CANDIDATE NAME

CLASS

CHEMISTRY

9729/02

Paper 2 Structured

9 September 2024

2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class in the spaces at the top of this page.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, 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.

For Examiner's Use	
1	/12
2	/7
3	/6
4	/6
5	/11
6	/11
7	/22
Total	/75

This document consists of **21** printed pages and **2** blank pages.

[Turn over

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

1(a) The Periodic Table usually shows hydrogen on its own and not a member of a group.

(i) Suggest why the element hydrogen could be placed at the top of Group 1.

....

....[1]

(ii) Suggest why the element hydrogen is **not** placed at the top of Group 1, in terms of
- its structure
- one physical property related to its structure

....

....

....

....

....

....

....

....

....[2]

The trihydrogen complex cation, H_3^+, was first discovered in 1911 when J.J. Thomson was performing his cathode ray tube experiments. In 1989, H_3^+ was detected in the ionosphere of Jupiter.

H_3^+ is mainly found in interstellar space where there is high cosmic radiation. In the presence of high energy gamma radiation, hydrogen gas can lose an electron to form H_2^+, which then reacts with molecular hydrogen to form H_3^+.

$$H_2 \rightarrow H_2^+ + e^-$$

$$H_2^+ + H_2 \rightarrow H_3^+ + H$$

(b) Describe and explain how the behaviour of beams of the ions H_2^+, H_3^+ and electrons differ in an electric field.
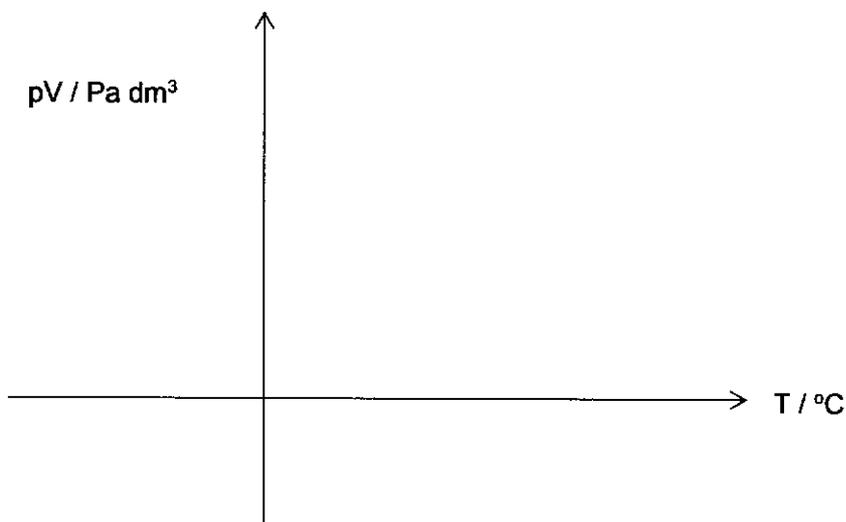
....

....

....

....

....[2]

(c) Given that hydrogen can exist as isotopes ^1H, ^2H and ^3H, complete Table 1.1.

Table 1.1

	number of protons	number of neutrons	number of electrons
^2H			
$^1H_2^+$			
$^3H_3^+$			

[3]

(d) Describe the reactions, if any, of the chlorides NaCl, $AlCl_3$ and PCl_5 with water.
Write equations for all the reactions that occur, and suggest the pH of the resulting solutions.

Relate the reactivity of these chlorides to their structure and bonding.

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....[4]

[Total: 12]

[Turn Over

2   Ozone, O_3, is a non-linear molecule present in the Earth's upper atmosphere. It absorbs ultraviolet radiation from the Sun and so protects living organisms from this type of radiation.

(a)   (i)   Draw the dot-and-cross diagram for the ozone molecule.

[1]

(ii)   State one harmful consequence to a person of increased exposure to ultraviolet radiation.

....[1]

Nitrogen oxides in aircraft emissions results in the depletion of the ozone layer. The reaction of nitrogen monoxide with ozone is given below.

$$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$$

(b)   (i)   Suggest and explain the following differences between NO_2 and O_3.

• Bond angle around central atom in O_3 is smaller than that in NO_2.

....

....

....

....

....

• Boiling point of O_3 is lower than that of NO_2.

....

....

....

....

....

....

....

....[2]

(ii) Suggest why the release of nitrogen oxides by vehicles does not affect the ozone layer.

....

....[1]

(c) On the axes given below, sketch two graphs to show how pV varies with T for O_3 and O_2 respectively. Assume ideal gas behaviour for both gases and a fixed mass of gas sample is used for each gas.

pV / Pa dm³

T / °C

[2]

[Total: 7]

[Turn Over

3 In heavily polluted air, nitrogen dioxide is often formed and it appears as a brown gas with a pungent odour.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g) \qquad \Delta H < 0$$

(a) The following results in Table 3.1 were obtained from a series of experiments carried out to investigate this reaction.

Table 3.1

experiment	[NO] / mol dm^{-3}	[O$_2$] / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	1.00×10^{-3}	0.100	7.00×10^{-4}
2	2.00×10^{-3}	0.100	2.80×10^{-3}
3	3.00×10^{-3}	0.200	1.26×10^{-2}

(i) Deduce the order of reaction with respect to each reactant by showing your working clearly and hence write the rate equation for the reaction.

....

....

....

....

....

....

....

....

....

....

....

....

....

.... [3]

(ii) Suggest, with reasoning, how the value of the rate constant, k, will be affected as the gases get cooler in the upper part of the atmosphere.

....

....

.... [1]

(b)   The removal of NO_2 is important because it has significant environmental consequences if emitted into the atmosphere.

Describe and explain with the aid of suitable equations, the role of NO_2 in the oxidation of atmospheric sulfur dioxide.

....

....

....

....

.... [2]

[Total: 6]

[Turn Over

4   The solubility product, K_{sp}, values for some insoluble salts, at 25 °C, are listed in Table 4.1.

Table 4.1

salt	K_{sp}
$Ag_2C_2O_4$	1.1×10^{-12}
CaC_2O_4	2.7×10^{-9}
$Zn(OH)_2$	2.0×10^{-17}

(a)   Write an expression for the K_{sp}, of $Ag_2C_2O_4$ giving its units.

.... [1]

(b)   Deduce whether $Ag_2C_2O_4$ is more or less soluble than CaC_2O_4. Show any working clearly.

[2]

(c)   Describe and explain how the solubility of CaC_2O_4 is affected by adding $CaCl_2(aq)$.

....

....

.... [1]

(d)   Describe and explain with the aid of equations, how the solubility of $Zn(OH)_2$ is affected by adding excess $NaOH(aq)$.

....

....

....

....

.... [2]

[Total: 6]

BLANK PAGE

5 Tulobuterol is a drug used in the management of asthma.

It can be produced in three steps as shown in Fig. 5.1
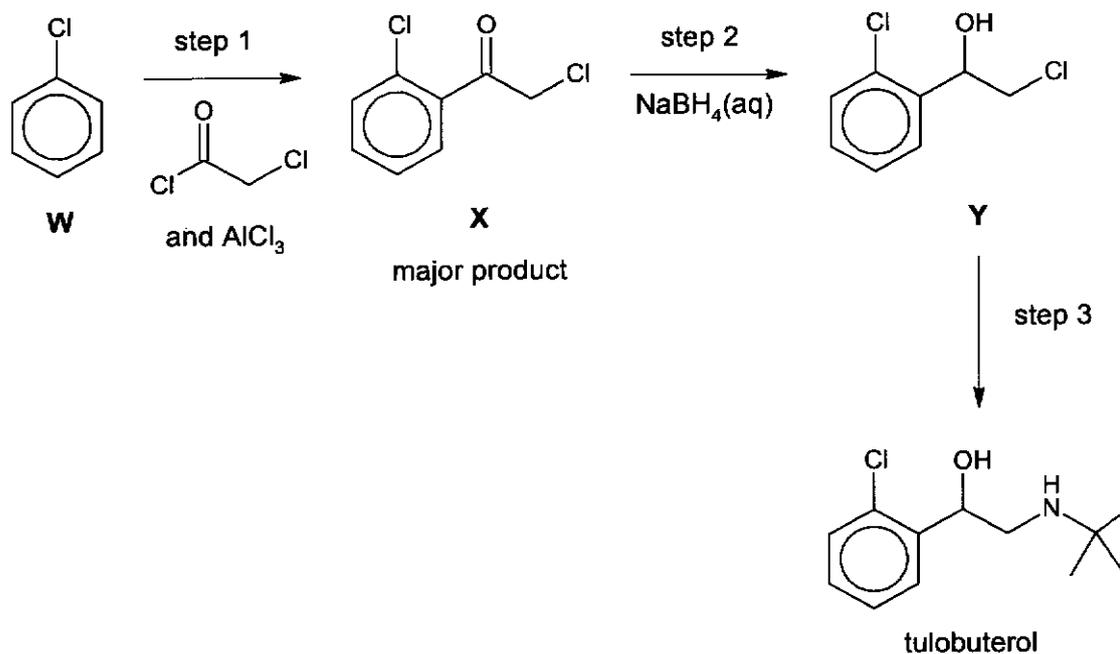
Fig. 5.1

(a) **(i)** ClCOCH$_2$Cl used in step 1 can be formed by reacting HOCOCH$_2$OH with an excess of SOCl$_2$.

