YISHUN INNOVA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
**Higher 2**

| | |
|---|---|
| CANDIDATE NAME | **SUGGESTED ANSWERS** |

| | | | |
|---|---|---|---|
| CG | | INDEX NO | |

# CHEMISTRY

**9729/02**

Paper 2 Structured Questions

**10 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.
You may use an HB pencil for any diagrams or graphs.
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** | | **/ 9** |
| **2** | | **/ 9** |
| **3** | | **/ 16** |
| **4** | | **/ 21** |
| **5** | | **/ 20** |
| **Penalty** | **units** | **significant figures** |
| | | |
| **Overall** | | **/ 75** |

This document consists of **17** printed pages and **3** blank pages.

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

**1 (a)** Calcium carbide, $CaC_2$ is a solid used in the production of ethyne, $C_2H_2$.

Calcium carbide is produced when calcium oxide reacts with carbon forming calcium carbide and carbon monoxide.

**(i)** Write the electronic configuration of calcium in calcium carbide.

$Ca^{2+}$: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

**(ii)** Write an equation, with state symbols for the formation of calcium carbide.

$CaO(s) + 3C(s) \longrightarrow CaC_2(s) + 3CO(g)$

**(iii)** Predict all possible intermolecular forces which could exist between carbon monoxide molecules. Explain how these forces arise.

Carbon monoxide has a simple molecular structure, with **instantaneous dipole-induced dipole interactions** and **permanent dipole-permanent dipole interactions** between the molecules.

As electrons in orbitals are in **constant random motion**, there is an **uneven distribution of electrons in a molecule/ distortion of the electron cloud**. This separation of charges creates an **instantaneous dipole** in the molecule.

Instantaneous dipole **induce neighbouring molecules to undergo electron cloud distortion/ induce the formation of dipoles in the neighbouring molecules** and hence instantaneous dipole – induced dipole attraction occurs.

Carbon monoxide being **polar**/ has **net dipole moment**/ has **permanent net separation of charges** due to **difference in electronegativity between C and O atoms**. Hence, permanent dipole-permanent dipole attraction occurs.

**(b)** The German chemist Friedrich Wohler discovered that calcium carbide, $CaC_2$ reacted with water releasing ethyne gas, $C_2H_2$ and calcium hydroxide.

The ethyne gas was burnt in miner's lamps and headlights of early motor vehicles for the purpose of illumination.

The equation for the formation of ethyne from calcium carbide is as shown.

$$CaC_2(s) + H_2O(l) \longrightarrow Ca(OH)_2(aq) + C_2H_2(g)$$

An impure sample of calcium carbide of mass 0.752 g was added to 50 $cm^3$ of water. After all the calcium carbide had reacted, 20.00 $cm^3$ of the reaction mixture was removed and titrated against 0.250 mol $dm^{-3}$ of hydrochloric acid and 34.60 $cm^3$ of hydrochloric acid was required to neutralise the sample. It can be assumed that none of the impurities reacted.

Calculate the percentage purity of calcium carbide.

$Ca(OH)_2 + 2HCl \longrightarrow CaCl_2 + 2H_2O$

Amount of HC*l* = 0.0346 × 0.250 = 0.00865 mol

Amount of $Ca(OH)_2$ in 20 $cm^3$ = 0.00865 × ½ = 0.004325 mol

Amount of $Ca(OH)_2$ in 50 $cm^3$ = 50/20 × 0.004325 = 0.01082 mol

Amount of $CaC_2$ = 0.01082 mol

Mass of $CaC_2$ = 0.01082 × (40.1 + 24.0) = 0.69308 g

% purity = $\frac{0.69308}{0.752} \times 100\ \% = 92.2\ \%$

[Total: 9]

