



VICTORIA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE
NAME

CT GROUP

CHEMISTRY

9729/02

Paper 2 Structured

11 September 2018

Candidates answer on the Question Paper.

2 hours

Additional Materials: *Data Booklet*

READ THESE INSTRUCTIONS FIRST

Write your name and CT group on all the work you hand in.

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, highlighters, glue or correction fluid.

Answer **all** questions.

The number of marks is given in brackets [] at the end of each question or part question.

For Examiner's Use	
1	/ 20
2	/ 20
3	/ 20
4	/ 15
Total	/ 75

This document consists of **20** printed pages.

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

- 1 (a) Bromine exists naturally as a mixture of two stable isotopes, ^{79}Br and ^{81}Br , in a 1:1 ratio.

- (i) Write down the full electronic configuration of $^{79}\text{Br}^{2+}$.

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$

[1]

- (ii) Define the term *relative isotopic mass*.

Mass of an atom of isotope relative to $\frac{1}{12}$ the mass of an atom of carbon-12 isotope.

[1]

- (b) Chlorine atom exists naturally as two isotopes, ^{35}Cl and ^{37}Cl , in a 3:1 ratio. When equimolar amounts of bromine and chlorine were mixed together, an interhalogen compound, BrCl , is formed. The product mixture contains four species with three different mass numbers 114, 116 and 118. $^{79}\text{Br}^{35}\text{Cl}$ is one of the four species.

- (i) With the help of the information given in (a), state the species that corresponds to each mass number. Hence, calculate the relative abundance for each mass number.

mass number	species	relative abundance
114	$^{79}\text{Br}^{35}\text{Cl}$	$\frac{1}{2} \times \frac{3}{4} = \frac{3}{8}$
116	$^{79}\text{Br}^{37}\text{Cl}$ and $^{81}\text{Br}^{35}\text{Cl}$	$(\frac{1}{2} \times \frac{1}{4}) + (\frac{1}{2} \times \frac{3}{4}) = \frac{1}{2}$
118	$^{81}\text{Br}^{37}\text{Cl}$	$\frac{1}{2} \times \frac{1}{4} = \frac{1}{8}$

[3]

- (ii) Explain whether BrCl or Cl_2 has a greater enthalpy change of vaporisation.

BrCl has a greater enthalpy change of vaporisation as it has stronger instantaneous dipole-induced dipole interactions due to the greater number of electrons in the larger BrCl molecule.

OR

BrCl has a greater enthalpy change of vaporisation as it is polar with stronger permanent dipole-permanent dipole interactions than the instantaneous dipole-induced dipole interactions in Cl_2 .

[1]

- (iii) Suggest with a reason how the first ionisation energy of ^{79}Br is compared to ^{81}Br .

First ionisation energy of ^{79}Br is the same as that of ^{81}Br because they have the same number of protons.

[1]

- (c) Bromine reacts with an element **A** to form a compound with empirical formula **ABr₃**. The percentage by mass of **A** in **ABr₃** is 4.31%. Calculate the relative atomic mass of **A**.

Let A_r of **A** be y .

Element	A	Br
No. of moles/mol	$\frac{4.31}{y}$	$\frac{100-4.31}{79.9}$

$$\text{Mole ratio of A : Br} = 1 : 3 = \frac{4.31}{y} : \frac{100-4.31}{79.9}$$

No. of moles of Br atoms = 3 × no. of moles of A atoms

$$\frac{100-4.31}{79.9} = 3 \times \frac{4.31}{y}$$

$$y = 10.8$$

[1]

- (d) Bromine and fluorine react to form the pale yellow liquid, bromine trifluoride, as shown in **Reaction 1**.



Some thermochemical data are given below.

Standard enthalpy change of formation of $\text{BrF}_3(\text{l})$ / kJ mol^{-1}	−301
Standard Gibbs free energy change of formation of $\text{BrF}_3(\text{l})$ / kJ mol^{-1}	−241
Standard entropy of $\text{Br}_2(\text{l})$, $S^\ominus(\text{Br}_2)$ / $\text{J mol}^{-1} \text{K}^{-1}$	152
Standard entropy of $\text{BrF}_3(\text{l})$, $S^\ominus(\text{BrF}_3)$ / $\text{J mol}^{-1} \text{K}^{-1}$	178

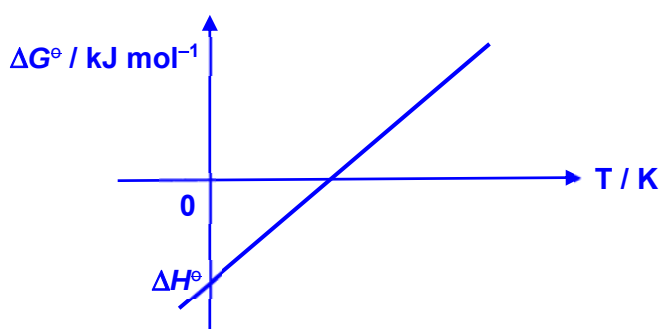
- (i) The above reaction is spontaneous at 298 K even though $\Delta S^\ominus$ is negative. Explain qualitatively why $\Delta H^\ominus$ is the predominant factor that causes the reaction to be spontaneous.

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus < 0 \text{ at } 298 \text{ K}$$

$\Delta H^\ominus$ is the predominant factor as it is exothermic (or negative) and drives the reaction.

