CHEMISTRY   **9729/02**

Paper 2 Structured Questions   **2 hours**

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

READ THESE INSTRUCTIONS FIRST

Write in dark blue or black pen.
You may use a HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.
DO **NOT** WRITE ON ANY BARCODES.

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.

This document consists of **14** printed pages and **2** blank pages.

[Turn Over

1 A famous science experiment shown to school children demonstrates how water may be "sucked" using a candle. A teacher demonstrates one such experiment conducted at room temperature and pressure. First, a tub half-filled with water was prepared. In the center of the tub, the teacher fixes a tall wax candle. The teacher then lit the candle. An inverted beaker with a height taller than the candle was then placed in the tub, covering the candle.

The candle burns for a short period of time, during which the water level in the inverted beaker rose negligibly. The candle then extinguishes. The water level in the inverted beaker then rose rapidly.

A common explanation found in the internet claims that the pressure of the air initially trapped by the inverted beaker dropped due to the burning candle consuming oxygen. This loss in pressure causes the water level in the inverted beaker to rise, lowering the volume of the air pocket until the pressure of the air pocket reaches atmospheric pressure.

(a) (i) The candle can be assumed to contain C_8H_{18}(s). Write a balanced equation for the complete combustion of C_8H_{18}. State symbols are not required.

.... [1]

(ii) State **two** reasons to explain why the flame of the candle extinguished by itself.

....

.... [1]

(iii) The drop in pressure of the air pocket, however, is **not** mainly due to the consumption of oxygen. Identify one piece of evidence found in the opening paragraphs of the question that supports this idea, and explain your answer.

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.... [2]

(iv) On Fig. 1.1, draw a graph of ΔG of the equation as written in your answer for **(a)(i)** against time, from the time the candle is lit (when $t = 0$) to the time the flame of the candle extinguishes (label on the time axis $t = t_1$). The intersection of the 2 axes is the origin (0, 0).

ΔG / kJ mol^{-1}

time, t

Fig. 1.1

[2]

(b) Heat produced by the candle creates a rise in pressure despite the consumption of oxygen by the burning candle. C_8H_{18} in the candle undergoes complete combustion.

Assume that all gases act ideally.

(i) No water vapour is produced by the complete combustion of C_8H_{18} and $O_2(g)$ has a 20% (by amount) composition in the air pocket. The air pocket has a volume of $200\,cm^3$. Use your answer to **(a)(i)** to find the decrease in the amount of gas trapped in the air pocket as a result of the burning of the candle.

[2]

(ii) The volume of the air pocket trapped by the inverted beaker remains at $200\,cm^3$. By assuming that the pressure in the air pocket remains the same, use your answer to **(b)(i)** to deduce the minimum rise in temperature of the air pocket.

[1]

(iii) Explain why your answer in **(b)(ii)** is the **minimum** rise in temperature.

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.... [1]

(iv) Explain quantitatively why the pressure of the air pocket dropped once the flame of the candle extinguished.

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.... [1]

(v) During the experiment, the temperature of the air pocket rose to a maximum of $75.0\,°C$. Calculate the percentage, by volume, of the air pocket that shrunk resulting in water being sucked into the inverted beaker.

[1]

[Turn Over

(c) The teacher repeats the experiment with the same setup and variables, except for one modification listed in each subpart. Suggest how each of these modifications, when separately applied, affects the final water level observed in the inverted beaker. Compare this final water level to that in the original experiment. An explanation is required. Your explanation should refer to the extent the air pocket trapped by the inverted beaker shrunk.

(i) Two candles, of the same composition and size, are used instead of one. Assume that the candles have negligible volume compared to the size of the air pocket.

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.... [2]

(ii) The candle fails to combust completely.

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.... [1]

[Total: 15]

2 **(a)** **(i)** Metallic elements often do not exist in their pure elemental state. Instead, they are found in ores where these metals are oxidised. A student suggests that s block metals can be isolated by electrolysing an aqueous solution of their respective nitrate salt with inert electrodes. Explain whether this is a viable method.

....

....

.... [2]

(ii) Name 2 d block metals where electrolysing an aqueous solution of their nitrate salt with inert electrodes will yield the respective d block metal.

.... [1]

(b) **(i)** When Na_2CO_3 is subjected to strong heat, it does not decompose. However, when Li_2CO_3 is subjected to strong heat, it decomposes. Suggest an explanation for the difference in behaviour.