**2** **(a)** Sodium halides are ionic compounds which have the same crystal structures.

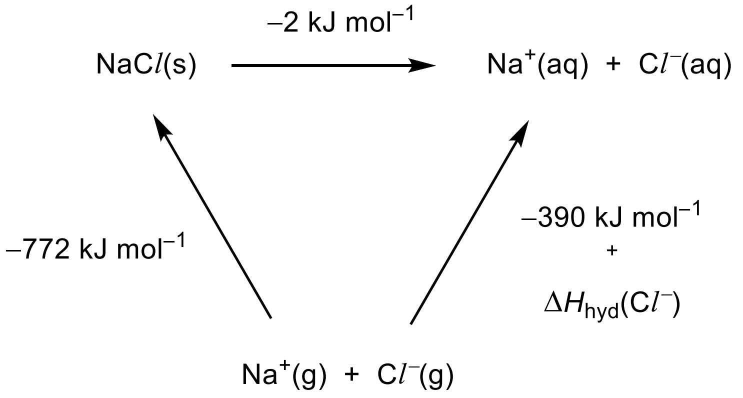
Table 2.1 shows data concerning solubility of sodium halides.

**Table 2.1**

| | value / kJ mol$^{-1}$ |
|---|---|
| enthalpy change of solution of NaC*l*(s) | –2 |
| enthalpy change of solution of NaI(s) | +2 |
| enthalpy change of hydration of Na$^+$(g) | –390 |
| lattice energy of NaC*l*(s) | –772 |
| lattice energy of NaI(s) | –694 |

**(i)** Use the data in Table 2.1, together with an appropriate energy cycle or otherwise, to calculate a value for the enthalpy change of hydration of the chloride ion.

Method 1



$\Delta H_{hyd}$(C*l*$^-$) = –384 kJ mol$^{-1}$

Method 2

$\Delta H_{sol}$ = [$\Delta H_{hyd}$(Na$^+$) + $\Delta H_{hyd}$(C*l*$^-$)] – lattice energy

–2 = [(–390) + $\Delta H_{hyd}$(C*l*$^-$)] – (–772)

$\Delta H_{hyd}$(C*l*$^-$) = –384 kJ mol$^{-1}$

**(ii)** By quoting appropriate data from the *Data booklet*, explain whether the magnitude of enthalpy change of hydration of iodide ion be larger or smaller compared to your answer in **(a)(i)**.

$\Delta H_{\text{hyd}} \propto \frac{\text{charge}}{\text{size of the ion}}$ (charge density)

$\text{I}^-$ which has an ionic radius of 0.216 nm while $\text{C}l^-$ has an ionic radius of 0.181 nm. Since the ionic radius of $\text{I}^-$ is larger than the ionic radius of $\text{C}l^-$, the charge density of $\text{I}^-$ is smaller than $\text{C}l^-$. $\text{I}^-$ attracts water less strongly or forms weaker ion–dipole attraction between $\text{I}^-$ and water and hence the magnitude of $\Delta H_{\text{hyd}}$ for $\text{I}^-$ is smaller.

**(b)** Lattice energies are not measured directly. By using Hess' Law and Born Haber cycle, they can be obtained from experimental data.

From the knowledge of the distances between cations and anions in the crystal structure, and the charge on each ion, it is possible to calculate the theoretical values for lattice energies.

Table 2.2 shows the numerical values of lattice energies of sodium chloride and sodium iodide.

**Table 2.2**

| compound | experimental value / kJ mol$^{-1}$ | theoretical value / kJ mol$^{-1}$ |
|---|---|---|
| $\text{NaC}l\text{(s)}$ | –772 | –776 |
| $\text{NaI(s)}$ | –699 | –685 |

**(i)** Define, using sodium chloride as an example, what is meant by the term *lattice energy*.

**Heat evolved** when **one mole of the solid ionic compound, $\text{NaC}l$** is formed from its **gaseous** ions, **$\text{Na}^+$** and **$\text{C}l^-$** at 298K and 1 bar.

**(ii)** There is close agreement between experimental and theoretical values of lattice energy for sodium chloride but not sodium iodide.

Suggest a reason for this.

$\text{I}^-$ has a larger ionic radius than $\text{C}l^-$ and hence $\text{I}^-$ is more readily polarised by $\text{Na}^+$ leading to some covalent character in the ionic bond of NaI.

*or*

NaI is an ionic compound with a higher degree of covalent character because $\text{I}^-$ is more polarisable than $\text{C}l^-$.