[1]

- (ii) Sketch a graph to show how $\Delta G^\ominus$ varies with temperature in K for **Reaction 1**. Label the y-intercept.



[1]

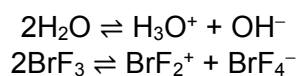
- (iii) Given that $\Delta S^\circ = 2 \times S^\circ(\text{BrF}_3) - [S^\circ(\text{Br}_2) + 3 \times S^\circ(\text{F}_2)]$ for **Reaction 1**, calculate the standard entropy of $\text{F}_2(\text{g})$, $S^\circ(\text{F}_2)$, at 298 K.

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ \Delta S^\circ &= (\Delta H^\circ - \Delta G^\circ) / T \\ &= 2(-301 + 241) \times 10^3 / 298 \\ &= -403 \text{ J mol}^{-1} \text{ K}^{-1}\end{aligned}$$

$$\begin{aligned}-403 &= 2(178) - [152 + 3S^\circ(\text{F}_2)] \\ S^\circ(\text{F}_2) &= 202 \text{ J mol}^{-1} \text{ K}^{-1}\end{aligned}$$

[2]

- (e) Similar to water, liquid BrF_3 can be used as a solvent and it undergoes minimal self-ionisation.



When $(\text{BrF}_2^+)_2(\text{SnF}_6^{2-})$ and $\text{Ag}^+(\text{BrF}_4^-)$ react in BrF_3 , an insoluble Ag_2SnF_6 is formed.

- (i) Construct an equation for the reaction between $(\text{BrF}_2^+)_2(\text{SnF}_6^{2-})$ and $\text{Ag}^+(\text{BrF}_4^-)$.



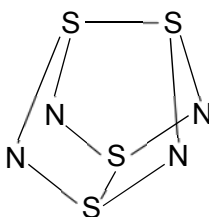
[1]

- (ii) State and draw the shapes of BrF_2^+ and BrF_4^- , including lone pairs of electrons.

bent BrF_2^+	square planar BrF_4^-
---	--

[2]

- (f) One of the most readily prepared sulfur nitrides is S_4N_4 , which can be made by passing dry $\text{NH}_3(\text{g})$ into a solution of SCl_2 in an organic solvent. A proposed structure of the molecule of S_4N_4 is shown below.



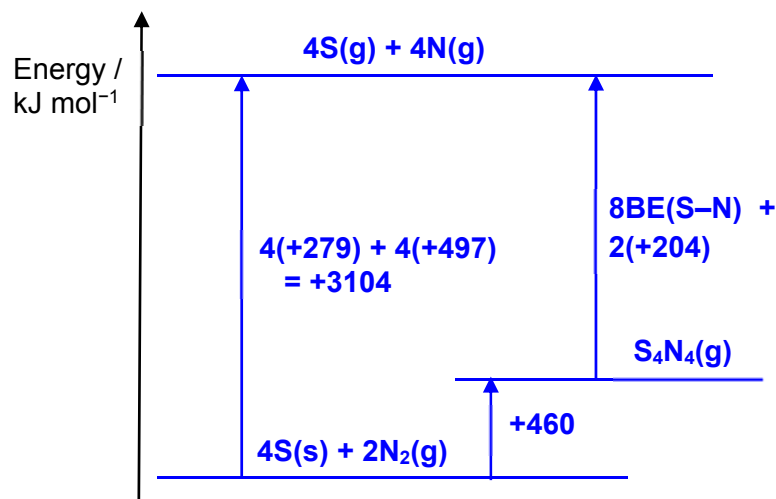
- (i) Using the data given below, construct a suitable energy level diagram to calculate the S–N bond energy in S_4N_4 .

$$\Delta H_f^\ominus [S_4N_4(g)] = +460 \text{ kJ mol}^{-1}$$

$$\Delta H_{at}^\ominus [S(s)] = +279 \text{ kJ mol}^{-1}$$

$$\Delta H_{at}^\ominus [\text{nitrogen}] = +497 \text{ kJ mol}^{-1}$$

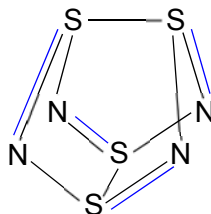
$$\text{Bond energy of (S–S) in } S_4N_4 = +204 \text{ kJ mol}^{-1}$$



By Hess's Law,
 $8BE(S-N) + 2(+204) = -(+460) + 3104$
 $BE(S-N) = +279.5 \text{ kJ mol}^{-1}$

[3]

- (ii) The nitrogen atoms in S_4N_4 show their usual valency of 3. All four sulfur atoms have the same oxidation number. Add to the structure below to show which sulfur–nitrogen bonds are single bonds and which are double bonds.



[1]

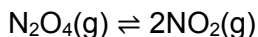
- (iii) Hence, explain why the calculated bond energy of sulfur–nitrogen bond in S_4N_4 from (f)(i) is between that of a S–N bond and a S=N bond.

This is due to the delocalisation of pi electrons / formation of resonance structures between the two sulfur–nitrogen bonds in S–N–S / N–S–N.

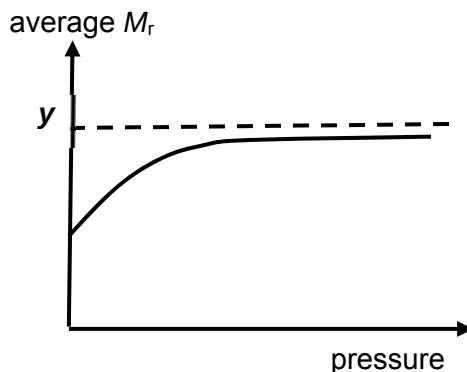
[1]

[Total: 20]

- 2 (a) Dinitrogen tetroxide, N_2O_4 , and nitrogen dioxide, NO_2 , exist in dynamic equilibrium with each other as shown below.



