^5 M^{-1} cm^{-1}. With the aid of the Beer-Lambert's Law, calculate the concentration of the concentrated C_{60} in mol dm^{-3}.

$A = \varepsilon c l$

$0.96 = 1.75 \times 10^5 \times c \times 1$

$c = 5.486 \times 10^{-6}$ M

$= 5.486 \times 10^{-6}$ mol dm^{-3} (concentration of diluted solution)

$c_1v_1 = c_2v_2$

$200 \times 5.486 \times 10^{-6} = 10 \times c_2$

$c_2 = 1.097 \times 10^{-4}$ mol dm^{-3}

[3]

(c) Fig. 5.2 shows that there is deviation from Beer-Lambert's Law at high concentration.

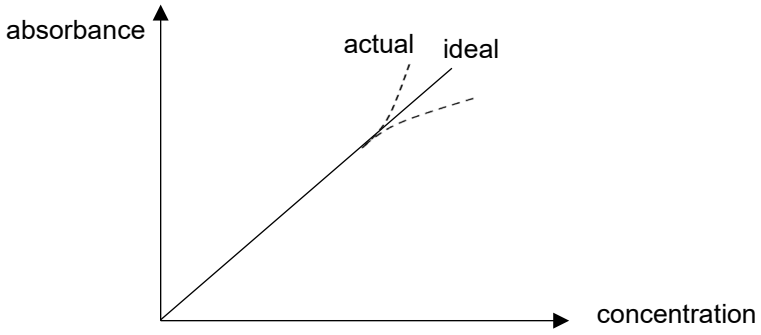


Fig. 5.2

Suggest a reason for this observation.

When the solution becomes increasingly concentrated,

- **light is unable to pass through the solution effectively** and hence unable to reach the detector.

OR

- the molecules will be more closely packed so there will be **significant intermolecular interactions** which causes the deviation from ideally.

[1]

C_{60} has been widely researched on its modification to give other fullerene derivatives such as *exofullerenes*, *endofullerenes* and *heterofullerenes* as shown in Fig. 5.3.

Exofullerenes have additional atoms or ions attached to the outer spheres while *endofullerenes* have them caged within the inner sphere. *Heterofullerenes* are formed when at least one carbon atom is replaced by another element.

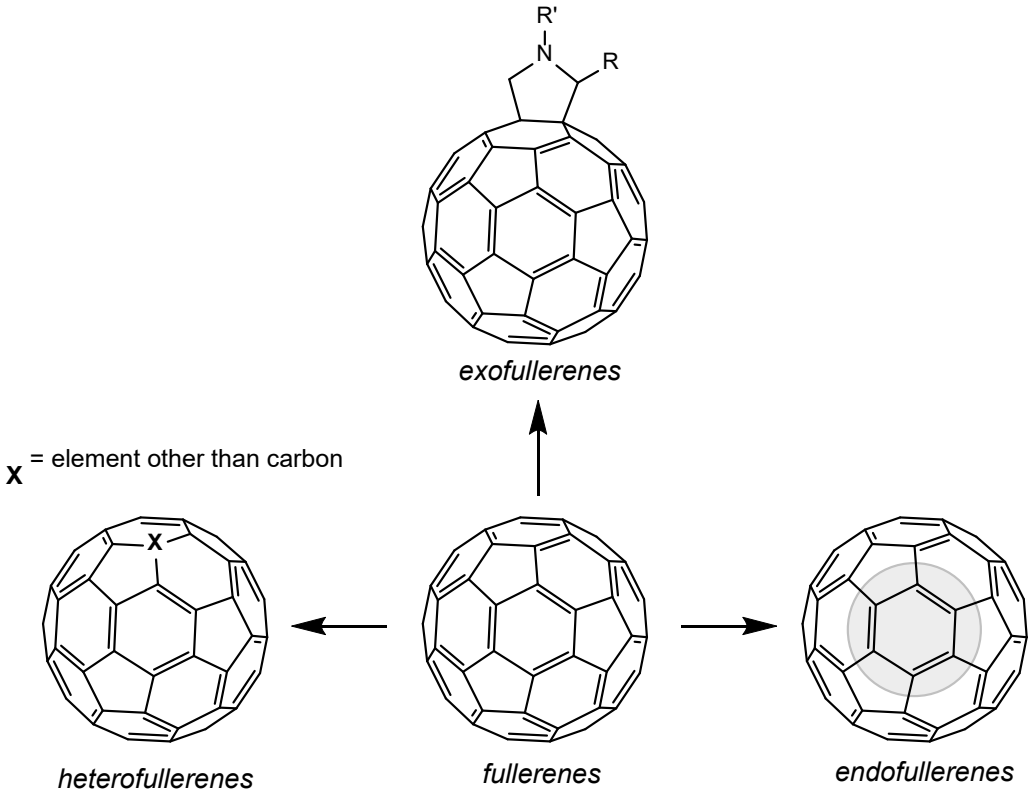


Fig. 5.1

(d) $C_{59}M$ is a *fullerene* derivative formed by reacting the ligand C_{60} with M^{n+}, where M^{n+} can be a metal ion such as Al^{3+} or Ni^{2+}.

(i) With reference to Fig. 5.3, state which of the three types of *fullerene* derivatives does $C_{59}M$ belongs to.

Heterofullerene

[1]

(ii) State the electronic configuration of Ni^{2+}.