Write an equation for this reaction.

.... [1]

(ii) Explain why step 1 forms the isomer shown in Fig. 5.1 as the major product, and the isomer shown in Fig. 5.2 as the minor product.
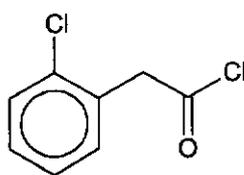
Fig. 5.2

....

....

.... [1]

(b) **(i)** The reaction between **X** and aqueous sodium borohydride in step 2 is a nucleophilic addition reaction.

Draw the mechanism for this reaction, assuming that sodium borohydride produces the hydride ion, $:H^-$, as the reacting species.

[3]

(ii) Many drug molecules are chiral but are often produced as a mixture of enantiomers.

Suggest, in terms of the mechanism of step 2, and the shape of molecule **X**, why tulobuterol does not rotate the plane of polarised light.

....

....

....

....

....

.... [2]

(iii)   Suggest a problem that might arise as a result of producing drug molecules as a mixture of enantiomers.

....

.... [1]

(c)   (i)   Suggest reagents and conditions for step 3.

.... [1]

(ii)   Explain why step 3 proceeds mainly via an S_N2 mechanism rather than an S_N1 mechanism.

....

....

....

....

....

.... [2]

[Total: 11]

BLANK PAGE

[Turn Over

6   Phenol can be made by first reacting phenylamine and nitrosonium ion, NO^+ to produce a diazonium salt. NO^+ is formed in situ from nitrous acid, HNO_2, and concentrated hydrochloric acid, HCl. The diazonium salt then undergoes hydrolysis with water in the presence of copper salts to form phenol.

diazonium salt

(a)   Step I of the reaction to obtain diazonium salt from phenylamine proceeds via the following mechanism shown in Fig. 6.1.

Fig. 6.1

(i)   The intermediate ion formed in Fig. 6.1 can be represented by two different structures, X and Y. The arrow ↔ indicates that the actual structure of the intermediate ion is somewhere in between these two structures, with the positive charge dispersed over N_1, N_2 and O atoms.

Suggest how dispersion of charge occurs in the intermediate ion. You may find it helpful to draw a diagram in your answer.

....

....

....

[2]

[Turn Over

(ii) Suggest why **Y** is considered to most closely resemble the actual structure of the intermediate ion.

....

....

....[1]

(b) In step II of the reaction, the diazonium salt reacted with copper(I) oxide in an aqueous solution of copper(II) nitrate to form phenol. This diazonio replacement reaction is believed to occur through homolytic fission instead of heterolytic fission of C–N bond.

(i) Explain what is meant by *heterolytic fission of C–N bond*.

....

....

....[1]

(ii) Suggest the different organic products formed after the C–N bond in diazonium salt undergoes homolytic and heterolytic fission respectively.

product after homolytic fission	product after heterolytic fission

[2]

(c) Compound **G**, a phenolic ester, can be formed from benzene via a 5-step synthesis.
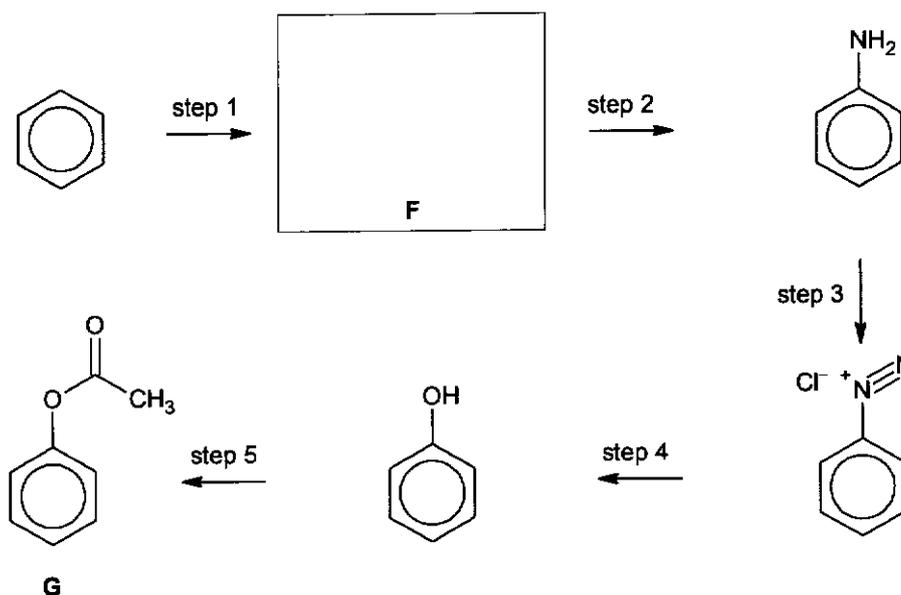
Fig. 5.2

(i) Step 1 is an electrophilic substitution reaction. Explain why benzene undergoes substitution reactions.

....

....

....[1]

(ii) Draw the structure of the intermediate **F** in the box above. [1]

(iii) Suggest the reagents and conditions for steps 1, 2 and 5.

step 1 ....

step 2 ....

step 5 ....[2]

(iv) In a reaction discovered just over 100 years ago by German chemist Karl Fries, compound **G** can be converted into compound **H** when heated with AlCl₃. Compound **H** is a constitutional isomer of **G**.

Compound **H** is a 1,4-disubstituted benzene derivative. It gives a white precipitate with Br₂(aq), and a yellow precipitate with alkaline aqueous iodine.

$AlCl_3$ → **H**

$(C_8H_8O_2)$

G

Deduce the structure of **H**.

[1]

[Total: 11]

7   It is likely that hydrogen vehicles will play a significant role in the near future. Table 7.1 shows the specifications of a hydrogen vehicle.

Table 7.1

number of tanks	2
operating pressure of a tank / MPa	70
volume of a tank / dm³	87

(a) **(i)** Use Table 7.1 to calculate the total amount of hydrogen molecules in a hydrogen vehicle under room temperature.

[1 MPa = 10^6 Pa]

[2]

(ii) Explain fully why hydrogen does not behave like an ideal gas in a tank of the hydrogen vehicle.

....

....

....

....

....

....[2]

(iii) Suggest one disadvantage for using hydrogen as an alternative source of energy.

....

....[1]
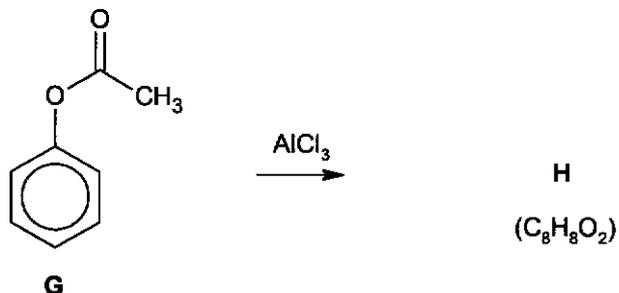
(iv) Methanol is also a possible alternative source of energy.

Write balanced equations for the combustion of methanol and hydrogen respectively. Hence, state and explain which is a cleaner source of energy.

....

....

....

....

....[2]

(b) In 2014, Jeffery Long, a chemist in University of California, Berkeley, and his colleagues reported a nickel-based Metal-Organic Framework (MOF). MOF is a class of porous polymers consisting of metal clusters coordinated to organic ligands. The organic ligands are largely made up of hydrocarbon chains.