**(c)** The ionic radii of some Group 1 metal cations and the halides ions are given in Table 2.3.

**Table 2.3**

| ion | radius, $r^+$/ nm |
|---|---|
| $Na^+$ | 0.098 |
| $K^+$ | 0.133 |
| $Rb^+$ | 0.148 |
| $Cs^+$ | 0.167 |

| ion | radius, $r^-$/ nm |
|---|---|
| $Cl^-$ | 0.181 |
| $Br^-$ | 0.196 |
| $I^-$ | 0.219 |

Complete Table 2.4 and use your results to predict the tastes of sodium bromide and potassium iodide.

**Table 2.4**

| salt | NaBr | KC*l* | NaI | RbC*l* | RbBr | CsC*l* | KI |
|---|---|---|---|---|---|---|---|
| ($r^+ + r^-$) | | | | | | | |
| taste | | salty | salty | salty<br>+<br>bitter | bitter | bitter | |

| salt | NaBr | KC*l* | NaI | RbC*l* | RbBr | CsC*l* | KI |
|---|---|---|---|---|---|---|---|
| ($r^+ + r^-$) | **0.294** | **0.314** | **0.317** | **0.329** | **0.344** | **0.348** | **0.352** |
| taste | **salty** | salty | salty | salty<br>+<br>bitter | bitter | bitter | **bitter** |

[Total: 9]

**3** **(a)** Write equations to show the acidic or basic property of

**(i)** phenylamine

$C_6H_5NH_2 + H^+ \longrightarrow C_6H_5NH_3^+$

*or*

$C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$

**(ii)** phenol

$C_6H_5OH + OH^- \longrightarrow C_6H_5O^- + H_2O$

*or*

$C_6H_5OH + H_2O \rightleftharpoons C_6H_5O^- + H_3O^+$

**(b)** Ethylamine, $CH_3CH_2NH_2$, is a weak base.

$$CH_3CH_2NH_2 + H_2O \rightleftharpoons CH_3CH_2NH_3^+ + OH^-$$

**(i)** Using the equation given, explain why ethylamine is a *Brønsted-Lowry* base.

Ethylamine is a proton acceptor (and produces $OH^-$ when in solution).

**(ii)** Identify the two different conjugate acid–base pairs in the equation given.

acid ........................................ conjugate base ........................................

base ........................................ conjugate acid ........................................

acid: $H_2O$ conjugate base: $OH^-$

base: $CH_3CH_2NH_2$ conjugate acid: $CH_3CH_2NH_3^+$

**(iii)** The degree of ionisation of $CH_3CH_2NH_2$ in 0.010 mol dm$^{-3}$ aqueous solution is 0.17. Calculate the concentration of $OH^-$ in the solution.

$[OH^-] = 0.17 \times 0.010 = 1.70 \times 10^{-3}$ mol dm$^{-3}$

**(iv)** Using your answer to **(b)(iii),** calculate a value of the base dissociation constant, $K_b$, for $CH_3CH_2NH_2$, stating its unit.

$$K_b = \frac{\left(1.7 \times 10^{-3}\right)^2}{0.01(1-0.17)} = 3.48 \times 10^{-4} \text{ mol dm}^{-3} \quad \textit{or} \quad K_b = \frac{\left(1.7 \times 10^{-3}\right)^2}{0.01} = 2.89 \times 10^{-4} \text{ mol dm}^{-3}$$