- (i) The diagram below shows the variation of the average molecular mass of the equilibrium mixture with pressure.



Predict a value for y and account for the shape of the graph.

$$y = 2(14.0) + 4(16.0) = 92.0$$

By Le Chatelier's Principle, as pressure increases, the position of equilibrium would shift left to decrease the amount of gaseous molecules. Hence, more N_2O_4 will be produced and average M_r increases. [2]

0.0100 mol of inert N_2 with a partial pressure of 0.27 bar and 0.0500 mol of N_2O_4 were placed in a sealed vessel of volume 1.00 dm^3 and temperature of 50°C . When equilibrium was established, the total pressure of all gases was 1.95 bar.

- (ii) With reference to the *Data Booklet*, calculate the average molecular mass, M_r , of the $\text{N}_2\text{O}_4/\text{NO}_2$ equilibrium mixture. Give your answer to **three** significant figures.

$$\begin{aligned} \text{Mass of } \text{N}_2\text{O}_4 \text{ initially} &= \text{Total mass of } \text{N}_2\text{O}_4 \text{ and } \text{NO}_2 \text{ at equilibrium} \\ &= 0.0500 \times 92.0 \\ &= 4.60 \text{ g} \end{aligned}$$

$$\begin{aligned} \text{Total pressure of } \text{N}_2\text{O}_4 \text{ and } \text{NO}_2 \text{ at equilibrium} \\ &= 1.95 - 0.27 \\ &= 1.68 \text{ bar} \end{aligned}$$

$$\begin{aligned} pV &= nRT = \frac{m}{M_r}RT \\ 1.68 \times 10^5 \times 1.00 \times 10^{-3} &= \frac{4.60}{M_r} \times 8.31 \times (273 + 50) \\ M_r &= 73.5 \end{aligned}$$

[2]

- (iii) Use your answer in (a)(ii) to calculate the mole fraction of NO_2 in the $\text{N}_2\text{O}_4/\text{NO}_2$ equilibrium mixture.

Let the mole fraction of NO_2 be z . Then the mole fraction of N_2O_4 is $(1 - z)$.

$$\begin{aligned} 46z + 92(1 - z) &= 73.5 \\ z &= 0.402 \end{aligned}$$

- (iv) Write an expression for the equilibrium constant, K_c , for this $\text{N}_2\text{O}_4/\text{NO}_2$ equilibrium. Calculate the value of K_c and give its units. [1]

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$

$$\begin{aligned} \text{Total number of moles of } \text{N}_2\text{O}_4 \text{ and } \text{NO}_2 \text{ at equilibrium} \\ &= 4.60 \div 73.5 \\ &= 0.0626 \text{ mol} \end{aligned}$$

$$\begin{aligned} n_{\text{NO}_2} \\ &= 0.402 \times 0.0626 \\ &= 0.0252 \text{ mol} \end{aligned}$$

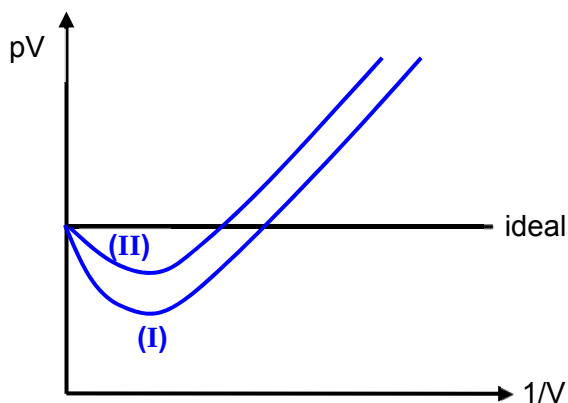
$$\begin{aligned} n_{\text{N}_2\text{O}_4} \\ &= 0.0626 - 0.0252 \\ &= 0.0374 \text{ mol} \end{aligned}$$

$$\begin{aligned} K_c &= \frac{(0.0252)^2}{0.0374} \\ &= 0.0170 \text{ mol dm}^{-3} \end{aligned}$$

[2]

- (v) Sketch and label on the same axes, a graph of variation of pV against $1/V$ at constant temperature for 1 mol of

- (I) N_2O_4 , and
(II) NO_2 .