MOF acts as a molecular sponge that could hold significant amounts of hydrogen at low pressures. Fig. 7.1 shows how a hydrogen molecule is stored in a unit of a MOF.
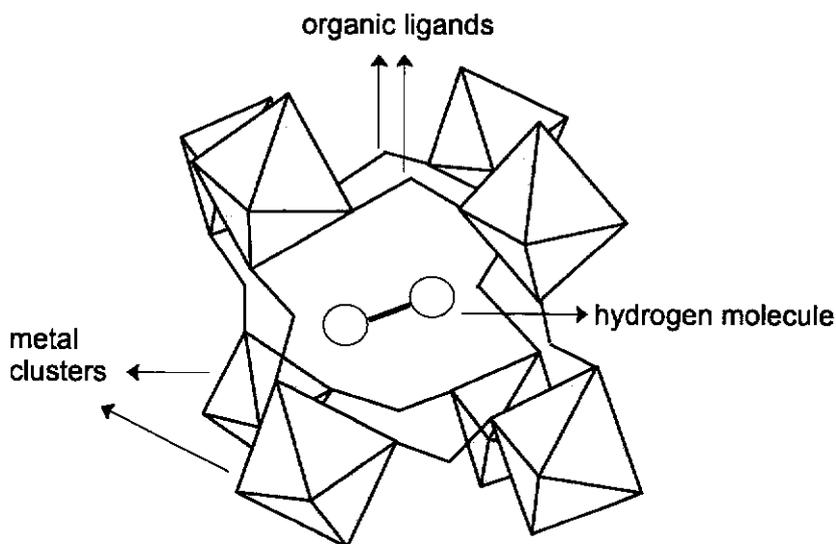
Fig. 7.1

(i) Suggest the type of bonding between MOF and hydrogen molecule. Explain your answer.

....

....

....[1]

An effective MOF not only needs to store hydrogen, it must also release hydrogen easily. Binding energy is the energy required to remove one mole of hydrogen molecules from the MOF. The ideal binding energy is between 15 to 25 kJ per mole of hydrogen molecules for hydrogen to be stored at room temperature. Below this range, the system must be cooled to prevent hydrogen from escaping the MOF. Above this range, the system must be heated to release the hydrogen from the MOF.

Table 7.2 lists some properties of a nickel-based and an aluminium-based MOFs.

Table 7.2

property	nickel-based MOF	aluminium-based MOF
binding energy	14 kJ mol^{-1}	8.6 kJ mol^{-1}
cost of 1 kg of MOF	$20	$2
mass of hydrogen stored per m^3	23 kg m^{-3}	15 kg m^{-3}

(ii)   Use the information in Table 7.2 to suggest whether aluminium-based MOF is a viable alternative to nickel-based MOF for hydrogen storage. Explain your answer.

....

....

....

....

....[2]

(c)   Hydrogen is also used as a fuel in hydrogen-oxygen fuel cells. A typical hydrogen-oxygen fuel cell is shown in Fig. 7.2.

H_2O

negative electrode ————— ⌐⌐ ↑↑ ⌐————— positive electrode

gas in ⇒   ⇐ gas in

concentrated NaOH in a hydroxide ion selective membrane
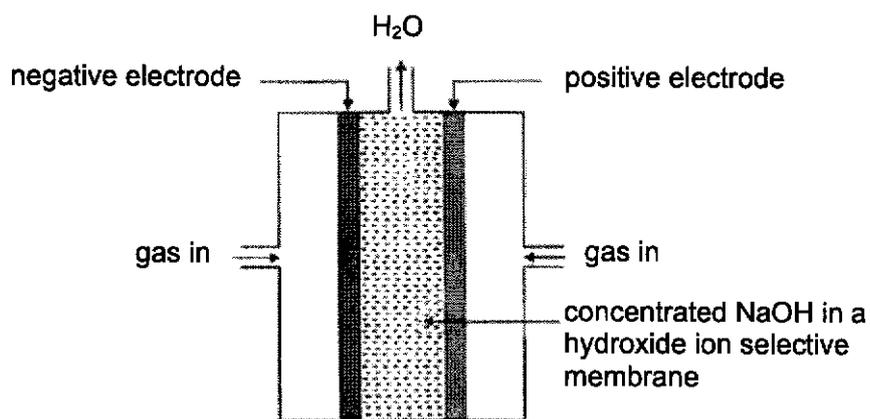
Fig. 7.2

(i)   Write balanced half-equations to show the reactions occurring in a hydrogen-oxygen fuel cell.

electrode	half-equation
negative	
positive	

Hence, explain why the pH of the electrolyte remains constant.

....

....

....[2]

(ii) Based on your answer in (c)(i), calculate the $E^\ominus_{cell}$ for the hydrogen-oxygen fuel cell.

[1]

(d) When electricity produced is more than what is required, the excess electricity can be stored to prevent wastage. An iron redox flow cell is one method to store electrical energy. It employs Fe(II)/Fe(III) and Fe(II)/Fe redox couples for the positive and negative half-cells respectively.

Stored electrical energy can be discharged when needed. During discharging, the following reactions occur.

Positive half-cell: $Fe^{3+}(aq) + e^- \downarrow Fe^{2+}(aq)$

Negative half-cell: $Fe(s) \downarrow Fe^{2+}(aq) + 2e^-$

(i) Write the overall balanced equation when the iron redox flow cell is charging.

Hence, suggest the observations at the respective half-cells during charging.

....

....

....

....**[3]**

(ii) In 1 hour of charging, 6100 C of electricity was delivered to the iron redox flow cell.

The Fe at the negative half-cell is then washed and dried. The change in mass of Fe is 1.740 g.

Using your answer in **(d)(i)**, calculate the change in mass of Fe at the negative half-cell during 1 hour of charging, assuming that the process is 100% efficient. Compare this theoretical value with the actual value and comment on the efficiency of the charging process.

[2]

(iii) The iron redox flow cell functions at an optimal pH value of 3. Otherwise, side products will be produced.

Suggest a possible side product for each of the following pH values of the electrolyte when the iron redox flow cell is charging.

	side product
pH 1	
pH 13	

[2]

(iv) When the concentrations of the ions in the electrolyte are not 1.0 mol dm^{-3}, the potential, E, of a half-cell can be calculated using equation 7.1.

equation 7.1 $E = E^{\ominus} + \left(\dfrac{0.0592}{n}\right) \lg \dfrac{[oxid]}{[red]}$

n = number of electrons transferred during the electrode reaction
[oxid] = the concentration of the oxidised species
[red] = the concentration of the reduced species

The concentration of Fe^{2+} ions in each half cell in a fully discharged iron redox flow cell is 2 mol dm^{-3}. The two half-cells are separated by a cation-selective membrane.

Use equation 7.1 to calculate the potential of each half-cell, and hence the total cell potential, when 80% of Fe^{2+} ions at the positive half-cell is converted during charging. You may assume the concentration of Fe to have a constant value of 1.

[2]

[Total: 22]
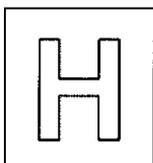
NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE
NAME

CLASS

CHEMISTRY

Paper 2 Structured

9729/02

9 September 2024

2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class in the spaces at the top of this page.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, 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.

For Examiner's Use	
1	/12
2	/7
3	/6
4	/6
5	/11
6	/11
7	/22
Total	**/75**

This document consists of **21** printed pages and **2** blank pages.

[Turn over

1(a) The Periodic Table usually shows hydrogen on its own and not a member of a group.

(i) Suggest why the element hydrogen could be placed at the top of Group 1.

Hydrogen atom has <u>one valence electron</u> and it has a <u>smaller number of protons</u>

<u>than lithium</u>..[1]

(ii) Suggest why the element hydrogen is **not** placed at the top of Group 1, in terms of
- its structure
- one physical property related to its structure

Hydrogen has a <u>simple molecular structure</u> with weak instantaneous dipole – induced dipole interaction between the molecules, while Group I elements have a <u>giant metallic structure</u> with strong metallic bonds between the metallic cations and sea of delocalised valence electrons. [1] (Difference in structure of hydrogen and Group I elements)

The <u>sea of delocalised valence electrons</u> in Group I elements act as <u>mobile charge carriers</u> to <u>conduct electricity</u>, while <u>hydrogen does not contain mobile charged carriers /electrons are localized in covalent bonds. Hence does not conduct electricity.</u> [1] (Difference in Physical property for hydrogen and Group I elements, accept other physical properties like mpt/bpt etc)

....[2]

The trihydrogen complex cation, H_3^+, was first discovered in 1911 when J.J. Thomson was performing his cathode ray tube experiments. In 1989, H_3^+ was detected in the ionosphere of Jupiter.

