Class | Adm No

Candidate Name: _____

H

millennia institute

2023 Preliminary Examination
Pre-University 3

H2 CHEMISTRY **9729/02**

Paper 2 Structured Questions **13 September 2023**

2 hours

Candidates answer on the Question paper.

Additional materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not turn over this question paper until you are told to do so

Write your name, class and admission number on all the work you hand in.

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.

The use of an approved scientific calculator is expected, where appropriate.

A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.

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

Question	1	2	3	4	Total
Marks	/20	/14	/20	/21	/75

For Examiners' Use

1 (a) The mercury cell is a non-rechargeable electrochemical battery making use of the reaction between mercuric oxide, HgO, and Zn electrodes. The reaction is performed in an alkaline electrolyte.

The main reaction of the battery is:

$$Zn + HgO \rightarrow ZnO + Hg \qquad \textbf{equation 1.1}$$

The ion-electron equation for the reaction of HgO is:

$$[R]: HgO + H_2O + 2e^- \rightarrow Hg + 2OH^- \qquad E_{HgO/Hg} = +0.10\ V$$

As mercury is toxic, the sale of mercury cells is now banned in many countries.

(i) Due to the alkaline conditions, the oxidation of Zn forms $Zn(OH)_4^{2-}$ as the product. It then undergoes another (non-redox) chemical reaction to form ZnO.

Write an ion-electron equation for the oxidation of Zn to $Zn(OH)_4^{2-}$.

[O]: ..... [1]

$Zn + 4H_2O \rightarrow Zn(OH)_4^{2-}$

$Zn + 4H_2O \rightarrow Zn(OH)_4^{2-} + 4H^+$

$Zn + 4H_2O \rightarrow Zn(OH)_4^{2-} + 4H^+ + 2e^-$

$Zn + 4H_2O + 4OH^- \rightarrow Zn(OH)_4^{2-} + 4H^+ + 4OH^- + 2e^-$

[O]: $Zn + 4OH^- \rightarrow Zn(OH)_4^{2-} + 2e^-$;

(ii) A voltmeter is placed across a button-sized mercury cell to measure the cell potential of **equation 1.1**. An enlarged schematic of the button-sized mercury cell is shown in **Fig 1.1**.

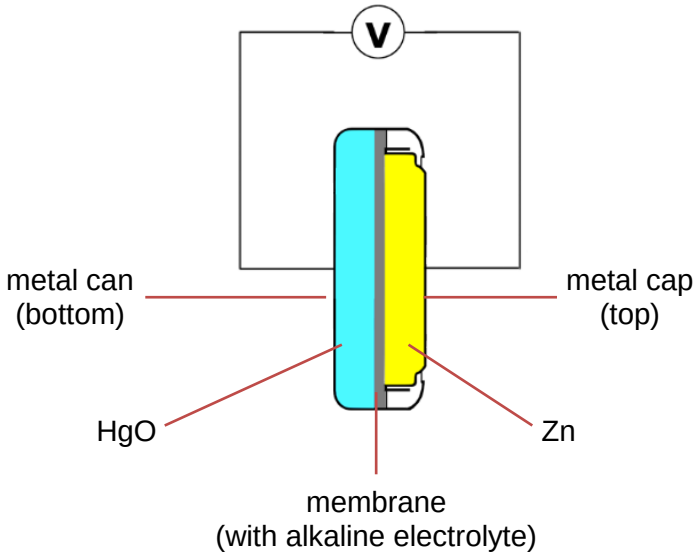


Fig 1.1

Determine the charges of the metal cap/can and identify which is the anode/cathode.

	charge	anode or cathode
metal cap		
metal can		

[2]

	charge	anode or cathode
metal cap	negative	anode
metal can	positive	cathode

charge pair ; electrode pair ;

(iii) Hence, label the flow of electrons in the external circuit of **Fig 1.1**. [1]

from cap to can (anticlockwise)

(iv) Suggest the function of the membrane.