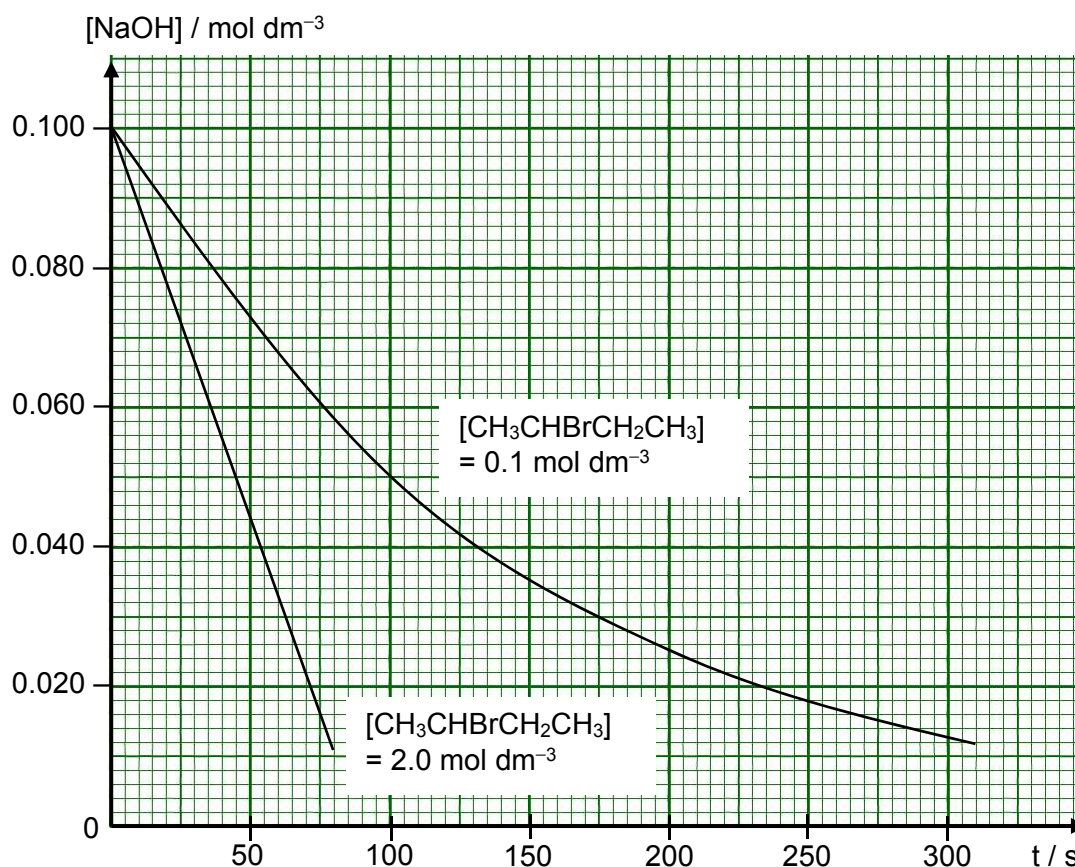


[1]

- (b) 2-bromobutane, $\text{CH}_3\text{CHBrCH}_2\text{CH}_3$, is hydrolysed by aqueous sodium hydroxide. The kinetics of the reaction was determined by monitoring the change in concentration of sodium hydroxide with time.

Two sets of experiments were performed using different initial concentrations of 2-bromobutane while the initial concentration of sodium hydroxide was kept at $0.100 \text{ mol dm}^{-3}$.

The following graphs are obtained.



- (i) Explain the terms *order of reaction* and *half-life*.

The order of reaction with respect to a given reactant is the power to which the concentration of that reactant is raised to in the rate equation.

The half-life ($t_{1/2}$) of a reaction is the time taken for the concentration of a reactant to decrease to half its initial value.

[2]

- (ii) Use the graphs to determine the order of reaction with respect to

(I) NaOH, and

When $[\text{CH}_3\text{CHBrCH}_2\text{CH}_3] = 2.0 \text{ mol dm}^{-3}$, $\text{CH}_3\text{CHBrCH}_2\text{CH}_3$ is in excess and has pseudo zeroth order. From the graph of $[\text{CH}_3\text{CHBrCH}_2\text{CH}_3] = 2.0 \text{ mol dm}^{-3}$, rate is a constant as seen from the constant gradient.

Thus, order of reaction wrt NaOH is zero.

(II) $\text{CH}_3\text{CHBrCH}_2\text{CH}_3$

From the graph of $[\text{CH}_3\text{CHBrCH}_2\text{CH}_3] = 0.1 \text{ mol dm}^{-3}$, $t_{1/2}$ is constant.

Thus, order of reaction wrt $\text{CH}_3\text{CHBrCH}_2\text{CH}_3$ is one.

[2]

- (iii) By determining the half-life for the graph of $[\text{CH}_3\text{CHBrCH}_2\text{CH}_3] = 0.1 \text{ mol dm}^{-3}$, calculate the initial rate at $t = 0 \text{ min}$, including its units.

$$t_{1/2} = 100 \text{ s}$$

$$k = \ln 2 \div 100$$

$$k = 6.93 \times 10^{-3} \text{ s}^{-1}$$

$$\begin{aligned} \text{Rate} &= k [\text{CH}_3\text{CHBrCH}_2\text{CH}_3] \\ &= 6.93 \times 10^{-3} \times 0.1 \\ &= 6.93 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1} \end{aligned}$$

[2]

- (iv) Write two elementary equations to show how $\text{CH}_3\text{CHBrCH}_2\text{CH}_3$ and NaOH react.



[1]

- (v) $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ reacts with $\text{NaOH}(\text{aq})$ via an $\text{S}_{\text{N}}1$ mechanism. Suggest why this may be so.

The carbocation from $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ is resonance-stabilised as the positive charge can delocalise into the benzene ring.

[1]

- (c) 2-iodobutane, $\text{CH}_3\text{CHICH}_2\text{CH}_3$, exists as two enantiomers, **A** and **B**, which rotate plane-polarised light in opposite directions.

An optically pure sample containing only isomer **A** rotates plane-polarised light by an angle of $+15.0^\circ$. It reacts with a solution of radioactive iodide, $^{131}\text{I}^-$, dissolved in a mixture of ethanol and water. The product mixture is found to rotate plane-polarised light by an angle of -6.4° . The reaction is found to proceed by both the $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ mechanisms. If $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ mechanisms proceed in a ratio of 1:1, the percentage composition of **B** is 75%.