H_3^+ is mainly found in interstellar space where there is high cosmic radiation. In the presence of high energy gamma radiation, hydrogen gas can lose an electron to form H_2^+, which then reacts with molecular hydrogen to form H_3^+.

$$H_2 \rightarrow H_2^+ + e^-$$
$$H_2^+ + H_2 \rightarrow H_3^+ + H$$

(b) Describe and explain how the behaviour of beams of the ions H_2^+, H_3^+ and electrons differ in an electric field.

ion	H_2^+	H_3^+
angle of deflection $\propto \frac{charge}{mass}$	1/2	1/3
Simplest ratio	3/2	1

Both H_2^+, H_3^+ are deflected towards the negative plate. Angle of deflection of H_2^+ will be greater than that of H_3^+ (3/2 times). [1]

An electron will be deflected towards positive plate by a <u>much larger angle of deflection</u> compared to H_2^+ and H_3^+ due to the <u>much smaller</u> mass of an electron compared to a proton. [1]

[2]

(c) Given that hydrogen can exist as isotopes ^1H, ^2H and ^3H, complete Table 1.1.

Table 1.1

	number of protons	number of neutrons	number of electrons	Explanation (not required in answer)
^2H	1	1	1	each ^2H atom has 1 electron, 1 proton and 1 neutron
$^1H_2^+$	2	0	1	each ^1H atom has 1 electron, 1 proton and 0 neutrons
$^3H_3^+$	3	3 atoms x 2 = 6	2	each ^3H atom has 1 electron, 1 proton and 2 neutrons

[3]

[1] for any 3 boxes correct

(d) Describe the reactions, if any, of the chlorides NaCl, $AlCl_3$ and PCl_5 with water.
Write equations for all the reactions that occur, and suggest the pH of the resulting solutions.

Relate the reactivity of these chlorides to their structure and bonding.

1. <u>NaCl has a giant ionic lattice structure where the Na^+ and Cl^- ions are held together by strong ionic bonds.</u>
2. Hence the ions are able to form ion – dipole interactions with water, thus NaCl undergoes <u>hydration</u> to form a neutral solution of hydrated ions.
3. pH = 7
4. $NaCl(s) + aq \rightarrow Na^+(aq) + Cl^-(aq)$ [state symbols are required]
5. <u>$AlCl_3$ has simple molecular structure with weak instantaneous dipole – induced dipole interactions between the molecules.</u>
6. $AlCl_3$ has a slight ionic character, allowing it to undergo <u>hydration</u>.
7. $AlCl_3(s) + 6H_2O(l) \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$
   $[Al(H_2O)_6]^{3+}$ then undergoes <u>hydrolysis</u> to give $[Al(H_2O)_5OH]^{2+}$ (aq) (part of marking pt 6)
8. $[Al(H_2O)_6]^{3+}$ (aq) + H_2O (l) ⇌ $[Al(H_2O)_5OH]^{2+}$ (aq) + H_3O^+ (aq)
   Al^{3+} in $[Al(H_2O)_6]^{3+}$ has a small size and high charge, thus has a high charge density and is highly polarising. Thus it is able to polarise the O–H bond in H_2O, causing H^+ to be released to give an acidic solution .
9. pH ≈ 2–3
10. <u>PCl_5 has simple molecular structure with weak instantaneous dipole – induced dipole interactions between the molecules.</u>
11. PCl_5 undergoes <u>hydrolysis</u> to give a highly acidic solution and white fumes of HCl gas.
    When PCl_5 dissolves, the slightly positive P atom attracts the slightly negative O atom from water, breaking the O–H bond and releasing a H^+ to make the solution acidic.
12. pH ≈ 1– 2
13. $PCl_5(s) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 5HCl(g)$

13 marking points in total. 3-4 marking pt – 1 mark, 5-8 marking pt – 2 marks, 9-11 marking pt – 3 marks, 12-13 marking pt – 4 marks (also subjected to no major conceptual error)

....[4]

[Total: 12]

2   Ozone, O_3, is a non-linear molecule present in the Earth's upper atmosphere. It absorbs ultraviolet radiation from the Sun and so protects living organisms from this type of radiation.

(a)   (i)   Draw the dot-and-cross diagram for the ozone molecule.

$\overset{..}{\underset{.}{O}} : \underset{x}{\overset{xx}{O}} \underset{x}{\overset{}{}} \overset{..}{\underset{..}{O}} :$ [1]

[1]
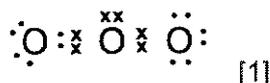
   (ii)   State one harmful consequence to a person of increased exposure to ultraviolet radiation.

uv radiation can penetrate the skin and reach the cells, resulting in <u>increased risk of skin cancer/sun burn</u>. [1]

Nitrogen oxides in aircraft emissions results in the depletion of the ozone layer. The reaction of nitrogen monoxide with ozone is given below.

$$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$$
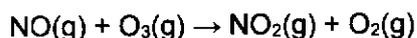
(b)   (i)   Suggest and explain the following differences between NO_2 and O_3.

- Bond angle around central atom in O_3 is smaller than that in NO_2.

There are <u>2 bond pairs and 1 lone pair around central O in O_3 while there is 1 lone electron and 2 bond pairs around N in NO_2</u>. There is <u>less repulsion between the lone electron and bond pairs</u> hence bond angle is $>120°$ (and $<180°$ since lone e exerts some repulsion vs Olp) while there is more repulsion between lone pair and bond pairs hence bond angle is $<120°$. [1]

FYI structure of NO_2: $O \overset{N}{=} O$
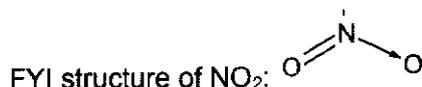
- Boiling point of O_3 is lower than that of NO_2.

Both have simple molecular structure and contains <u>permanent dipole-permanent dipole interactions</u> between polar molecule. There is a <u>larger difference in electronegativity between N and O</u> resulting in a <u>larger dipole</u>. Hence <u>more energy is needed to break</u> the <u>stronger pd-pd between NO_2 molecules</u>. [1] OR

Both have simple molecular structure. <u>NO_2 is able to dimerise</u> and form N_2O_4 which has a <u>larger electron cloud</u> that is <u>more easily polarised/more polarisable</u>. Hence <u>more energy is needed to break</u> the <u>stronger instantaneous dipole-induced dipole interactions</u> between NO_2 molecules than that between O_3 molecules. [1] OR

Both have simple molecular structure and have similar M_r. <u>Less energy is required to break the weaker instantaneous dipole-induced dipole interactions</u> between non-polar O_3 molecule compared to the <u>strong permanent dipole-permanent dipole interactions</u> between polar NO_2 molecule. [1]

(ii)   Suggest why the release of nitrogen oxides by vehicles does not affect the ozone layer.

The <u>free radicals NO/NO$_2$</u> contain an unpaired electron and are <u>highly reactive/ reacts readily with other species in the environment</u> and will not reach the ozone layer. [1]
OR

NO/NO$_2$ are reduced to non-toxic N2 in catalytic converters installed in vehicles. [1]
BOD given as aircrafts may also have similar catalytic converters too.

(c)   On the axes given below, sketch two graphs to show how pV varies with T for O$_3$ and O$_2$ respectively. Assume ideal gas behaviour for both gases and a fixed mass of gas sample is used for each gas.

pV / Pa dm^3

O$_2$

O$_3$

T / °C
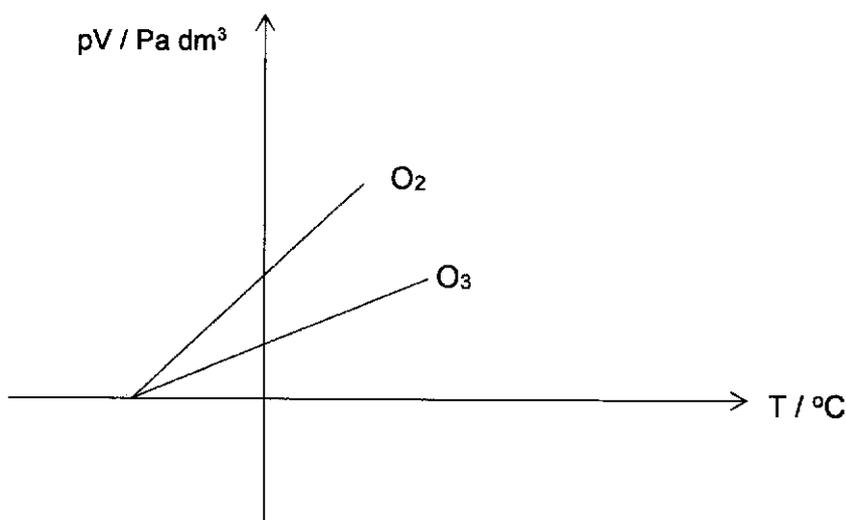
Explanation for understanding (not required in answer).