……[1]

It acts as the salt bridge to maintain electrical neutrality. OR

To separate the HgO and Zn to allow electron flow via the external circuit. ;

(v) The cell potential of **equation 1.1** is found to be +1.35 V.

Calculate the reduction potential of the $Zn(OH)_4^{2-}/Zn$ half-cell.

[1]

$E_{cell} = E_{cat} - E_{an}$
$= E_{red} - E_{ox}$

$+1.35 = E_{HgO/Hg} - E_{Zn(OH)42-/Zn}$

$E_{Zn(OH)42-/Zn} = +0.10 - (+1.35)$
$= -1.25$ V ;

(vi) Deduce how the cell potential of **equation 1.1** will change if the $[Zn(OH)_4^{2-}]$ is increased.

……

……

……

……

……

……[2]

$Zn(OH)_4^{2-} + 2e^- \rightleftharpoons Zn + 4OH^-$ --- Equilibrium 1

A increase in $[Zn(OH)_4^{2-}]$ shifts position of Equilibrium 1 to the right. ;

$E_{Zn(OH)42-/Zn}$ will become less negative, leading to E_{cell} becoming less positive. ;

(b) Mercury is typically unreactive and does not react with most acids. However, it dissolves in 'aqua regia', which is a mixture of nitric acid and hydrochloric acid.

When nitric acid and hydrochloric acid are mixed together, nitrosyl chloride and chlorine gas are formed:

$$HNO_3 + 3HCl \rightarrow NOCl + Cl_2 + 2H_2O$$

(i) Suggest the shape about the central N atom of NOC*l*.

shape: …… [1]

bent ;

(ii) Explain, with reference to the Valence Shell Electron Pair Repulsion theory, the shape of the NOC*l* molecule.

……

……

……

……[2]

There are 3 electron pairs / 2 bond pairs 1 lone pair around the central atom, N.

VSEPR states that to minimise repulsion, ;

the electron pairs are arranged as far apart as possible about the central atom (bent for 3 electron pairs). ;

(iii) At 500 K, NOC*l* readily dissociates into NO and Cl_2:

$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$ **equation 1.2**

0.05 mol of NOC*l* and 0.05 mol Cl_2 were introduced into a 1 dm^3 reaction vessel at 500 K and left to equilibrate. The total amount of gases at equilibrium was found to be 0.122 mol, and the total pressure of gases was 5.00 atm.

Calculate the value of K_p for **equation 1.2** at 500 K.

[4]

	$2NOCl(g)$	$\rightleftharpoons$	$2NO(g)$	+	$Cl_2(g)$
I / mol	0.05		0		0.05
C / mol	-2x		+2x		+x
E / mol	0.05-2x		2x		0.05+x

;

0.05-2x + 2x + 0.05+x = 0.122
x = 0.022 mol ;

	$2NOCl(g)$	$\rightleftharpoons$	$2NO(g)$	+	$Cl_2(g)$
E / mol	0.006		0.044		0.072

$K_p = \frac{\left(\frac{0.044}{0.122}\times 5\right)^2 \left(\frac{0.072}{0.122}\times 5\right)}{\left(\frac{0.006}{0.122}\times 5\right)^2}$; *generic K_p expression*

= 159 atm (3sf) ;

(c) **Fig 1.2** shows the graph of *pV/RT* against varying pressures, *p*, for 1.0 mol of O_2.