- (i) Determine the percentage composition of **B** in the product mixture. Hence, deduce the predominant mechanism for the above reaction.

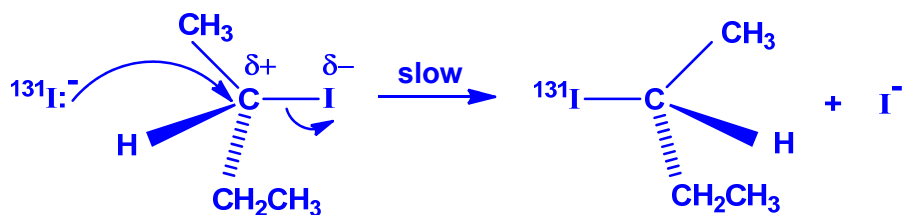
Let the percentage composition of **B** be $z\%$ and the percentage composition of **A** be $(100 - z)\%$.

$$\begin{aligned} (-15.0^\circ)\left(\frac{z}{100}\right) + (+15.0^\circ)\left(\frac{100 - z}{100}\right) &= -6.4^\circ \\ z &= 71.3\% \end{aligned}$$

Since percentage composition of **B** is less than 75 %, the predominant mechanism is $\text{S}_{\text{N}}1$.

[2]

- (ii) Describe the S_N2 mechanism for the reaction of CH₃CHICH₂CH₃ with ¹³¹I⁻.



[2]

[Total: 20]

- 3 Nickel is widely used as components of fuel cells and batteries. It often occurs in ores along with iron as metal oxides. After the initial reduction of the ore with carbon, a nickel–iron alloy is formed. It can then be purified by an electrolysis technique.

- (a) On the other hand, Group 2 metal oxides such as magnesium oxide, are not reduced by carbon. Use relevant data from the *Data Booklet* to explain why carbon can reduce oxides of nickel and iron but not magnesium oxide.

From *Data Booklet*,
 $E^\circ(\text{Mg}^{2+} | \text{Mg}) = -2.38 \text{ V}$
 $E^\circ(\text{Ni}^{2+} | \text{Ni}) = -0.25 \text{ V}$
 $E^\circ(\text{Fe}^{2+} | \text{Fe}) = -0.44 \text{ V}$
 $E^\circ(\text{Fe}^{3+} | \text{Fe}) = -0.04 \text{ V}$

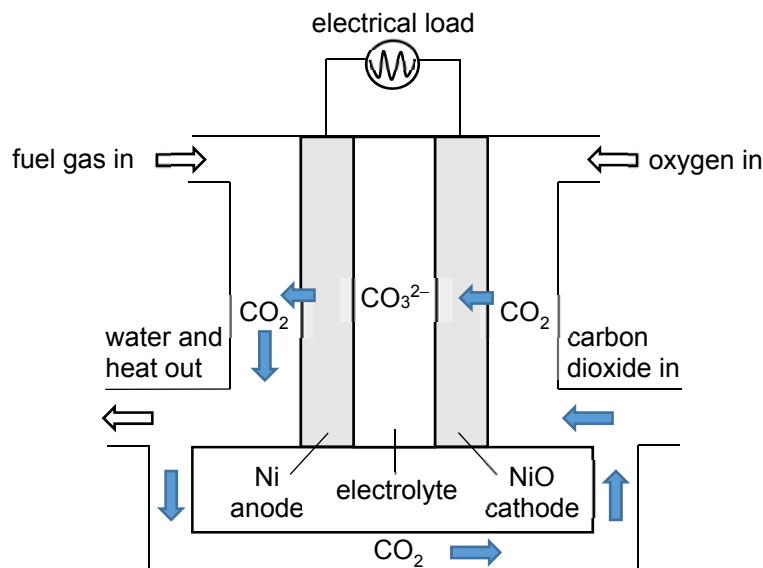
Standard reduction potential, E° , for nickel and iron are both much less negative than that of magnesium.

[2]

- (b) Nickel and nickel(II) oxide are used as electrodes in molten carbonate fuel cells (MCFC).

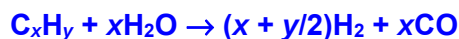
MCFC operates at temperatures above 650 °C to ensure ionic conductivity of its electrolyte, which is a mixture of lithium carbonate and potassium carbonate.

The high temperature also allows fuel reforming which produces hydrogen gas at the anode for the electrochemical reaction. Fuel gases, such as natural gas and other higher hydrocarbons derived from biomass, could be used with MCFC. The CO₂ generated at the anode is recycled to the cathode where it is consumed as shown in the schematic diagram of MCFC below.



- (i) When a hydrocarbon C_xH_y is used as the fuel gas, it undergoes fuel reforming with H_2O at the anode to produce hydrogen gas and carbon monoxide.

Write a balanced equation for the fuel reforming of the hydrocarbon, C_xH_y .



[1]

- (ii) The fuel reforming is catalysed by the nickel. Explain the mode of action of the nickel catalyst.

Nickel is a heterogeneous catalyst.

Gaseous reactants are adsorbed on the Ni surface through forming weak bonds with the active sites of the catalyst.

This weakens the covalent bonds within the reactant molecules.