- pV = nRT = pV = $\frac{m}{M}$RT. The graph of pV against T is a linear graph: y = mx.
- When temperature is expressed in °C instead of K, the graph is shifted left as 0 K = –273 °C. The graph shouldn't have a negative pV value (BOD) as the lowest temperature is 0K. The units of V (dm^3 instead of m^3) will not affect shape of the graph.
- For a fixed mass of gas, n(O$_2$) is higher than n(O$_3$) hence the graph of O$_2$ has a higher/steeper gradient (=nR) OR gradient = $\frac{mR}{M}$ is higher for NO$_2$ that has a lower molar mass M than O$_3$.

Check in graph all 3 pts [2]. Any 2 [1]

[2]

[Total: 7]

3   In heavily polluted air, nitrogen dioxide is often formed and it appears as a brown gas with a pungent odour.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g) \qquad \Delta H < 0$$

(a) The following results in Table 3.1 were obtained from a series of experiments carried out to investigate this reaction.

Table 3.1

experiment	[NO] / mol dm^{-3}	[O$_2$] / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	1.00×10^{-3}	0.100	7.00×10^{-4}
2	2.00×10^{-3}	0.100	2.80×10^{-3}
3	3.00×10^{-3}	0.200	1.26×10^{-2}

(i) Deduce the order of reaction with respect to each reactant by showing your working clearly and hence write the rate equation for the reaction.

Comparing Expt 1 & 2,
When [NO] increased by 2 times or doubles ($2.00 \times 10^{-3}/1.00 \times 10^{-3} = 2$), the initial rate increases by 4 times ($2.80 \times 10^{-3}/7.00 \times 10^{-4} = 4$).
Rate is directly proportional to [NO]^2
Hence, the reaction is <u>second order</u> of reaction with respect to <u>NO</u>. [1]

Let the rate equation be rate = k [NO]^2[O$_2$]^n
Comparing Expt 2 & 3,

$$\frac{2.80 \times 10^{-3}}{1.260 \times 10^{-2}} = \frac{k(2.00 \times 10^{-3})^2(0.100)^n}{k(3.00 \times 10^{-3})^2(0.200)^n}$$

$$\frac{2}{9} = (\frac{4}{9})(\frac{1}{2})^n$$

$$\frac{1}{2} = (\frac{1}{2})^n$$

$n = 1$
Hence, the reaction is first order of reaction with respect to O$_2$. [1]

$\therefore$ rate equation is   rate = k [NO]^2[O$_2$]   **[1]**

....

....

....

....

....

.... [3]

(ii) Suggest, with reasoning, how the value of the rate constant, k, will be a⁓ ˙ ˙ ˙ ⁓
gases get cooler in the upper part of the atmosphere.

[Turn Over

When the gases get cooler in the upper part of the atmosphere means that there is a <u>decrease in temperature</u>. The <u>rate</u> of reaction will <u>decrease</u> since concentration remains constant hence <u>rate constant, k</u> also <u>decreased</u>. [1]
Or

From the <u>Arrhenius equation</u> ($k = Ae^{-\frac{E_a}{RT}}$), when <u>temperature decreases</u>, the value of <u>k decreases</u> exponentially, hence decreasing the rate greatly. [1]

....[1]

(b)   The removal of NO_2 is important because it has significant environmental consequences if emitted into the atmosphere.

Describe and explain with the aid of suitable equations, the role of NO_2 in the oxidation of atmospheric sulfur dioxide.

NO_2 functions as a homogeneous <u>catalyst</u> as it is in the same phase as the gaseous reactants (SO_2) and products (SO_3 and NO).

Step 1: $SO_2 + NO_2 \rightarrow SO_3 + NO$
Step 2: $NO + \frac{1}{2}O_2 \rightarrow NO_2$
Overall: $SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$
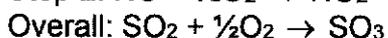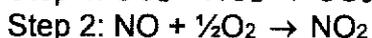
Role + step 1 + step 2 eqns: 2 marks
Role + step 1 or step 2 eqn: 1 mark

....

....

....

....

....[2]

[Total: 6]

4 The solubility product, K_{sp}, values for some insoluble salts, at 25 °C, are listed in Table 4.1.

Table 4.1

salt	K_{sp}
$Ag_2C_2O_4$	1.1×10^{-12}
CaC_2O_4	2.7×10^{-9}
$Zn(OH)_2$	2.0×10^{-17}

(a) Write an expression for the K_{sp}, of $Ag_2C_2O_4$ giving its units.

$Ag_2C_2O_4(s) \rightleftharpoons 2Ag^+(aq) + C_2O_4{}^{2-}(aq)$ ....

$K_{sp} = [Ag^+]^2[C_2O_4{}^{2-}] \ mol^3 \ dm^{-9}$ [1]...[1]

(b) Deduce whether $Ag_2C_2O_4$ is more or less soluble than CaC_2O_4. Show any working clearly.

Let solubility of $Ag_2C_2O_4$ be x mol dm^{-3}
$K_{sp} = [Ag^+]^2[C_2O_4{}^{2-}]$
$1.1 \times 10^{-12} = (2x)^2(x)$
$1.1 \times 10^{-12} = 4x^3$
$x = 6.502 \times 10^{-5}$ mol dm^{-3}
$\approx 6.50 \times 10^{-5}$ mol dm^{-3}

Let solubility of CaC_2O_4 be y mol dm^{-3}
$K_{sp} = [Ca^{2+}][C_2O_4{}^{2-}]$
$2.7 \times 10^{-9} = (y)(y)$
$2.7 \times 10^{-9} = y^2$
$y = 5.196 \times 10^{-5}$ mol dm^{-3}
$\approx 5.20 \times 10^{-5}$ mol dm^{-3}

$Ag_2C_2O_4$ is <u>more soluble</u> than CaC_2O_4.

[2]: both correct calculations + correct conclusion
[1]: 1 correct calculation + correct conclusion

[2]

(c) Describe and explain how the solubility of CaC_2O_4 is affected by adding $CaCl_2(aq)$.

The solubility of $CaC_2O_4(s)$ will <u>decrease</u>. Due to the addition of <u>common ion Ca^{2+}</u>, the <u>position of equilibrium</u> $CaC_2O_4(s) \rightleftharpoons Ca^{2+}(aq) + C_2O_4{}^{2-}(aq)$ will shift to the <u>left</u> to removed the added Ca^{2+}. [1]

....[1]

(d) Describe and explain with the aid of equations, how the solubility of $Zn(OH)_2$ is affected by adding excess $NaOH(aq)$.
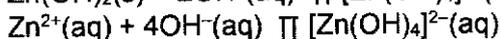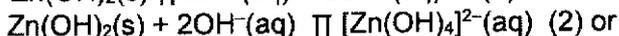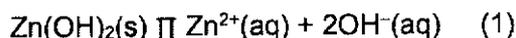
$Zn(OH)_2(s) \rightleftharpoons Zn^{2+}(aq) + 2OH^-(aq)$ (1)
$Zn(OH)_2(s) + 2OH^-(aq) \rightleftharpoons [Zn(OH)_4]^{2-}(aq)$ (2) or
$Zn^{2+}(aq) + 4OH^-(aq) \rightleftharpoons [Zn(OH)_4]^{2-}(aq)$
The solubility of $Zn(OH)_2$ will <u>increase</u>. The <u>formation of soluble complex</u> [1],
$[Zn(OH)_4]^{2-}(aq)$ causes the concentration of $Zn^{2+}(aq)$ in (1) to decrease
By Le Chatelier's Principle, the position of equilibrium will shift right to compensate the decrease in $[Zn^{2+}(aq)]$ hence $Zn(OH)_2$ is more soluble.

....[2]

[Total: 6]

2 equations + explanation: 2 marks

[Turn Over

2 equations or 1 equation + explanation: 1 mark

....

....

....

....

.... [2]

[Total: 6]

BLANK PAGE

5   Tulobuterol is a drug used in the management of asthma.

It can be produced in three steps as shown in Fig. 5.1

Fig. 5.1

(a)   **(i)**   ClCOCH$_2$Cl used in step 1 can be formed by reacting HOCOCH$_2$OH with an excess of SOCl$_2$.

Write an equation for this reaction.