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....

.... [2]

(ii) Deduce the s block carbonates, up to the sixth Period, that do **not** decompose under strong heating.

.... [1]

(c) A piece of copper ore contaminated with some metallic zinc and silver may be purified using electrolysis. The copper ore is made the anode, and electrolysed in a dilute solution of $CuSO_4$. A piece of pure copper metal is the cathode.

(i) State the expected observations during the course of the electrolysis.

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.... [1]

(ii) Explain fully how copper is purified during the electrolysis.

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.... [3]

[Total: 10]

[Turn Over

3 (a) **A** is an aromatic compound with molecular formula $C_{11}H_{15}Cl$. When $SnCl_4$ is added to **A** at room temperature, **B** is obtained. **B** is an aromatic compound containing 2 rings, one of which is a 5-membered ring, with molecular formula $C_{11}H_{14}$. When **B** is heated with concentrated $KMnO_4$ in acid conditions, a dicarboxylic acid **C** with molecular formula $C_{11}H_{12}O_4$ is obtained. **C** is the only organic product in this reaction.

(i) By comparing the molecular formula of **B** and **C**, and considering the type of reaction of the transformation of **B** to **C**, deduce the structure of **B**. Draw **B** in the box provided in **(a)(ii)**.

[3]

(ii) Given that $SnCl_4$ can act as a Lewis acid, draw the structure of **A**. **A** is a primary chloroalkane.

A	**B**

[1]

(iii) When **A** is heated with ethanolic NaOH, products with molecular formula $C_{11}H_{14}$ are obtained. State the type of isomerism these products exhibit with **B**.

.... [1]

(iv) Distinguish these products from **B** using a simple chemical test without the use of any halogens.

....

.... [2]

(b) C_2H_2 polymerises in different conditions to form hydrocarbons with different behaviours. Cyclic hydrocarbons **D** and **E** are 2 such compounds. Both **D** and **E** have only 1 ring, and all carbon atoms are not sp^3 hybridised. The M_r of **D** is 78.0 and that of **E** is 104.0.

(i) When Br_2(aq) is added to separate portions of **D** and **E**, only **E** decolourises Br_2(aq). Explain what this suggests about the distribution of pi electrons within the ring of **D**.

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.... [1]

(ii) The structure of **E** is symmetrical, and **E** has 2 carbon-carbon (C-C) bond lengths. Draw an accurate structure of **D** and **E**, ensuring that your answer reflects all information given in **(b)** so far.

D	**E**
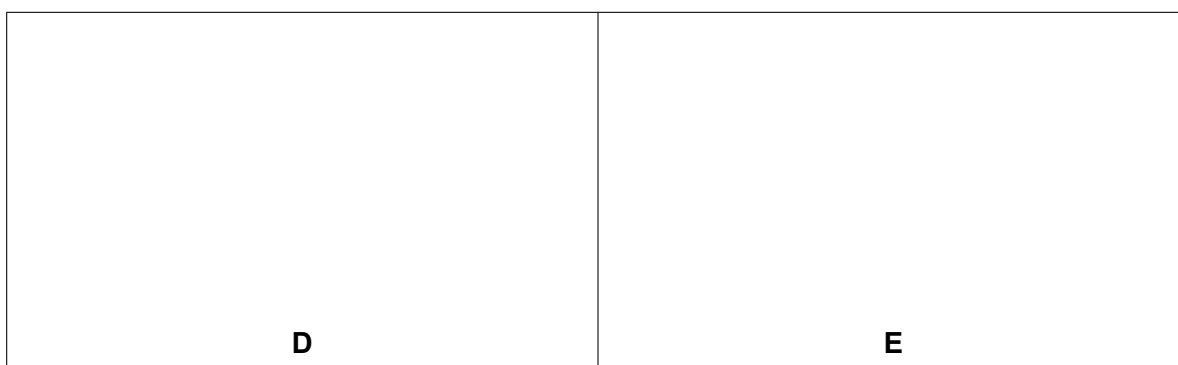
[2]

(iii) Take the standard enthalpy change of formations of **D** and **E** and divide them by the number of carbons in **D** and **E** respectively. State which of these values is lower in magnitude and explain your answer. Assume that the standard enthalpy change of formations are positive.
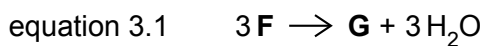
....

....