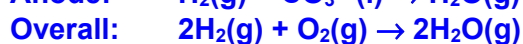
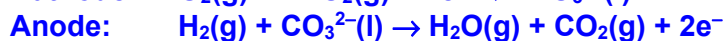
High concentration of reactants on the catalyst surface come into close contact with proper orientation for reaction to occur.

Products desorb from the surface of the catalyst.

[2]

- (iii) Carbonates are generated at the cathode by the reaction between oxygen and carbon dioxide. The carbonate ions then diffuse across the electrolyte to the anode and react with hydrogen gas, generating steam and carbon dioxide.

Write the half-equations at both electrodes and hence give the overall equation for the MCFC.



[2]

- (iv) The temperature of MCFC is kept constant.

With reference to your answer from (b)(iii), state and explain the effect of increasing the partial pressure of oxygen on the cell potential of this MCFC.

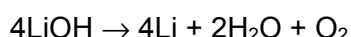
Higher partial pressure of O₂ would cause the position of equilibrium of the overall reaction to shift to the right to decrease the amount of gaseous oxygen.

The cell potential becomes more positive.

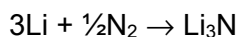
[2]

- (c) Biomass from farms could be used to produce fuel gases for MCFC to power an ammonia-making plant for the farming community. The ammonia is manufactured in the following three-step process.

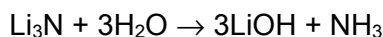
Step 1: Electrolysis of molten lithium hydroxide at 750 K to form lithium metal.



Step 2: Reaction of lithium metal with nitrogen to form lithium nitride.



Step 3: Reaction of lithium nitride with water to re-form lithium hydroxide and ammonia.



Thus, the lithium hydroxide formed in **Step 3** can be re-used in **Step 1** and the process can be repeated.

- (i) The electrolysis will only proceed at an appreciable rate when the applied potential exceeds the cell potential by 0.60 V.

Use appropriate E° values from the *Data Booklet* to calculate the minimum potential that should be applied in **Step 1**.

$$E^\circ(\text{Li}^+ | \text{Li}) = -3.04 \text{ V}$$

$$E^\circ(\text{O}_2 | \text{OH}^-) = +0.40 \text{ V}$$

$$\begin{aligned} E^\circ_{\text{cell}} &= |-3.04 - (+0.40)| \\ &= 3.44 \text{ V} \end{aligned}$$

$$\begin{aligned} \text{Minimum potential} &= 3.44 + 0.60 \\ &= 4.04 \text{ V} \end{aligned}$$

[2]

- (ii) State the ratio between the lithium produced in **Step 1** and the ammonia produced in **Step 3**.

$$\text{Ratio of Li : NH}_3 = 3 : 1$$

[1]

- (iii) A farm requires 0.0770 tonnes of ammonia per acre annually.

If the lithium hydroxide was not recycled at the end of the process, calculate the total mass of lithium (in tonnes) that would have to be produced to generate the required mass of ammonia for a farm of 100 acres in a year.

[1 tonne = 10^6 g]

Mass of NH_3 needed for 100 acres in a year
 $= 0.0770 \times 10^6 \times 100$
 $= 7.70 \times 10^6 \text{ g}$

Amount of NH_3
 $= 7.70 \times 10^6 \div 17.0$
 $= 4.53 \times 10^5 \text{ mol}$

Amount of Li required
 $= 3 \times 4.53 \times 10^5$
 $= 1.36 \times 10^6 \text{ mol}$

Mass of Li required
 $= 1.36 \times 10^6 \times 6.9$
 $= 9.38 \times 10^6 \text{ g}$
 $= 9.38 \text{ tonnes}$

[2]

- (d) Unlike lithium carbonate and potassium carbonate, a mixture of Group 2 carbonates consisting of magnesium carbonate and barium carbonate is **not** a suitable electrolyte for the molten carbonate fuel cell (MCFC) in (b). For each of the carbonates, suggest a reason why it is not a suitable electrolyte.

Magnesium carbonate:

Mg^{2+} ion has greater charge density than Group 1 ion and hence polarising the electron cloud of CO_3^{2-} to a greater extent. This causes lower thermal stability.

MgCO_3 may undergo thermal decomposition at the high operating temperature of the fuel cell, forming CO_2 , depleting the source of CO_3^{2-} .

Barium carbonate:

BaCO_3 may have a higher melting point than the operating temperature.

There will be no charge carriers in the electrolyte if the carbonate does not melt.

[2]

- (e) A solution contains $0.100 \text{ mol dm}^{-3}$ magnesium nitrate and $0.100 \text{ mol dm}^{-3}$ barium nitrate. Solid sodium carbonate is added slowly to 100 cm^3 of this solution.
 $[K_{\text{sp}}(\text{MgCO}_3) = 3.5 \times 10^{-8} \text{ mol}^2 \text{ dm}^{-6}$; $K_{\text{sp}}(\text{BaCO}_3) = 5.1 \times 10^{-9} \text{ mol}^2 \text{ dm}^{-6}]$

- (i) State which metal ion is first precipitated. Calculate the concentration of carbonate ions in the solution needed for the first trace of precipitate to be seen.