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^8$

[2]

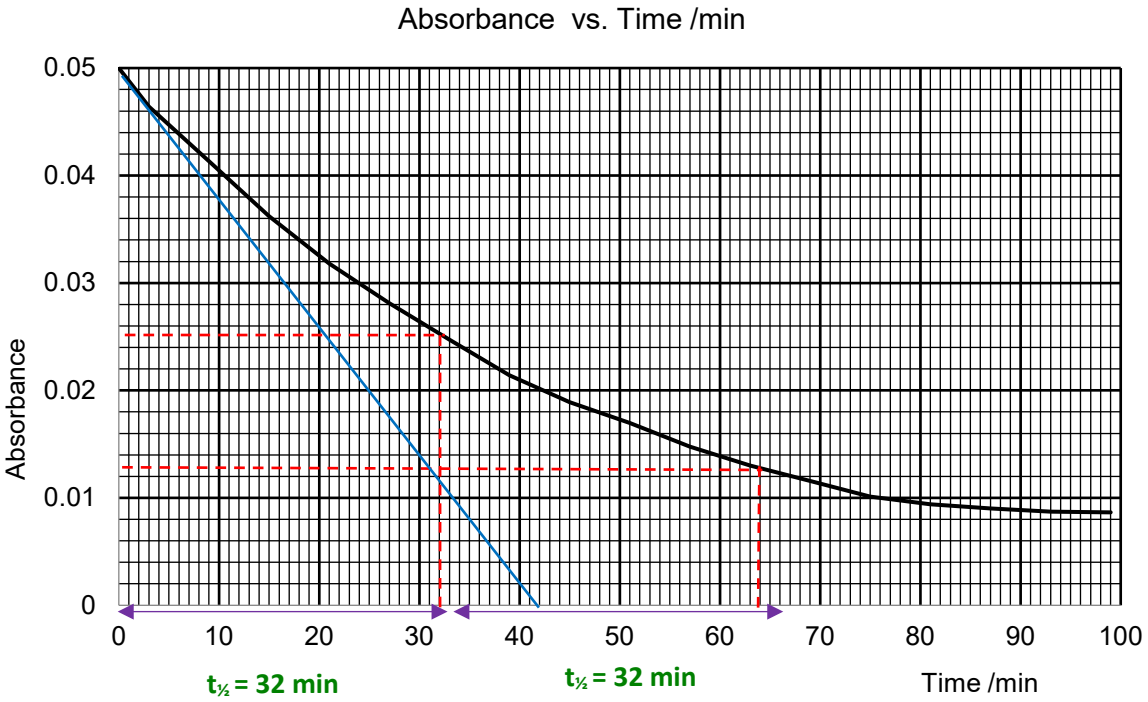
(iii) Explain why complexes formed with Al^{3+} are usually not coloured whereas those containing Ni^{2+} are coloured.

The wavelength of light absorbed during electron transition in Al^{3+} is **not within the visible light region** of the electromagnetic spectrum.

OR

Ni^{2+} absorbed visible light during the electron (*d*-*d*) transition. [1]

(e) $C_{60}O_3$ is an *exofullerene* which can undergo decomposition in methylbenzene to give $C_{60}O$ and oxygen gas. The rate of decomposition of $C_{60}O_3$ is measured using the ultraviolet-visible spectroscopy. An absorbance versus time graph is plotted as shown in Fig. 5.4.



(i) Use the graph in Fig. 5.4 to deduce the order of reaction with respect to $C_{60}O_3$. Hence, write a rate equation for the reaction.

The graph has a **constant half-life of 32 minutes**.
Order of reaction with respect to $C_{60}O_3$ is **1**.
Rate = **$k[C_{60}O_3]$**

[3]

(ii) Calculate the rate constant of the reaction, stating its units.

$$t_{\frac{1}{2}} = \frac{\ln 2}{k}$$

$$k = \frac{\ln 2}{32} = \mathbf{0.0217\ min^{-1}}$$

OR

$$\text{Initial rate} = \left|\frac{(0.05 - 0)}{(0 - 42)}\right| \quad \textit{(based on the gradient at time = 0 and absorbance at 0.05)}$$

$$= 1.19 \times 10^{-3}\ \text{min}^{-1}$$

Since rate = $k[C_{60}O_3]$

$k = 1.19 \times 10^{-3} \div 0.05 = \mathbf{0.0238\ min^{-1}}$

[2]

(iii) State the effect, if any, on the half-life of $C_{60}O_3$ when

I the concentration of $C_{60}O_3$ is halved.

Half-life remains constant when $[C_{60}O_3]$ is halved .

Reason: Since the order of reaction with respect to $[C_{60}O_3]$ is 1, the half-life is independent on the $[C_{60}O_3]$.

$$t_{\frac{1}{2}} = \frac{\ln 2}{k}$$

.....

II the reaction temperature is increased.

Half-life will be **shorter/smaller** .

Reason: When temperature is increased, the rate of reaction is increased. Hence, the time taken for the reaction to occur and the half-life should be shorter.

..... [2]

(iv) Apart from absorbance, state one other variable that could be measured over time to monitor the rate of this reaction.

State how this variable could be measured in a laboratory.

Volume of O_2 gas. O_2 gas can be collected using a **gas syringe** at regular time intervals during the reaction.

Or

Measure the **pressure of O_2** gas with a **pressure gauge** at regular rime intervals during the reaction.

....[1]

[Total: 16]