**(c)** Fig 3.1 shows a possible reaction sequence with bromomethane as the starting material to form ethylamine.

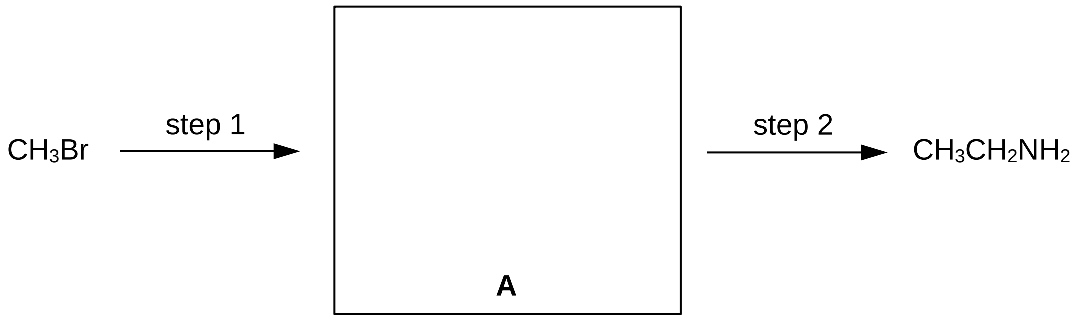


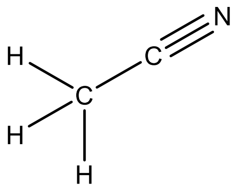
**Fig. 3.1**

**(i)** Suggest the reagents and conditions for step 1 and step 2.

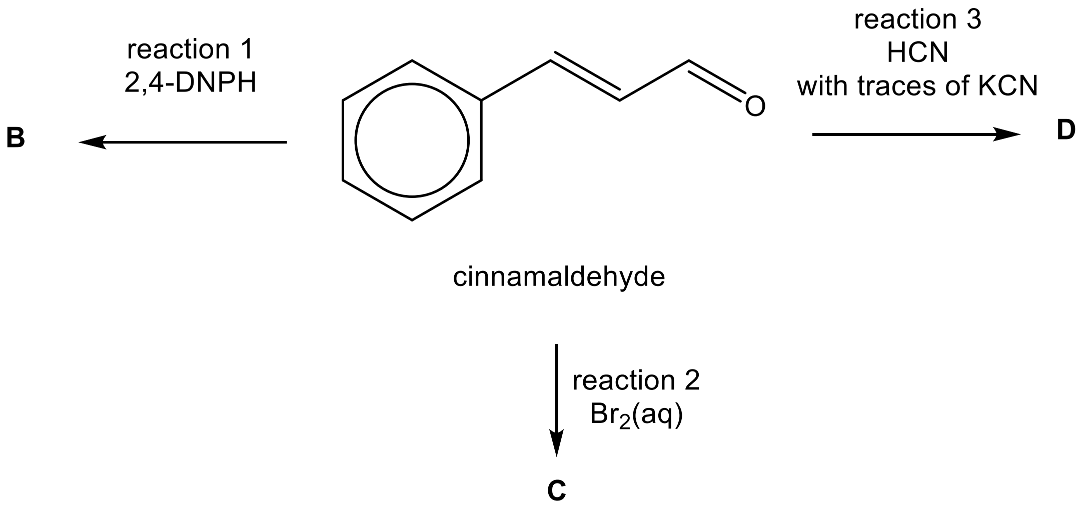
step 1: NaCN or KCN in ethanol, heat

step 2: LiA*l*$H_4$ in dry ether, room temperature *or* $H_2$(g), Ni, heat *or* $H_2$(g), Pt, room temperature

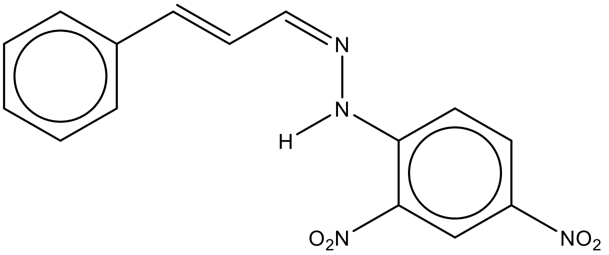
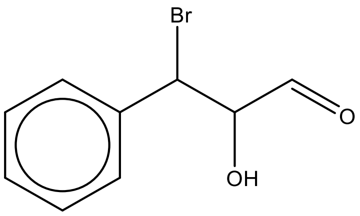
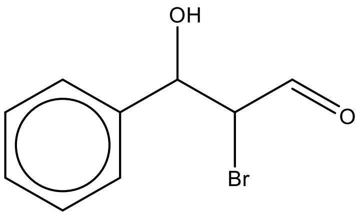
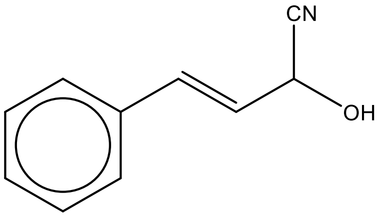
**(ii)** Draw the displayed formula of **A** in the box provided in Fig. 3.1.