.... [2]

(iv) Suggest whether **E** is planar. Explain your answer in terms of the C-C-C bond angles in **E**.

....

.... [2]

[Turn Over

(c) Under the action of concentrated H_2SO_4, **F** undergoes a condensation reaction to form hydrocarbon **G**. **G** contains a benzene ring. The balanced equation for the reaction is given in equation 3.1.

equation 3.1 $3\,\textbf{F} \longrightarrow \textbf{G} + 3\,H_2O$

(i) When **F** is reacted with warm alkaline I_2(aq), a yellow precipitate is formed. **F** reacts with 2,4-DNPH to give an orange precipitate. Given that **F** has 3 carbons, draw the structure of **F**.

Further given that **G** has a 1,3,5-trisubstituted benzene ring, draw the structure of **G**.

F	**G**

[2]

(ii) Another hydrocarbon **H** containing 3 carbons may polymerise to form **G**, similar to the reaction described in **(b)**. However, another aromatic product, **J**, may be formed. Draw the structures of **H** and **J**.

H	**J**

[2]

(iii) Explain whether **G** or **J** is more easily synthesised directly from methylbenzene.

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.... [2]

[Total: 20]

4 A nucleophile may act as a Brønsted-Lowry base. However, some factors affecting the strength of a nucleophile are different to that of the factors affecting the strength of a base.

(a) H_2O and OH^- are two nucleophiles that may act as a Brønsted-Lowry base. OH^- is a stronger Brønsted-Lowry base than H_2O.

(i) H_2O and OH^- may act as suitable nucleophiles in an S_N2 reaction of CH_3Br. State, with explanation, the stronger nucleophile, H_2O or OH^-, in the S_N2 reaction.

....

.... [1]

(ii) Suggest a neutral species isoelectronic to H_2O and OH^- that is a stronger nucleophile than H_2O. Explain your answer.

....

.... [1]

(b) The strength of Brønsted-Lowry bases may vary in various solvents. The pK_a of selected Brønsted-Lowry acids at 25 °C are shown in Table 4.1.

Table 4.1

Acid	pK_a in H_2O	pK_a in $(CH_3)_2S{=}O$
$(CH_3CH_2)_3NH^+$	10.7	9.0
NH_4^+	9.2	10.5

(i) Use Table 4.1 to determine the stronger Brønsted-Lowry base, $(CH_3CH_2)_3N$ or NH_3, in the solvents H_2O and $(CH_3)_2S{=}O$. Explain your answer.

....

.... [1]

(ii) State the predominant intermolecular forces of attraction between H_2O and the conjugate acid cations in Table 4.1. State, with explanation, which cation has the stronger interaction with H_2O.

....

....

.... [2]

(iii) Hence, account for the relative Brønsted-Lowry basicities of $(CH_3CH_2)_3N$ and NH_3 in the different solvents H_2O and $(CH_3)_2S{=}O$.

....

....

.... [2]

[Turn Over

(c) The strength of a nucleophile may be measured by its rate of reaction with an electrophile. Equation 4.1 relates the strength of a nucleophile (defined as n) relative to the strength of water as a nucleophile. k is the rate constant of the reaction where the nucleophile performs a S_N2 reaction with CH_3Br in H_2O. k_0 is the rate constant of the reaction where water performs a S_N2 reaction with CH_3Br.

$$\text{equation 4.1} \qquad \frac{k}{k_0} = 10^n$$

Various n values for different nucleophiles are shown in Table 4.2.

Table 4.2

Nucleophile	Cl^-	$C_6H_5NH_2$	I^-
n	3.0	4.5	5.0

(i) State the value of n for H_2O.

.... [1]

(ii) By considering your answer in **(b)(ii)**, suggest an explanation for the relative strength of the nucleophiles I^- and Cl^- in H_2O medium.

....

.... [2]

(iii) Deduce the conditions where Cl^- is a stronger nucleophile than I^-.

....

.... [1]

(iv) Deduce from Table 4.2 whether a stronger Brønsted-Lowry base is always a stronger nucleophile.

....

.... [1]

(d) (i) $(CH_3)_3CO^-$ is a strong base but a very weak nucleophile. Suggest why $(CH_3)_3CO^-$ is a weaker nucleophile than OH^-.

....

.... [1]

(ii) When 2-bromobutane is treated with $(CH_3)_3CO^-$ in the presence of heat, but-1-ene is obtained as the product. Using information offered in **(d)(i)**, write a balanced equation for this reaction.

