H

NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

| | |
|---|---|
| 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.

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 $^{1}H$, $^{2}H$ and $^{3}H$, complete Table 1.1.

**Table 1.1**

| | number of protons | number of neutrons | number of electrons |
|---|---|---|---|
| $^{2}H$ | | | |
| $^{1}H_2^+$ | | | |
| $^{3}H_3^+$ | | | |

[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]

**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 $NO_2$.

..........................................................................................................

..........................................................................................................

..........................................................................................................

..........................................................................................................

..........................................................................................................

..........................................................................................................

..........................................................................................................

..........................................................................................................

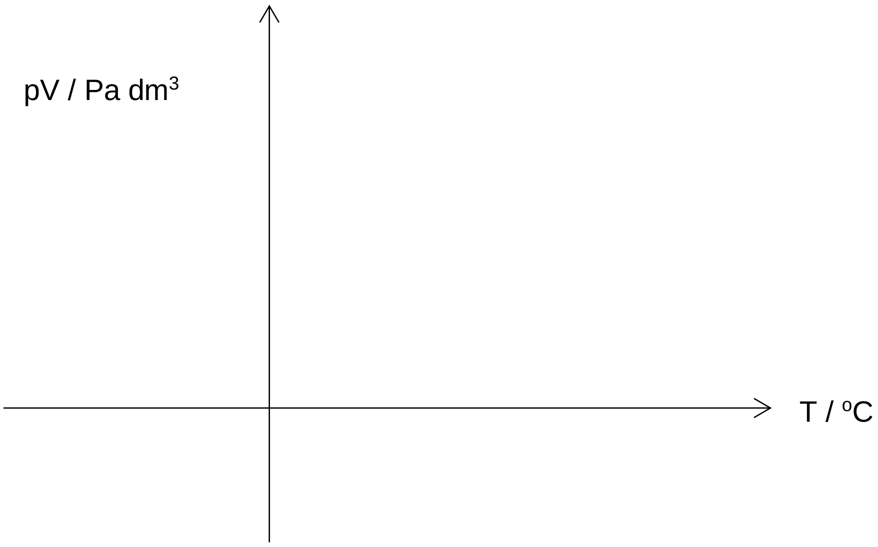
.......................................................................................................... [2]

**(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.



[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 | $1.00 \times 10^{-3}$ | 0.100 | $7.00 \times 10^{-4}$ |
| 2 | $2.00 \times 10^{-3}$ | 0.100 | $2.80 \times 10^{-3}$ |
| 3 | $3.00 \times 10^{-3}$ | 0.200 | $1.26 \times 10^{-2}$ |

**(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]

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

**Table 4.1**

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

**(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

*For Examiner's Use*

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

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

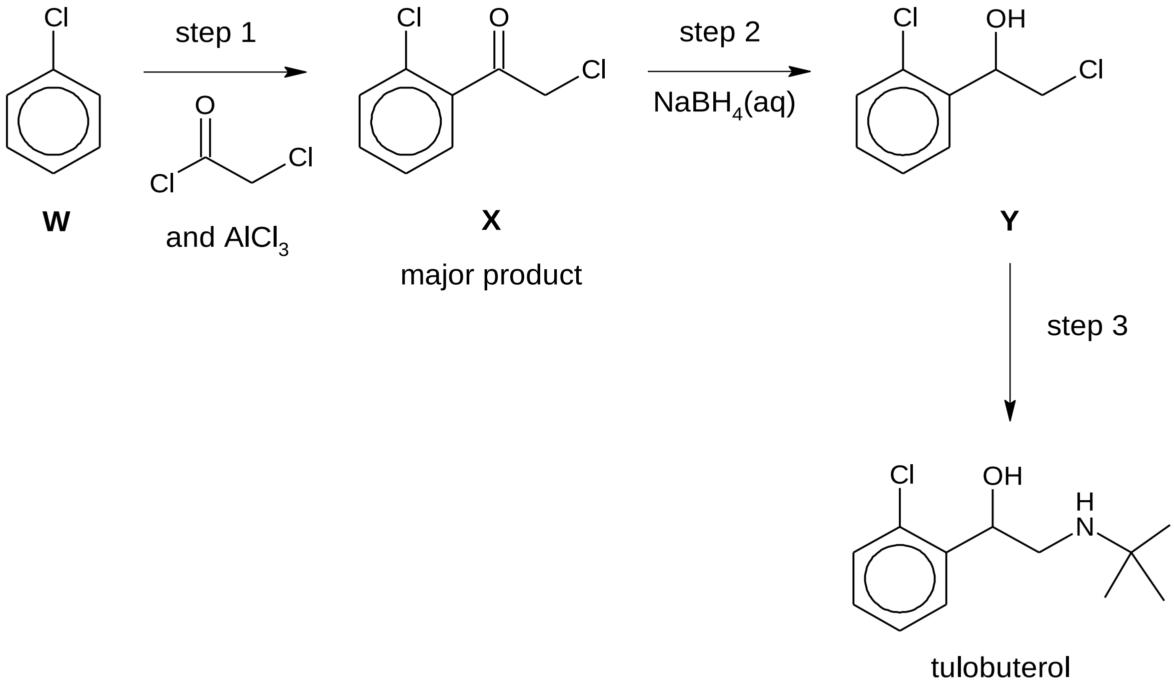


**Fig. 5.1**

**(a)** **(i)** $ClCOCH_2Cl$ used in step 1 can be formed by reacting $HOCOCH_2OH$ 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.