**(d)** Separate samples of cinnamaldehyde are added to an excess of 3 different reagents.



**(i)** Suggest the structures of the organic products, **B**, **C** and **D**.

| | |
|---|---|
| **B** |  |
| **C** |  *or*  |
| **D** |  |

**(ii)** State the *types of reaction* that occur during each of the reactions 1, 2 and 3.

reaction 1: condensation
reaction 2: electrophilic addition
reaction 3: nucleophilic addition

[Total: 16]

**4** Nitrogen dioxide, $NO_2$ is important in the atmospheric oxidation of sulfur dioxide to sulfur trioxide.

**(a)** **(i)** Describe and explain, with the aid of suitable equations, the role of $NO_2$.

$SO_2 + NO_2 \longrightarrow SO_3 + NO$
$NO + \frac{1}{2}O_2 \longrightarrow NO_2$

$NO_2$ function as a **homogenous** catalyst as it is **regenerated** at the end of the reaction.

**(ii)** Describe the reaction of $SO_3$ with $H_2O$.
Write an equation to show this reaction and state the pH of the resultant solution.

$SO_3 + H_2O \longrightarrow H_2SO_4$

$SO_3$ is a **covalent** oxide and **dissolves** readily in water to form a strong acid which has a **pH of 2** (***or*** **1**).

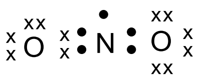
**(b)** At room temperature of 25 °C, gaseous dinitrogen tetraoxide and nitrogen dioxide are in dynamic equilibrium as shown in the equation.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

**(i)** Explain what is meant by the term *dynamic equilibrium*.

Dynamic equilibrium refers to a **reversible reaction** in which the **forward and reverse reactions are continuing at the same rate** and **concentrations of both reactants and products are constant**.

**(ii)** Draw a dot-and-cross diagram showing the bonding in $NO_2$, clearly indicating any co-ordinate (dative covalent) bonds it contains.



**(iii)** Explain, in terms of bond breaking and bond forming, why the decomposition of $N_2O_4$ is endothermic.

Energy is absorbed to **break the N – N bond** in $N_2O_4$ but no energy is released as **no new bonds are formed** in $NO_2$.

**(c)** At a temperature of 25 °C, 1.00 g of a mixture of $N_2O_4$ and $NO_2$ takes up a volume of $3.17 \times 10^{-4}$ m$^3$ at a pressure of 101 kPa.

**(i)** Calculate the average relative molecular mass of the mixture.

$pV = nRT = (\text{mass}/M_r)RT$
$101000 \times (3.17 \times 10^{-4}) = (1.00 / M_r) \times 8.31 \times 298$
$M_r = 77.3$

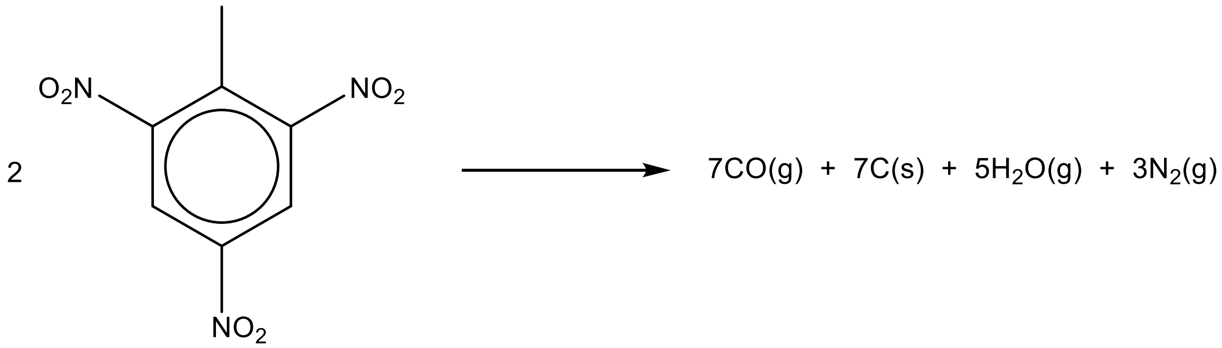
**(ii)** Deduce qualitatively the effect on the average molecular mass, $M_r$ of the gaseous mixture for each of the following changes.