Since K_{sp} of BaCO_3 is smaller (lower solubility), Ba^{2+} is precipitated first.

$$\begin{aligned} K_{\text{sp}} &= [\text{Ba}^{2+}][\text{CO}_3^{2-}] = 5.1 \times 10^{-9} \\ 0.100 \times [\text{CO}_3^{2-}] &= 5.1 \times 10^{-9} \\ [\text{CO}_3^{2-}] &= 5.1 \times 10^{-8} \text{ mol dm}^{-3} \end{aligned}$$

[1]

- (ii) Determine the concentration of the metal ion stated in (e)(i) when the other metal ion just begins to precipitate.

$$\begin{aligned} &[\text{CO}_3^{2-}] \text{ when } \text{Mg}^{2+} \text{ starts to precipitate} \\ &= 3.5 \times 10^{-8} \div 0.100 \\ &= 3.5 \times 10^{-7} \text{ mol dm}^{-3} \end{aligned}$$

$$\begin{aligned} &\text{Using } K_{\text{sp}} \text{ of } \text{BaCO}_3, \\ &[\text{Ba}^{2+}] \times 3.5 \times 10^{-7} = 5.1 \times 10^{-9} \\ &[\text{Ba}^{2+}] = 0.0146 \text{ mol dm}^{-3} \end{aligned}$$

[2]

- (iii) The separation is considered effective when less than 1% of the metal ion remains in the solution. Hence, deduce if the above separation is effective.

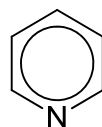
$$\begin{aligned} &\text{Percentage of } \text{Ba}^{2+} \text{ ions remained} \\ &= \frac{0.0146}{0.100} \times 100\% \text{ (ecf)} \\ &= 14.6\% \gg 1\% \end{aligned}$$

The above separation is not effective.

[1]

[Total: 20]

- 4 (a) Pyridine is an aromatic planar molecule similar to benzene. Unlike benzene, pyridine can act as a Bronsted–Lowry base and a nucleophile.



pyridine

- (i) State the type of hybridisation of the nitrogen atom in pyridine.

sp^2 hybridisation

[1]

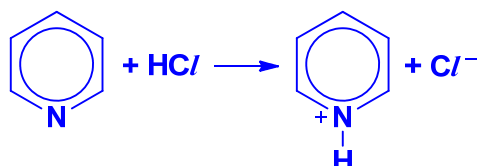
- (ii) Hence, explain why pyridine has a higher pK_b than ethylamine, $\text{CH}_3\text{CH}_2\text{NH}_2$.

The nitrogen atom in pyridine is sp^2 hybridised while that in ethylamine is sp^3 hybridised.

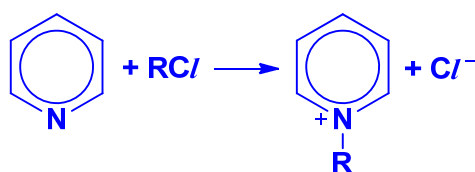
Hence, the lone pair of electrons in pyridine is less available for donation as it is more strongly attracted by / closer to the nucleus.

[1]

- (iii) Write a balanced equation to show that pyridine is acting as a Bronsted–Lowry base

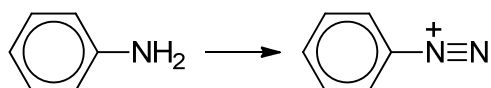


a Lewis base but not a Bronsted–Lowry base



[2]

- (b) Phenylamine and substituted phenylamines are used to make dyes and food colourants. The first step in this process is the production of a diazonium ion as shown.

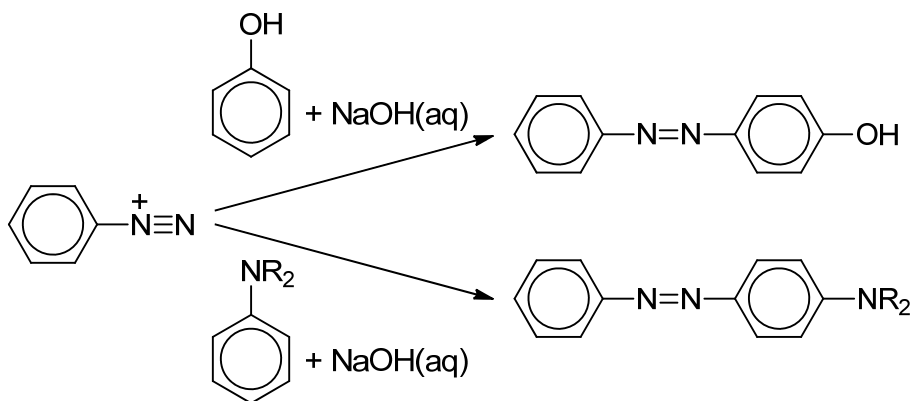


- (i) State the type of reaction.