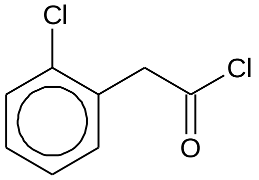


**Fig. 5.2**

..................................................................................................................

..................................................................................................................

.................................................................................................................. [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.

..........................................................................................................................................

..........................................................................................................................................

..........................................................................................................................................

..........................................................................................................................................

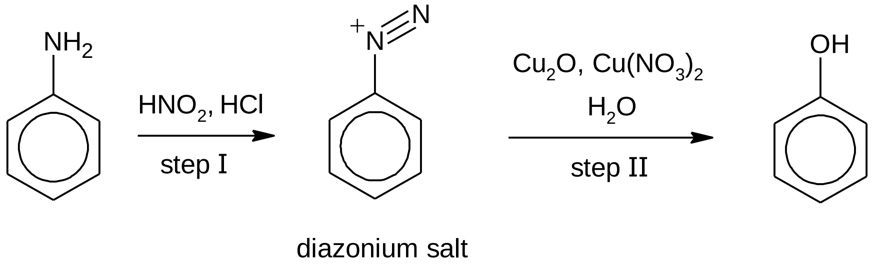
..........................................................................................................................................

.................................................................................................................................... [2]

[Total: 11]