- increasing pressure,
- increasing temperature.

When pressure increases, equilibrium position shifts to the **left** to **decrease the total pressure**, as the backward reaction involves a **decrease in the total number of gas molecules** hence $\boldsymbol{M_r}$ of the gaseous mixture **increases** as the $M_r$ of $N_2O_4$ is larger than the $M_r$ of $NO_2$.

When temperature increases, the equilibrium position will shift to the **right** to **absorb the heat** added, as the forward reaction is **endothermic** hence $\boldsymbol{M_r}$ of the gaseous mixture **decreases** as the $M_r$ of $N_2O_4$ is larger than the $M_r$ of $NO_2$.

**(d)** Trinitrotoluene, TNT, is used as an explosive. It can decompose according to the equation shown.



**(i)** Deduce the molecular formula of TNT.

$C_7H_5N_3O_6$

**(ii)** When TNT explodes, a black smoke is observed.

Suggest the identity of the black smoke.

Carbon/ Soot

**(iii)** In practice, TNT is mixed with potassium chlorate(VII), $KClO_4$ for use as an underground explosive to reduce the **hazardous risk**.

Suggest how $KClO_4$ helps to reduce the hazardous risk.

$KClO_4$ oxidises harmful carbon monoxide to carbon dioxide.

**(iv)** The decomposition of Group 1 and Group 2 chlorates(VII) are similar to Group 2 carbonates. Explain why $KClO_4$ decomposes less readily than $Ca(ClO_4)_2$.

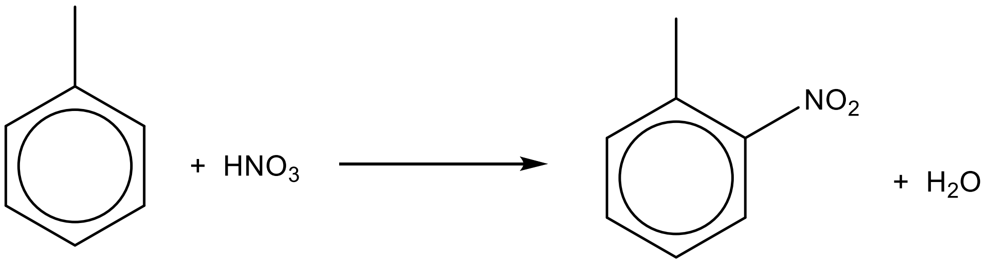
$K^+$ has a **smaller charge and larger ionic radius** than $Ca^{2+}$ and hence $K^+$ has a **lower charge density** and hence **lower polarising power** than $Ca^{2+}$.

Thus, the **electron cloud** of the large **$ClO_4^-$** anion is **distorted (or polarised) to a smaller** extent and a **smaller weakening effect on the Cl–O** bonds within the $ClO_4^-$ **by the $K^+$**.

Hence thermal decomposition of $KClO_4$ is more difficult and higher temperature is required for the decomposition to occur.

**(e)** TNT is made by reacting methylbenzene with concentrated $HNO_3$ in the presence of concentrated $H_2SO_4$ at 30 °C.

**(i)** Methylbenzene can react with concentrated $HNO_3$ in the presence of concentrated $H_2SO_4$ as shown in the equation.



Name the type of reaction and describe the mechanism for this reaction. Show relevant lone pair of electrons, all charges and using curly arrows to show the movement of electron pairs.