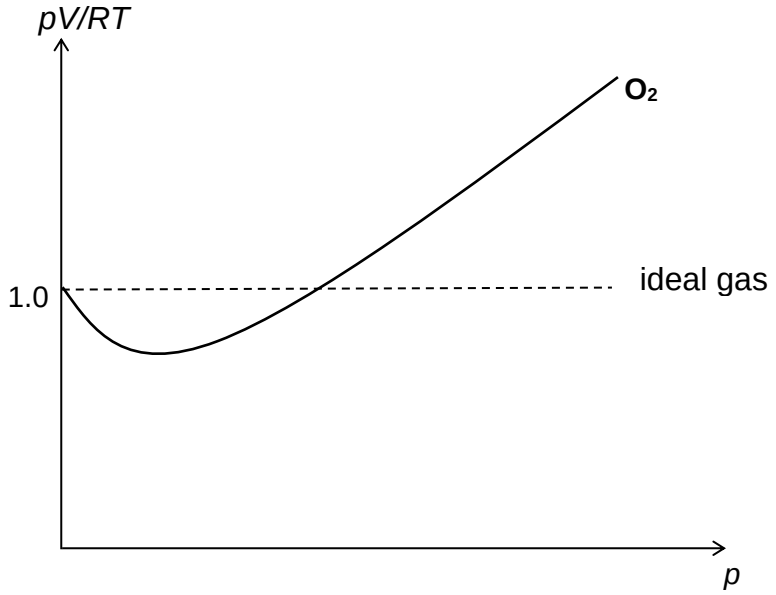


Fig 1.2

(i) State the two main assumptions of the kinetic theory of ideal gases.

……

……

……[2]

Vol of gas particles are negligible compared to volume of the container. ;
Intermolecular forces between gas particles is negligible. ;

(ii) Explain the shape of the graph for the 'ideal gas' in **Fig 1.2**.

……

……

……[1]

pV = nRT
pV/RT = n = constant (1 mol)
The ideal gas curve is a horizontal line of constant value (pV/RT = 1) OR

Ideal gases always obey the ideal gas equation pV=nRT ;

don't mark for "1 mol"

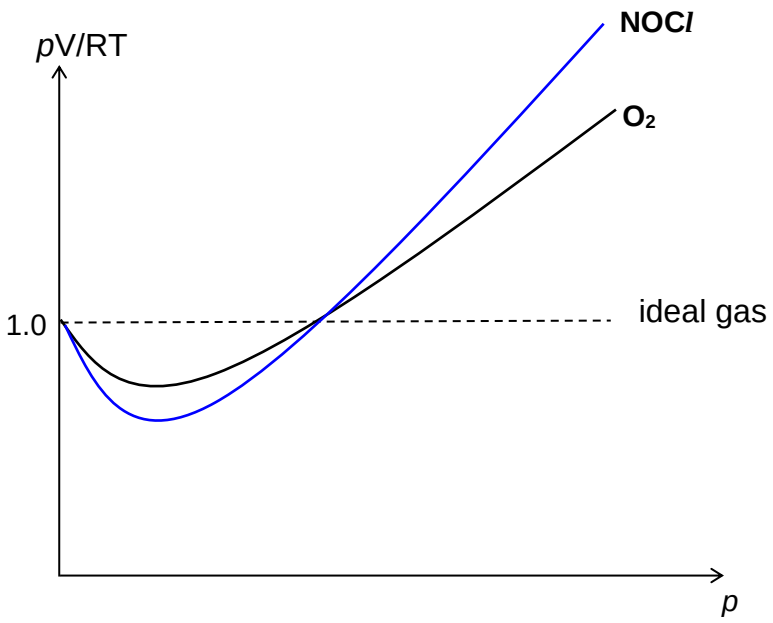
(iii) Sketch the graph for NOC*l* on **Fig 1.2**, explaining your reasoning.

……

……

……

.....[2]

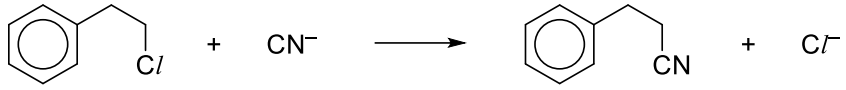


NOC*l* deviates more from ideality as the permanent dipole–permanent dipole interactions / instantaneous dipole-induced dipole interactions between its molecules are stronger than the instantaneous dipole–induced dipole interactions between O_2 molecules. ;

[Total: 20]

2 Kinetics studies, especially for organic reactions, provide strong evidence of their hypothesised mechanisms.

In one study, the kinetics of a nucleophilic substitution reaction involving $C_6H_5CH_2CH_2Cl$ and CN^- was investigated.