HOCOCH$_2$OH + 2SOCl$_2$ → ClCOCH$_2$Cl + 2SO$_2$ + 2HCl [1]
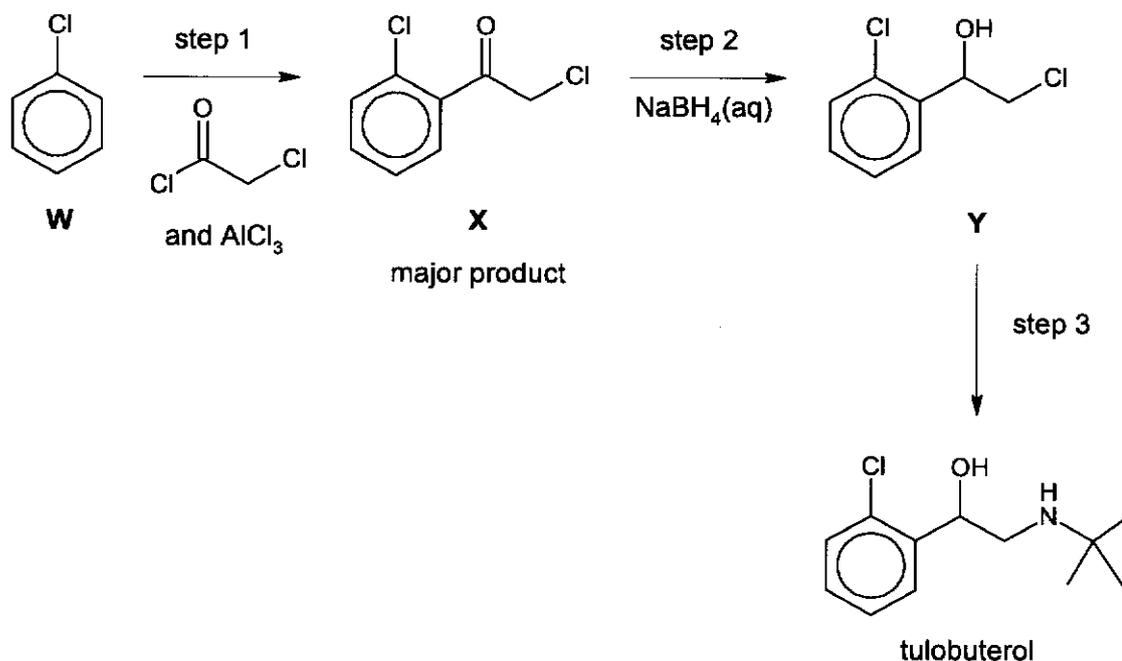
(ii)   Explain why step 1 forms the isomer shown in Fig. 5.1 as the major product, and the isomer shown in Fig. 5.2 as the minor product.
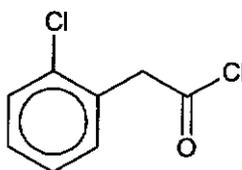
Fig. 5.2

• C atom in –COCl is attached to two highly electronegative atoms, O and Cl while C atom in C–Cl is attached to only one electronegative atom, Cl.
• C atom in –COCl is more electron deficient (i.e. carries a larger partial positive charge δ+) than C atom in C–Cl.

[1]

Or

 is more likely to form than as an electrophile

- as is more stable than

- and will attack the π electron ring system in benzene.

....

....

.... [1]

....

(b) **(i)** The reaction between **X** and aqueous sodium borohydride in step 2 is a nucleophilic addition reaction.

Draw the mechanism for this reaction, assuming that sodium borohydride produces the hydride ion, :H⁻ , as the reacting species.
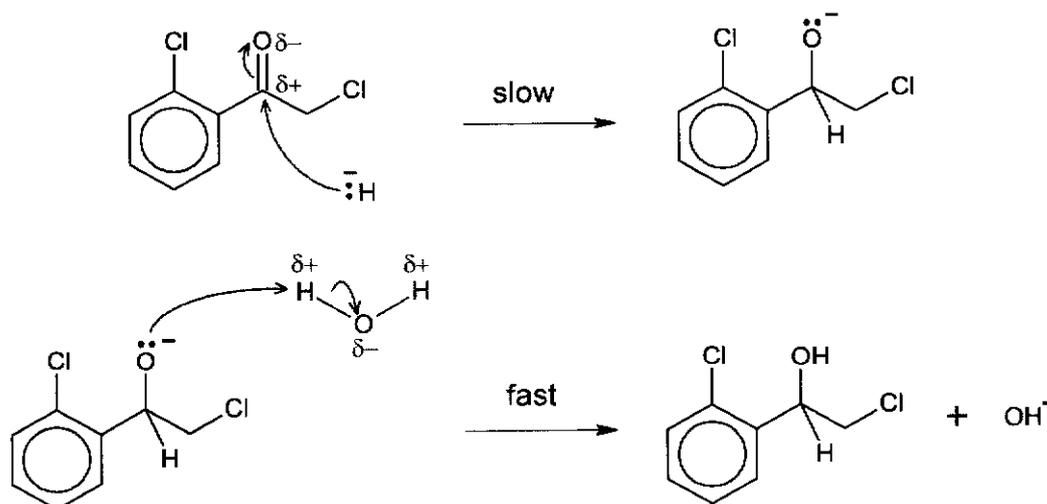
- labelling of slow step
- partial charges and lone pair
- correctly drawn intermediate
- curly arrows in both steps
- balanced equations

(2 points – 1 mark; 3 to 4 points – 2 marks; 5 points – 3 marks)

[3]

(ii) Many drug molecules are chiral but are often produced as a mixture of enantiomers.

Suggest, in terms of the mechanism of step 2, and the shape of molecule **X**, why tulobuterol does not rotate the plane of polarised light.

The carbonyl carbon in **X** is sp² hybridised and trigonal planar.
The H⁻ nucleophile can attack this electron deficient carbonyl carbon from either above or below the plane in equal probabilities yielding equal quantities of both enantiomers. Thus the product mixture is racemic. [1]

Tulobuterol is optically inactive and unable to rotate plane-polarised light as each enantiomer rotates light in the opposite direction by the same magnitude hence their rotating powers cancel out. [1]

....

.... [2]

(iii) Suggest a problem that might arise as a result of producing drug molecules as a mixture of enantiomers.

One enantiomer may cause harm or side effects to the body.
Drug has lower biological efficiency.
Larger dose is required as drug is less potent.
Any one [1]

....

.... [1]

(c) **(i)** Suggest reagents and conditions for step 3.

H_2N
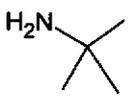
ethanolic / C(CH₃)₃NH₂ / 2-methylpropan-2-amine , heat under reflux [1]

.... [1]

(ii) Explain why step 3 proceeds mainly via an S$_N$2 mechanism rather than an S$_N$1 mechanism.

- Step 3 involves a primary alkyl halide.
- It can undergoes S$_N$2 mechanism since there is little steric hindrance around the electron deficient (δ+) carbon as it is attached to only 1 bulky group and hence the nucleophile can attack the electron deficient (δ+) carbon readily.
- There is absence of multiple electron donating alkyl groups that stabilise the carbocation intermediate, thus S$_N$1 mechanism is not favoured.
3● for [2] and 2● for [1]

....

.... [2]

[Total: 11]

BLANK PAGE

[Turn Over

6   Phenol can be made by first reacting phenylamine and nitrosonium ion, NO⁺ to produce a diazonium salt. NO⁺ is formed in situ from nitrous acid, HNO₂, and concentrated hydrochloric acid, HCl. The diazonium salt then undergoes hydrolysis with water in the presence of copper salts to form phenol.

diazonium salt

(a)   Step I of the reaction to obtain diazonium salt from phenylamine proceeds via the following mechanism shown in Fig. 6.1.

Fig. 6.1

(i)   The intermediate ion formed in Fig. 6.1 can be represented by two different structures, X and Y. The arrow ↔ indicates that the actual structure of the intermediate ion is somewhere in between these two structures, with the positive charge dispersed over N₁, N₂ and O atoms.

Suggest how dispersion of charge occurs in the intermediate ion. You may find it helpful to draw a diagram in your answer.

....

In X, the nitrogen atom directly bonded to the benzene ring, N₁ (is sp² hybridised) has its lone pair of electrons in its unhybridised p orbital. This p orbital overlap sideways with the π orbital/π e cloud of N₂=O resulting in the delocalisation of the lone pair of electrons on N₁ into the π orbital across N₂=O, hence the charge on O atom is dispersed over both N₁, N₂ and O. [1]

or

[1]
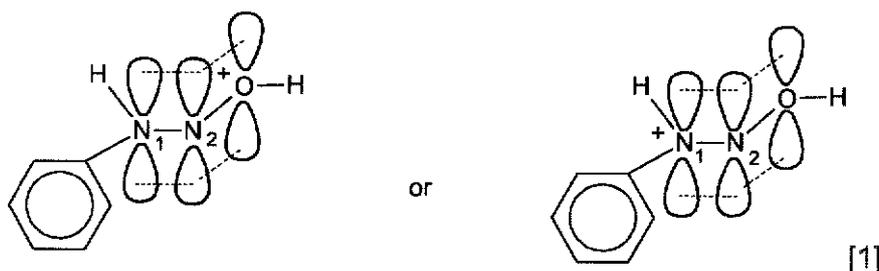
[2]

(ii) Suggest why **Y** is considered to most closely resemble the actual structure of the intermediate ion.