Type of reaction: electrophilic substitution

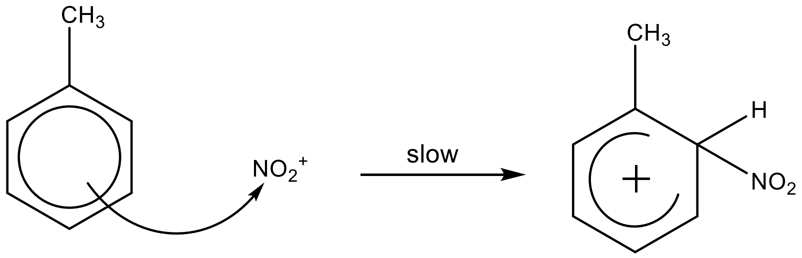
**Step 1**

$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + 2HSO_4^- + H_3O^+$

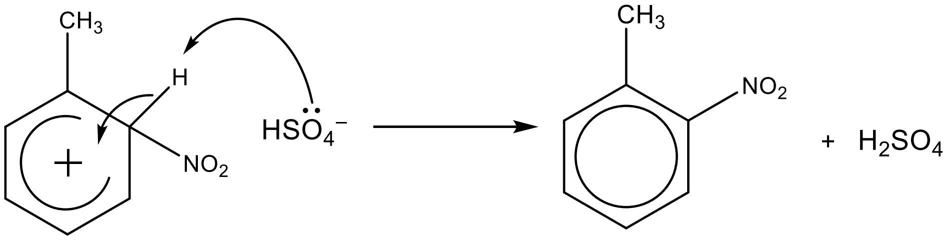
*or*

$HNO_3 + H_2SO_4 \rightleftharpoons NO_2^+ + HSO_4^- + H_2O$

**Step 2**



**Step 3**



**(ii)** The reaction of benzene with concentrated $HNO_3$ in the presence of $H_2SO_4$ takes place at 60 $^oC$.
Explain why methylbenzene reacts at lower reaction temperature of 30 °C.

The methyl group is an activating group.

Hence, it increases the electron density on benzene, making it more susceptible towards electrophilic reaction with concentrated $HNO_3$.

[Total: 21]

**5** Lithium-ion batteries have intercalated lithium compounds as the electrode material. Intercalation is the reversible inclusion or insertion of a molecule (or ion) into materials with layered structures.

When a battery discharges, the cathode is cobalt oxide with intercalated lithium ions, and the anode is graphite with intercalated lithium ions.

In the process of charging and discharging, lithium ions move from one electrode to the other through an electrolyte which is usually lithium salt dissolved in an organic solvent.

If the battery is handled according to the manufacturer's instructions, the elemental lithium is never found in the battery.

**(a)** When being discharged, the half reaction at the cathode may be assumed to be

$$CoO_2 + Li^+ + e^- \longrightarrow LiCoO_2$$

State the oxidation state of cobalt, Co, in $CoO_2$ and in $LiCoO_2$.

oxidation state of Co in $CoO_2$ +4

oxidation state of Co in $LiCoO_2$ +3

**(b)** If the battery is overcharged, Li metal can form on one of the electrodes and this can pose a serious fire risk.

State which electrode would Li be formed.

Lithium will be formed at the **cathode** which is the **graphite electrode**.

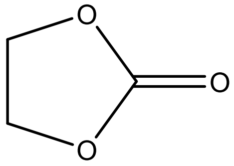
**(c)** The commonly used organic solvent for the electrolyte is called EC.

EC has a molecular formula of $C_3H_4O_3$. One of the products of the hydrolysis of EC is 1,2-ethanediol, $HOCH_2CH_2OH$.

**(i)** Suggest the reagents and conditions in the hydrolysis of EC.

$H_2SO_4$(aq) and heat

**(ii)** Draw the skeletal formula of EC.



**(d)** Lithium burns violently in air producing a mixture of lithium oxide and lithium peroxide, $Li_2O_2$.

Write the equation for the combustion of lithium assuming the two products are formed in a 1:1 molar ratio.

$4Li + 3/2O_2 \longrightarrow Li_2O + Li_2O_2$

**(e)** On the international space station, compound **F** is used for oxygen storage.
Elemental analysis of compound **F** contains 6.52% lithium and 33.32% chlorine by mass.
When decomposed, all the oxygen in compound **F** is converted to molecular oxygen.