A series of 4 experiments was conducted using different concentrations of $C_6H_5CH_2CH_2Cl$ while keeping the concentration of CN^- constant at 2.00 mol dm^{-3}. **Fig 2.1** shows the results:

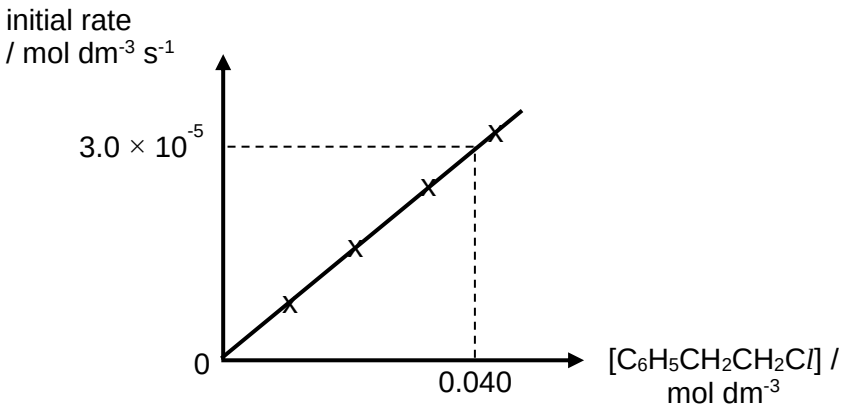


Fig 2.1

(a) **(i)** The order of reaction with respect to $C_6H_5CH_2CH_2Cl$ is 1.

Explain how the graph of **Fig 2.1** shows this.

……

……

…… [2]

The graph is a straight line of positive gradient passing through the origin, ;

thus rate is directly proportional to the [$C_6H_5CH_2CH_2Cl$]. ;

(ii) Briefly explain why the concentration of CN^- has to be kept constant.

……

…… [1]

[CN^-] has to be kept constant to confirm that any change in rate is solely due to [$C_6H_5CH_2CH_2Cl$] changing. ; *OWTTE*

do not accept large excess / pseudo-order reaction

(iii) The rate equation for the reaction was found to be:

$$\text{rate} = k[C_6H_5CH_2CH_2Cl][CN^-]$$

Determine a value for the rate constant, k, stating its units clearly.

[2]

rate = $k[C_6H_5CH_2CH_2Cl][CN^-]$
$3.00 \times 10^{-5} = k(0.04)(2)$
$k = 3.75 \times 10^{-4}$ mol^{-1} dm^3 s^{-1} ;;

(iv) Explain how the rate of reaction is expected to change when the reaction is carried out at a higher temperature.

……

……

……

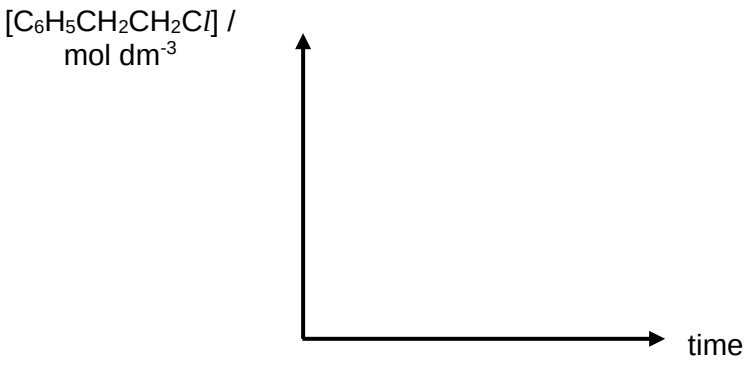
……

……[2]