N atom is less electronegative than O atom. Hence, more likely for the positive charge to reside on the N atom, increasing the stability the intermediate ion Y.
Or
N atom is less electronegative than O atom. Positive change residing on O atom decrease the stability of intermediate ion X.

....

....[1]

(b) In step II of the reaction, the diazonium salt reacted with copper(I) oxide in an aqueous solution of copper(II) nitrate to form phenol. This diazonio replacement reaction is believed to occur through homolytic fission instead of heterolytic fission of C–N bond.

(i) Explain what is meant by *heterolytic fission of C–N bond*.

When the covalent bond breaks, the more electronegative N atom takes both of the bonding electrons to form an anion, leaving a carbocation present in diazonium salt.

....[1]

(ii) Suggest the different organic products formed after the C–N bond in diazonium salt undergoes homolytic and heterolytic fission respectively.

product after homolytic fission	product after heterolytic fission

[2]

(c) Compound **G**, a phenolic ester, can be formed from benzene via a 5-step synthesis.
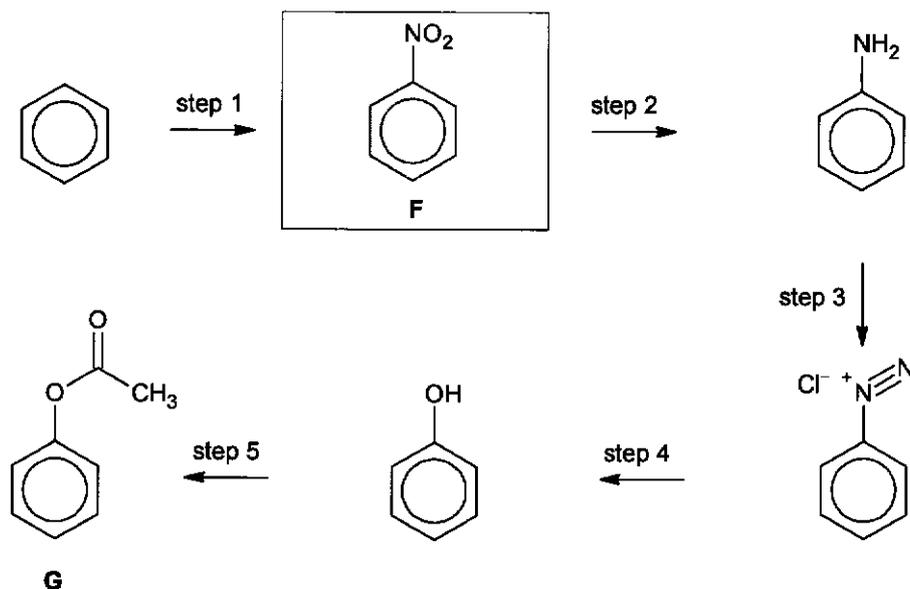
Fig. 5.2

(i) Step 1 is an electrophilic substitution reaction. Explain why benzene undergoes substitution reactions.

Benzene undergoes substitution reaction to <u>maintain the ring of delocalised π electrons, hence retaining its aromatic stability</u>.

.... [1]

(ii) Draw the structure of the intermediate **F** in the box above.   [1]

(iii) Suggest the reagents and conditions for steps 1, 2 and 5.

step 1 conc. H_2SO_4, conc. HNO_3, 55 °C (accept heat) ....

step 2 Sn, conc. HCl, heat under reflux, followed by NaOH(aq), room temperature ...

step 5 CH_3COCl, room temperature.. [2]

[2] 3 correct R&C
[1] 2 correct R&C

(iv) In a reaction discovered just over 100 years ago by German chemist Karl Fries, compound **G** can be converted into compound **H** when heated with AlCl₃. Compound **H** is a constitutional isomer of **G**.

Compound **H** is a 1,4-disubstituted benzene derivative. It gives a white precipitate with Br₂(aq), and a yellow precipitate with alkaline aqueous iodine.

Deduce the structure of H.
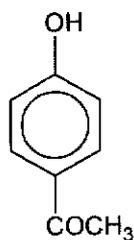
[1]

[Total: 11]

[Turn Over

7   It is likely that hydrogen vehicles will play a significant role in the near future. Table 7.1 shows the specifications of a hydrogen vehicle.

Table 7.1

number of tanks	2
operating pressure of a tank / MPa	70
volume of a tank / dm³	87

(a)   (i)   Use Table 7.1 to calculate the total amount of hydrogen molecules in a hydrogen vehicle under room temperature.

[1 MPa = 10^6 Pa]

pV = nRT
$(70 \times 10^6)(87/1000) = n \times 8.31 \times 293$
n = 2501 mol (amount of H_2 in one tank) [1]

total amount of H_2 in a car (i.e. 2 tanks) = 2501 × 2 = 5002 mol [1]

[2]

(ii)   Explain fully why hydrogen does not behave like an ideal gas in a tank of the hydrogen vehicle.

Due to high pressure, there are <u>significant intermolecular forces of attraction between hydrogen molecules</u> as they are closer to one another. [1]

Therefore, the <u>volume of the hydrogen gas molecules is significant</u> (not negligible) <u>compared to the volume of the container.</u> [1]

....

....

....

....

....[2]

(iii)   Suggest one disadvantage for using hydrogen as an alternative source of energy.

Disadvantage: Hydrogen makes it highly flammable/explosive.
Or
The tanks have high maintenance cost to withstand high pressure. [1]

....

....[1]

(iv) Methanol is also a possible alternative source of energy.

Write balanced equations for the combustion of methanol and hydrogen respectively. Hence, state and explain which is a cleaner source of energy.

$2CH_3OH + 3O_2 \rightarrow 2CO_2 + 4H_2O$
$2H_2 + O_2 \rightarrow 2H_2O$ [1]
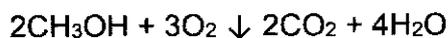
Hydrogen is a better alternative as it combusts to produce water which is a non-pollutant while methanol combusts to produce carbon dioxide which is a greenhouse gas. [1]

....

....[2]

(b) In 2014, Jeffery Long, a chemist in University of California, Berkeley, and his colleagues reported a nickel-based Metal-Organic Framework (MOF). MOF is a class of porous polymers consisting of metal clusters coordinated to organic ligands. The organic ligands are largely made up of hydrocarbon chains.

MOF acts as a molecular sponge that could hold significant amounts of hydrogen at low pressures. Fig. 7.1 shows how a hydrogen molecule is stored in a unit of a MOF.
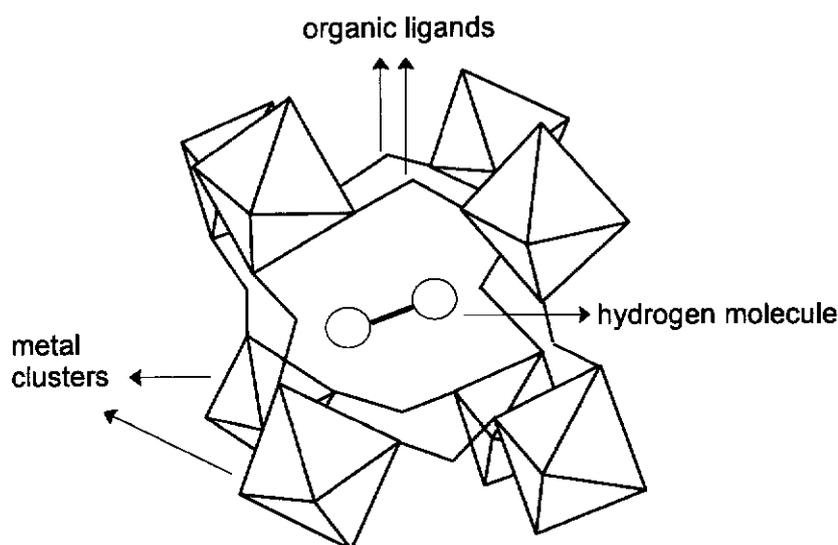

Fig. 7.1

(i) Suggest the type of bonding between MOF and hydrogen molecule. Explain your answer.

MOF is largely non-polar due to its hydrocarbon chains. Hence, there is instantaneous dipoles – induced dipoles forces of attraction between MOF and the non-polar hydrogen molecule. [1]

....