Determine the empirical formula of compound **F**.

Percentage mass of oxygen = 100 – 6.52 – 33.32 = 60.16%

| | Li | C*l* | O |
|---|---|---|---|
| percentage by mass | 6.52 | 33.32 | 60.16 |
| relative atomic mass | 6.9 | 35.5 | 16.0 |
| mole | $\frac{6.52}{6.9} = 0.945$ | $\frac{33.32}{35.5} = 0.939$ | $\frac{60.16}{16.0} = 3.76$ |
| mole ratio | 1 | 1 | 4 |

empirical formula: $LiClO_4$

**(f)** The efficiency of a compound to store molecular oxygen is given by its oxygen : volume ratio (OV).

$$\text{OV} = \frac{\text{volume of molecular oxygen released}}{\text{volume of compound that released molecular oxygen}}$$

**(i)** Using your answer to **5(e)**, write the equation for the decomposition of compound **F**.

$LiClO_4 \longrightarrow 2O_2 + LiCl$

**(ii)** The density of compound **F** is 2.42 g cm$^{-3}$.

Calculate the OV of compound **F** at room temperature and pressure.

Amount of $O_2$ produced from decomposition of 1 mol of compound **F** = 2.00 mol

Volume of $O_2$ at r.t.p = 2.00 × 24 = 48.0 dm$^3$
Molar mass of compound F = 6.9 + 35.5 + 4(16.0) = 106.4 g mol$^{-1}$

$$\text{Volume of compound } \mathbf{F} = \frac{\text{molar mass of compound } \mathbf{F}}{\text{density of compound } \mathbf{F}} = \frac{106.4}{2.42} = 43.97 \text{ cm}^3$$

$$\text{OV} = \frac{48 \times 1000}{43.97} = 1091.7 \approx 1092$$

**(g)** The Haber process is used to make ammonia, the main use of which is fertilisers that are sprayed on crops. Around 1% of the entire global energy supply is used in the Haber process and hence research groups are looking to find more sustainable methods of producing ammonia.

One recently published approach to making ammonia was the following 3–step method:

step 1: electrolysis of molten lithium hydroxide at 750 K to form lithium metal.

step 2: reaction of Li metal with $N_2$ to form lithium nitride, $Li_3N$.

step 3: reaction of lithium nitride with water to reform lithium hydroxide and ammonia.

Lithium hydroxide formed in step 3 can be re-used in step 1 and the process can be repeated.

**(i)** State the two half-equations that combine to give the overall equation in step 1.

cathode: $Li^+ + e^- \longrightarrow Li$
anode: $4OH^- \longrightarrow 2H_2O + O_2 + 4e^-$

In a small-scale experiment, researchers applied a current of 0.200 A for 1000 seconds.
The yield of Li production in this process was 88.3%.
The yield of step 2 and step 3 can be assumed to be 100%.

**(ii)** Calculate the mass of Li generated in step 1.

$Li^+ + e^- \longrightarrow Li$

$$\frac{96500}{0.200 \times 1000} = \frac{1}{n}$$

Amount of electrons = 0.00207 mol = Theoretical amount of Li

Actual amount of Li produced = (88.3/100) × 0.00207 = 0.00183 mol

Mass of Li generated = 0.00183 × 6.9 = 0.0126 g

**(iii)** Write balanced equations to show the reaction in step 2 and step 3.

step 2 ……………………………………………………………………………………

step 3 ……………………………………………………………………………………

step 2: $3Li + \frac{1}{2}N_2 \longrightarrow Li_3N$
step 3: $Li_3N + 3H_2O \rightarrow 3LiOH + NH_3$

**(iv)** Calculate the volume of $NH_3$ produced in $cm^3$ at s.t.p.

Mole ratio of Li : $Li_3N$ : $NH_3$ = 3 : 1 : 1

Amount of $NH_3$ = 1/3 × 0.00183 = $6.1007 \times 10^{-4}$ mol
Volume of $NH_3$ = $(6.1007 \times 10^{-4}) \times 22.7 = 0.013847\ dm^3 = 13.8\ cm^3$

[Total: 20]