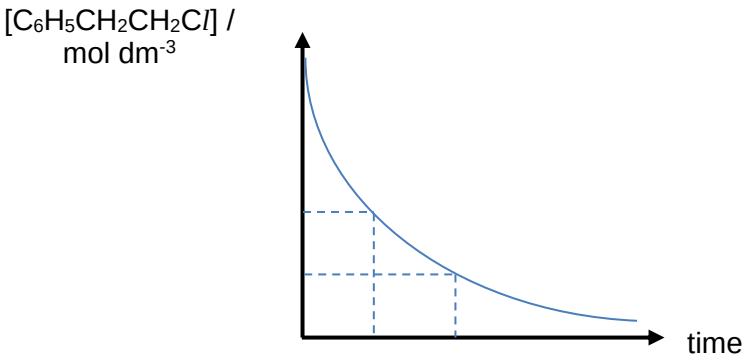
A higher temperature results in an increase in the average kinetic energy of the reactant particles. There is now a larger fraction of reactant particles with energy greater or equal to activation energy, leading to an increase in the frequency of effective collisions and hence faster rate. ;;

3pts 2m, 2pts 1m

(v) On the axes provided, sketch how you would expect the concentration-time graph of $C_6H_5CH_2CH_2Cl$ to look like for the reaction.



[2]

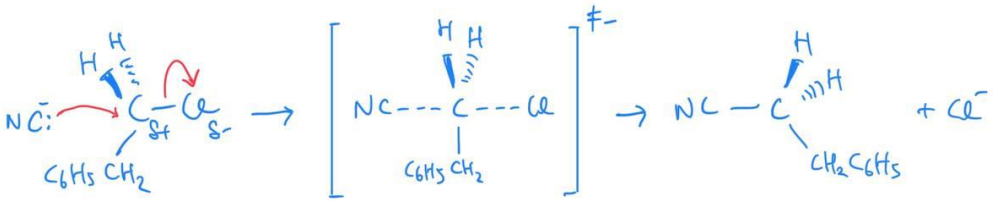


shape; constant half-life shown;

(b) **(i)** Outline the mechanism for the reaction between $C_6H_5CH_2CH_2Cl$ and CN^-. Show clearly any relevant charges, lone pairs of electrons, and movement of electrons.

[3]

Nucleophilic Substitution (S_N2) *no mark for just N.S.*



(ii) When $C_6H_5CHClCH_3$ was used in place of $C_6H_5CH_2CH_2Cl$, the rate equation was found as:

$$\text{rate} = k[C_6H_5CHClCH_3]$$

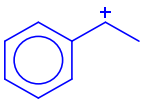
Explain this observation.

……

……

……

……[2]

The carbocation formed,  , is stabilised due to the p-orbital overlap with the adjacent pi-electron cloud of benzene. ;

This favours the nucleophilic substitution reaction taking place via an S_N1 reaction mechanism. ;

[Total: 14]

3 (a) **Table 3.1** shows the reduction potentials, atomic radii, and ionic radii for three Group 2 elements.

element	$E^{\ominus}$ [M^{2+}/M] / V	atomic radii of M / nm	ionic radii of M^{2+} / nm
Mg	–2.38	0.160	0.065
Ca	–2.87	0.197	0.099
Sr	–2.89	0.215	0.113

Table 3.1

(i) Rank and give an explanation for the relative reactivity of the Group 2 elements in **Table 3.1** as reducing agents.

……

……

……

……

……[2]

Reducing power: Mg < Ca < Sr ;

Down the group, $E^{\ominus}$ becomes more negative, hence the elements are themselves more readily oxidised, becoming stronger reducing agents. ;

OR

Down the group, both nuclear charge and shielding effect increases, so effective nuclear charge remains relatively constant. As the number of principal quantum shells increases, valence electrons are further away from the nucleus and less strongly attracted. Less energy is required to remove the valence electron when the Group 2 element is itself oxidised. ;

(ii) Explain how the ionic radius of Mg^{2+} would compare to that of Na^{+}.