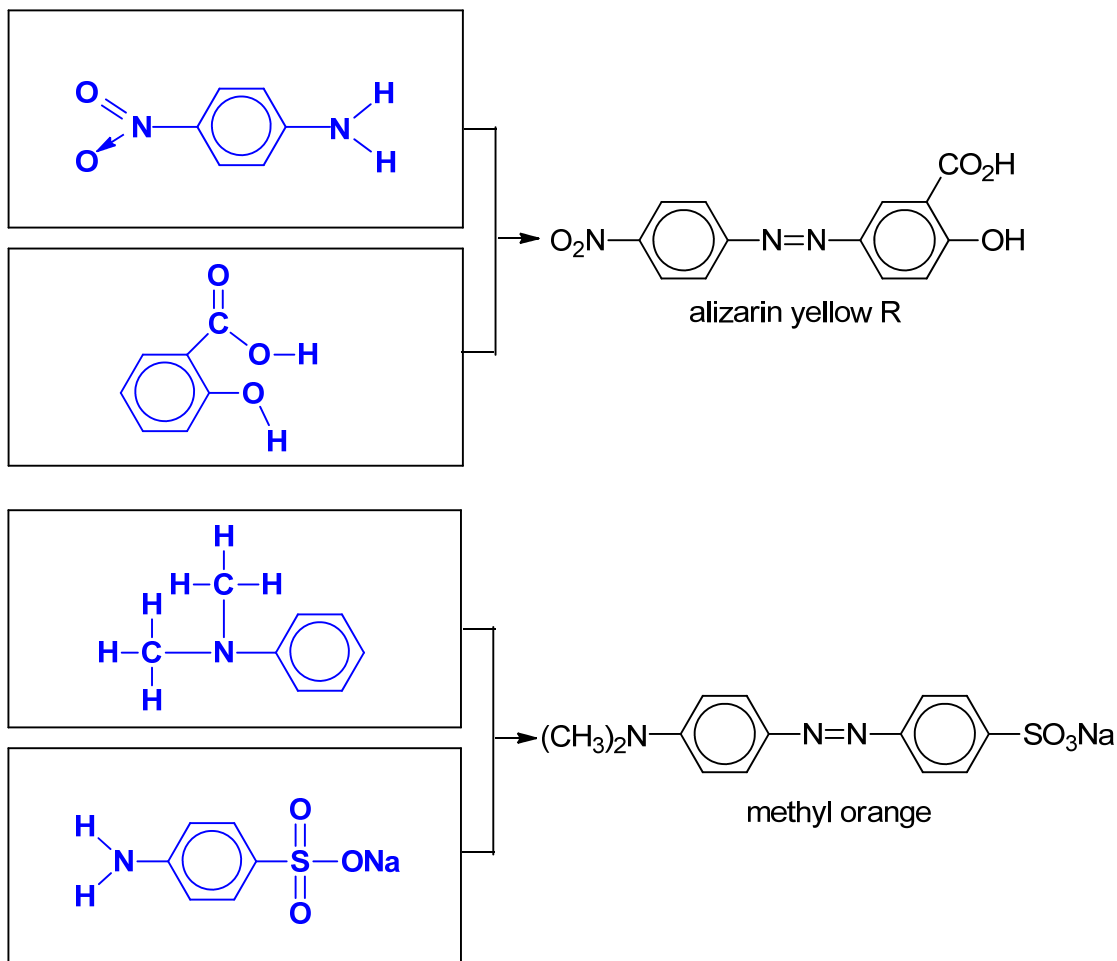
Oxidation

[1]

The diazonium ion is then reacted with a phenol or an arylamine in alkaline solution.



- (ii) Suggest the starting compounds needed to synthesise the following dyes. Draw their full structural formulae in the boxes provided.



[4]

- (iii) The benzene ring containing the NaO_3S^- group in methyl orange is less reactive towards bromine than the other benzene ring. Suggest **two** reasons.

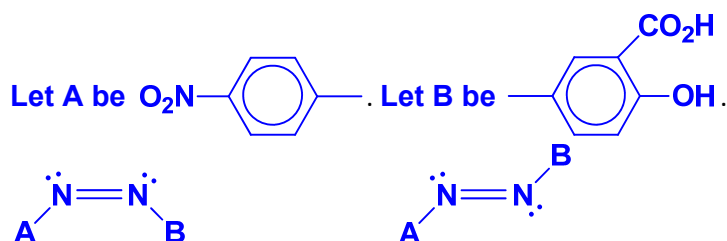
NaO_3S^- group is an electron withdrawing group, making the benzene ring less electron-rich and less susceptible to electrophilic attack.

Lone pair of electrons on $-\text{N}(\text{CH}_3)_2$ can delocalise into the benzene ring, making the benzene ring more electron-rich and more susceptible to electrophilic attack.

[2]

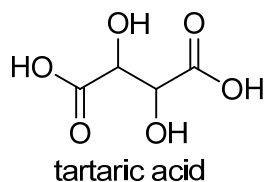
- (iv) Alizarin yellow R exhibits stereoisomerism and is a common indicator for acid-base titrations.

Draw the stereoisomers of alizarin yellow R.



[1]

- (c) Tartaric acid is present in many plants.

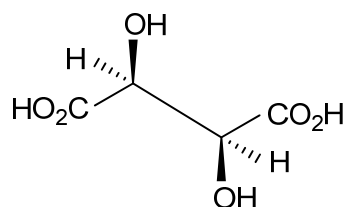


- (i) Tartaric acid has two acid dissociation constants, K_{a1} and K_{a2} , for which the pK_a values are 2.99 and 4.40. Draw the species present at pH 4.40.

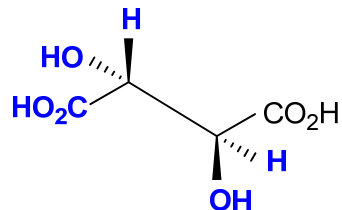
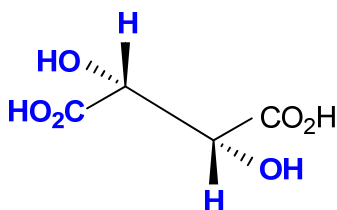


[1]

- (ii) One stereoisomer of tartaric acid is shown below.



Complete the diagrams below to show two other stereoisomers of tartaric acid.



[2]

[Total: 15]