## BLANK PAGE

**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.



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

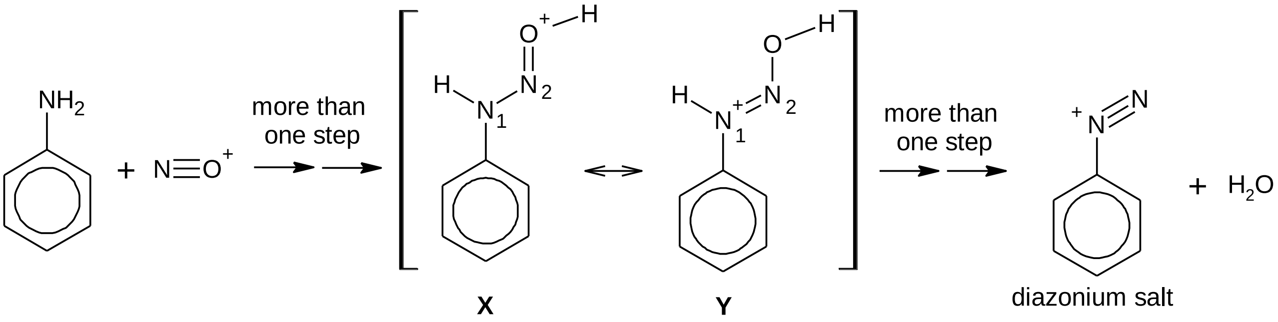


**Fig. 6.1**

**(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]

**(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.

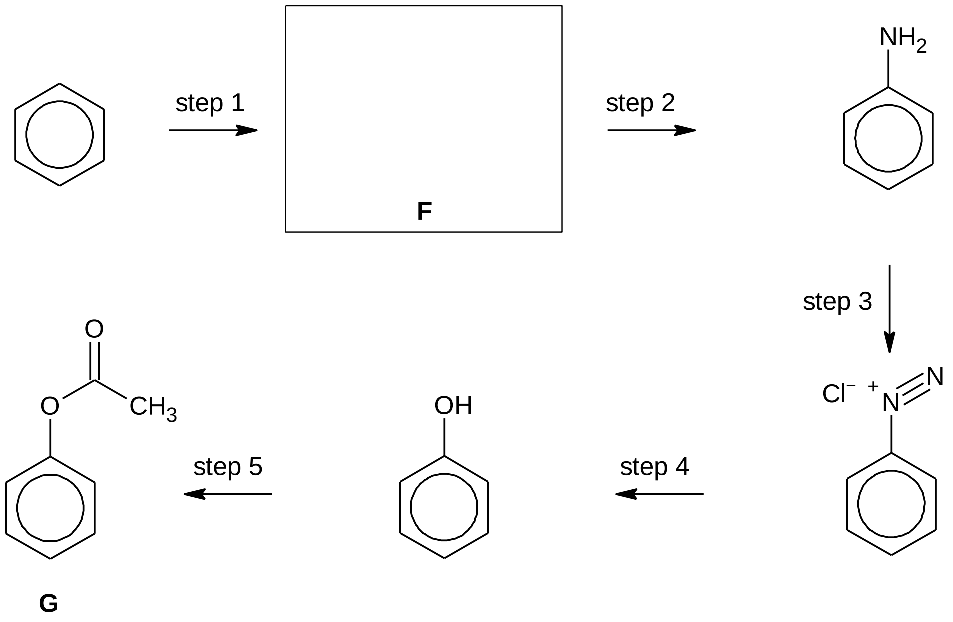


**Fig. 5.2**

**(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.

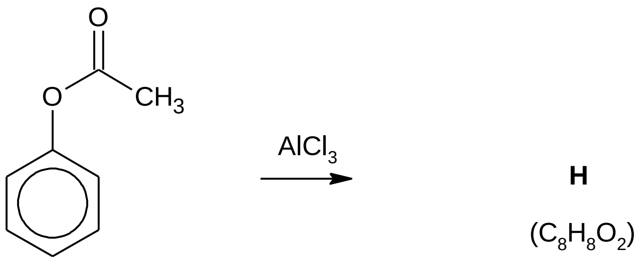
step 1 ..........................................................................................................................

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 $AlCl_3$. Compound **H** is a constitutional isomer of **G**.

Compound **H** is a 1,4-disubstituted benzene derivative. It gives a white precipitate with $Br_2(aq)$, and a yellow precipitate with alkaline aqueous iodine.



**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 / $dm^3$ | 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.

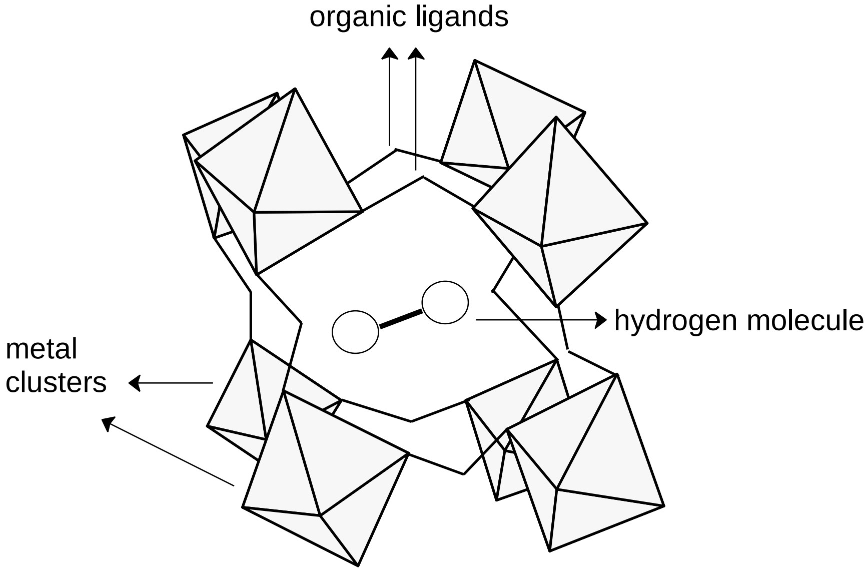


**Fig. 7.1**

**(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.

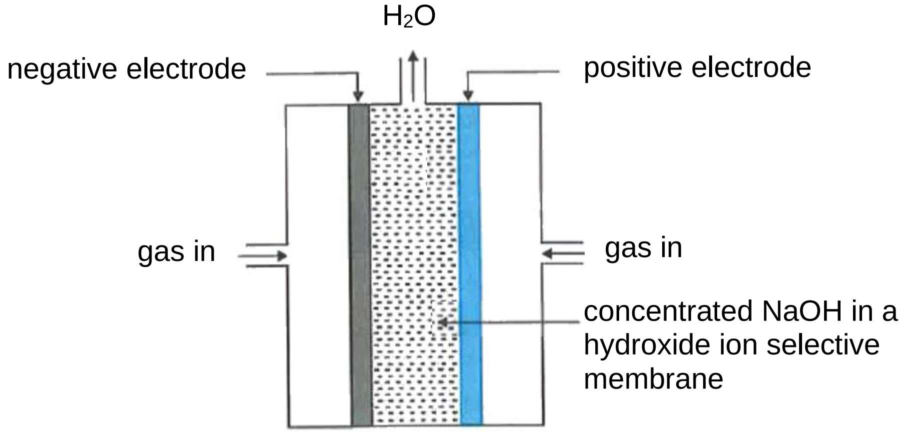


**Fig. 7.2**

**(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 $E^{\ominus}_{\text{cell}}$ 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 $$E = E^{\ominus} + \left(\frac{0.0592}{n}\right) \lg \frac{[\text{oxid}]}{[\text{red}]}$$

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]

**[End of Paper]**