....[1]

An effective MOF not only needs to store hydrogen, it must also release hydrogen easily. Binding energy is the energy required to remove one mole of hydrogen molecules from the MOF. The ideal binding energy is between 15 to 25 kJ per mole of hydrogen molecules for hydrogen to be stored at room temperature. Below this range, the system must be cooled to prevent hydrogen from escaping the MOF. Above this range, the system must be heated to release the hydrogen from the MOF.

Table 7.2 lists some properties of a nickel-based and an aluminium-based MOFs.

Table 7.2

property	nickel-based MOF	aluminium-based MOF
binding energy	14 kJ mol⁻¹	8.6 kJ mol⁻¹
cost of 1 kg of MOF	$20	$2
mass of hydrogen stored per m³	23 kg m⁻³	15 kg m⁻³

(ii) Use the information in Table 7.2 to suggest whether aluminium-based MOF is a viable alternative to nickel-based MOF for hydrogen storage. Explain your answer.

- As the <u>binding energy for aluminium-based MOF is lower (1.6 times lower) than that of nickel-based MOF, higher cost will be incurred to continuously cool down the tanks</u> to prevent the release of hydrogen from MOF.
- It also <u>stores less (1.5 times lesser) mass of hydrogen per m³</u>.
- Hence, aluminium-based MOF <u>may not be a viable alternative</u> to nickel-based MOF for hydrogen storage.

Or

- As the <u>binding energy for aluminium-based MOF is slightly lower (1.6 times lower) than that of nickel-based MOF, higher cost will be incurred to continuously cool down the tanks</u> to prevent the release of hydrogen from MOF. Or It also <u>stores</u> 1.5 times <u>less mass of hydrogen per m³</u>.
- However, <u>it costs</u> 10 times <u>much cheaper</u>. Hence, <u>overall cost may be much lower</u>.
- Hence, aluminium-based MOF <u>could be used as a viable alternative</u> to nickel-based MOF for hydrogen storage.

3 points – [2]; 2 points – [1]

....

....

....

....

....[2]

(c) Hydrogen is also used as a fuel in hydrogen-oxygen fuel cells. A typical hydrogen-oxygen fuel cell is shown in Fig. 7.2.

H_2O

negative electrode ----- positive electrode

gas in ===> <=== gas in

concentrated NaOH in a
hydroxide ion selective
membrane

Fig. 7.2

(i) Write balanced half-equations to show the reactions occurring in a hydrogen-oxygen fuel cell.

electrode	half-equation
negative	$H_2 + 2OH^- \downarrow 2H_2O + 2e^-$
positive	$O_2 + 2H_2O + 4e^- \downarrow 4OH^-$

[1]

Hence, explain why the pH of the electrolyte remains constant.

Since the amount of electrons (4 mol) transferred must be the same for both half-cells, there will be no net change in the amount of OH^-. Hence, there is no net change to the concentration of OH^-, causing the pH to remain constant.
Or
$2H_2 + O_2 \rightarrow 2H_2O$
OH^- is not present in the above overall equation. Hence, there is no net change to the concentration of OH^-, causing the pH to remain constant. [1]
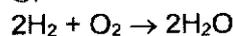
....

....

....[2]

(ii) Based on your answer in **(c)(i)**, calculate the $E^{\ominus}_{cell}$ for the hydrogen-oxygen fuel cell.

$E^{\ominus}_{cell} = (+0.40) - (-0.83) = +1.23 \text{ V}$ [1]

[1]

[Turn Over

(d) When electricity produced is more than what is required, the excess electricity can be stored to prevent wastage. An iron redox flow cell is one method to store electrical energy. It employs Fe(II)/Fe(III) and Fe(II)/Fe redox couples for the positive and negative half-cells respectively.

Stored electrical energy can be discharged when needed. During discharging, the following reactions occur.
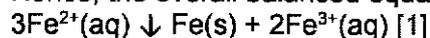
Positive half-cell: $Fe^{3+}(aq) + e^- \downarrow Fe^{2+}(aq)$

Negative half-cell: $Fe(s) \downarrow Fe^{2+}(aq) + 2e^-$

(i) Write the overall balanced equation when the iron redox flow cell is charging.

Hence, suggest the observations at the respective half-cells during charging.

During charging:
Positive half-cell: $Fe^{2+}(aq) \downarrow Fe^{3+}(aq) + e^-$ (x2)
Negative half-cell: $Fe^{2+}(s) + 2e^- \downarrow Fe(aq)$
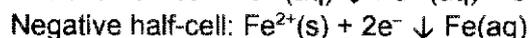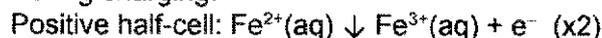
Hence, the overall balanced equation is
$3Fe^{2+}(aq) \downarrow Fe(s) + 2Fe^{3+}(aq)$ [1]

At the positive half-cell, the electrolyte will change from pale green to yellow. [1]
At the negative half-cell, the black solid of iron metal will be deposited on the electrode. [1]

....

....[3]

(ii) In 1 hour of charging, 6100 C of electricity was delivered to the iron redox flow cell.

The Fe at the negative half-cell is then washed and dried. The change in mass of Fe is 1.740 g.

Using your answer in **(d)(i)**, calculate the change in mass of Fe at the negative half-cell during 1 hour of charging, assuming that the process is 100% efficient. Compare this theoretical value with the actual value and comment on the efficiency of the charging process.

- $Q = n_{e-} \times F$
  $6100 = n_{e-} \times 96500$
  $n_{e-} = 0.06321$ mol
- $n(Fe) = \frac{1}{2} \times n_{e-} = \frac{1}{2} \times 0.06321 = 0.03160$ mol
- Change in $m(Fe) = 0.03160 \times 55.8 = 1.763$ g
- Efficiency of the charging process $= \frac{1.740}{1.763} \times 100\% = 98.7\%$
  Hence, the charging process is considered to be efficient.

4 points – [2]; 2 points – [1]

[2]

(iii) The iron redox flow cell functions at an optimal pH value of 3. Otherwise, side products will be produced.

Suggest a possible side product for each of the following pH values of the electrolyte when the iron redox flow cell is charging.

	side product
pH 1	H_2 [1]
pH 13	O_2 or $Fe(OH)_2$ or $Fe(OH)_3$ [1]

[2]

(iv) When the concentrations of the ions in the electrolyte are not 1.0 mol dm^{-3}, the potential, E, of a half-cell can be calculated using equation 7.1.

equation 7.1 $\qquad E = E^{\ominus} + \left(\dfrac{0.0592}{n}\right) \lg \dfrac{[oxid]}{[red]}$

n = number of electrons transferred during the electrode reaction
[oxid] = the concentration of the oxidised species
[red] = the concentration of the reduced species

The concentration of Fe^{2+} ions in each half cell in a fully discharged iron redox flow cell is 2 mol dm^{-3}. The two half-cells are separated by a cation-selective membrane.

Use equation 7.1 to calculate the potential of each half-cell, and hence the total cell potential, when 80% of Fe^{2+} ions at the positive half-cell is converted during charging. You may assume the concentration of Fe to have a constant value of 1.

Reaction during charging: $3Fe^{2+} \rightarrow Fe + 2Fe^{3+}$

When the cell is 80% of Fe^{2+} ions is converted at the positive half-cell (anode), 20% Fe^{2+} remains and 80% is converted to Fe^{3+}.

At the positive half-cell (i.e. anode during charging so oxidation taking place):

Conc./mol dm^{-3}	$2Fe^{2+}$	$\rightarrow$	$2Fe^{3+}$	+	$2e^-$
Initial	2		0		0
Change	-0.8×2		+0.8×2		+0.8×2
Final	0.4		1.6		1.6

$E = E_1 + \left(\dfrac{0.0592}{n}\right) \log \dfrac{[Fe^{3+}]}{[Fe^{2+}]} = +0.77 + \left(\dfrac{0.0592}{1}\right) \lg\dfrac{1.6}{0.4} = +0.8056$ V

At the negative half-cell (i.e. cathode during charging so reduction taking place):

Conc./mol dm^{-3}	Fe^{2+}	+	$2e^-$	$\rightarrow$	Fe
Initial	2		1.6		1
Change	-1.6/2		-1.6		– (e$^-$ gained at cathode = e$^-$ lost at anode)
Final	1.2		0		1

$E = E_1 + \left(\dfrac{0.0592}{n}\right) \lg \dfrac{[Fe^{2+}]}{[Fe]} = -0.44 + \left(\dfrac{0.0592}{2}\right) \lg\dfrac{1.2}{1} = -0.4376$ V [1]

$E_{cell} = (+0.8056) - (-0.4376) = +1.24$ V [1]

[2]

For
Examiner's
Use

[Total: 22]

[End of Paper]

[Turn Over