.... [1]

[Total: 14]

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5 In 2000, a dam failure in a gold mine spilled cyanide-containing (CN^-) waste water into the river Szamos. The pollution wave, which later reached the Central European rivers Tisza and Danube, killed massive amounts of fish.

Certain complex metal ions containing CN^- are toxic to aquatic life.

In this question, you may assume that any buffers do not contain any cyanide-containing species.

(a) The concentration of CN^- is determined through a cyanide-selective electrode. When the electrode is inserted into a solution and connected to a reference electrode, a potential difference, E, is recorded. Using E, $[CN^-]$ can be found with reference to equation 5.1.

equation 5.1 $\quad E = E^{\ominus} - a\log_{10}([CN^-]/\text{mol dm}^{-3})$

(i) At 25 °C, the K_a of HCN is $6.15 \times 10^{-10}\,\text{mol dm}^{-3}$. The potential difference recorded when x mg of NaCN(s) is added into $1\,\text{dm}^3$ of a pH 7.5 buffer at 25 °C is shown in Table 5.1.

Table 5.1

x	E / mV
1.00	598.9
10.0	539.8
100	480.7

Find $E^{\ominus}$ and a with their units, if any.

[3]

(ii) When the concentration of a cyanide-containing compound in a solution exceeds a certain limit, the solution is lethal enough to kill 50% of aquatic life within 24 hours. This is known as the LC_{50}. For simplicity, assume that concentrations above LC_{50} will result in aquatic life being killed, while concentrations below LC_{50} will result in all aquatic life being preserved. Table 5.2 contains the LC_{50} of 2 cyanide compounds.

Table 5.2

| compound	LC_{50} / mg dm^{-3}
non-complexed CN^- (sum of [HCN] and [CN^-])	2.1
$Na_4[Fe(CN)_6] \cdot 3\,H_2O$	6×10^3

State the maximum mass of NaCN that can be dissolved in a $1.0\,dm^3$ pH 7.5 buffer before the LC_{50} threshold is reached. Explain your answer.

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.... [1]

(b) A popular Hungarian TV show suggested that $FeSO_4$ should have been used to lower the environmental impact of the dam failure. A demonstration was conducted.

1. $98.0\,mg$ NaCN(s) was dissolved in $200\,cm^3$ of pH 7.5 buffer to simulate the contaminated river.
2. The pH 7.5 buffer was found to have $[O_2(aq)] = 8.00\,mg\,dm^{-3}$.
3. The buffer was separated into 2 equal portions, namely portion 1 and portion 2.
4. To portion 1, $40.0\,g$ of $FeSO_4 \cdot 7\,H_2O$ was added. Nothing was added to portion 2.
5. Some fish was placed in both portions. Only the fish in portion 1 survived.

Fe^{2+} ions may complex with CN^- to form $[Fe(CN)_6]^{4-}$ according to equation 5.2 bearing equilibrium constant β_6.

equation 5.2 $\qquad Fe^{2+} + 6\,CN^- \rightleftharpoons [Fe(CN)_6]^{4-}$ $\qquad\qquad\qquad\qquad\qquad\qquad$ β_6
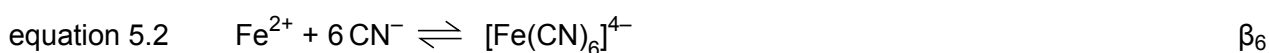
The electrode reading of portion 1 at equilibrium is 585.9 mV.

(i) At pH 7.5, Fe^{2+} ions may react with O_2 to form a brown precipitate. Write a balanced equation for this reaction. State symbols are not required.

.... [1]

(ii) Find β_6, stating its units clearly. Assume that the reaction in **(b)(i)** goes to completion.

[4]

(iii) Determine whether the outcome of the demonstration agrees with the toxicity data presented in Table 5.2. Support your answer with suitable calculations.

[4]

(c) When the same demonstration was conducted with water extracted from the contaminated river, the fish did not survive. It turns out that the presence of Cu^+ ions results in the toxic complexes $[Cu(CN)_2]^-$ and $[Cu(CN)_3]^{2-}$ being formed.

(i) Explain why copper(I) complexes are often colourless.

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.... [1]

(ii) Suggest why copper(I) species found in the solution are complexed and not in the form of aqueous Cu^+ ions.

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.... [2]

[Total: 16]

[Turn Over

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