……

……

……

……

……[2]

Ionic radii: $Mg^{2+} < Na^{+}$;

Across the isoelectronic series, nuclear charge increases while shielding effect remains constant, leading to an increase in effective nuclear charge. Attraction of the valence electrons for the nucleus increases, leading to a decrease in ionic radius. ;

(iii) Write, with state symbols, a chemical equation when solid MgO dissolves in water. State the pH of the resultant solution.

chemical equation: ……..

resultant pH: ……..... [2]

chemical equation: $MgO(s) + H_2O(l) \rightleftharpoons Mg(OH)_2(aq)$;
resultant pH = 9 ;

(iv) A water sample is known to contain small amounts of Ca^{2+}. To determine the concentration of Ca^{2+}, the following procedure is used:

1. An excess of alcoholic oxalate ($C_2O_4^{2-}$) solution is added to 25.0 cm^3 of the water sample to precipitate all of the Ca^{2+} as its metal oxalate salt.

2. The calcium oxalate is then converted to calcium carbonate solid via heat, and the solid is separated from solution via centrifugation followed by decanting.

3. To the calcium carbonate, 25.0 cm^3 of 0.10 mol dm^{-3} HC*l*(aq) was added, followed by titration with 0.02 mol dm^{-3} NaOH(aq).

Given that 23.20 cm^3 of NaOH(aq) was used in the titration, determine the concentration of Ca^{2+} in the 25.0 cm^3 water sample.

[4]

Amount of NaOH = $0.02 \times \frac{23.20}{1000}$
= 0.000464 mol ;
= Amount of HC*l* in excess

Amount of HC*l* reacted = Initial – Excess
= $(0.10 \times \frac{25.0}{1000}) - (0.000464)$
= 0.002036 ;

$2HCl + CaCO_3 \rightarrow CaCl_2 + H_2O + CO_2$

Amount of Ca^{2+} = Amount of $CaCO_3$

= ½ x Amount of HC*l* reacted
= 0.001018 mol ;

$[Ca^{2+}] = \frac{0.001018}{25.0/1000}$
= 0.0407 mol dm^{-3} (3sf) ;

(v) Suggest why calcium oxalate is not very soluble in alcoholic solution.

……

……

……

……

……[2]

Alcohols are generally less polar than water due to its additional hydrocarbon chains.

Energy released from formation of the less favourable ion-dipole interactions between the calcium / oxalate ions with alcohol is ;

insufficient to overcome the stronger hydrogen bonding between alcohol molecules / electrostatic forces of attraction between calcium and oxalate ions. ;

(b) Pure water is said to be *neutral* regardless of its temperature, even as its pH varies. The pH of liquid water at different temperatures is shown below:

temperature / °C	pH
0	7.47
10	7.26
25	7.00
40	6.76
50	6.63

Table 3.2

(i) Explain what it means for a solution to be *neutral*.

……[1]

$[H^+] = [OH^-]$;

(ii) Using the pH values in **Table 3.2**, calculate a value for the pK_w of water at 40 °C.

[1]

$K_w = [H^+][OH^-]$ OR $pK_w = pH + pOH$

pK_w at 40°C = pH at 40°C + pOH at 40°C
= 6.76 + 6.76
= 13.5 (3sf) ;

(iii) The pH of water decreases as temperature increases.

Deduce the sign of the enthalpy change of reaction of dissociation of water and fully explain the above observation.

……

……

……

……

……

…….. [2]

$H_2O \rightleftharpoons H^+ + OH^- \quad \Delta H > 0$

Since [H^+] increases, position of equilibrium shifts to the right as temperature increases. By LCP, the system favours the endothermic reaction to remove excess heat, ;

hence the forward reaction is endothermic. ;

Note also that only bonds are broken in the dissociation of water.

(iv) Compare and explain the relative densities of ice and water at 0 °C.

……

……

……

…….. [2]

Ice is less dense than water. ;

The water molecules in ice are regularly arranged in a tetrahedral fashion due to hydrogen bonding between the molecules, and this results in an open structure that has higher volume per unit mass. ;

(v) Pure water has a density of 1.0 g cm^{-3}.

Calculate the concentration of pure water.

[2]

Amount of H_2O in 1 g = $\frac{1.0}{2.0+16.0}$
= 0.05555 mol ;

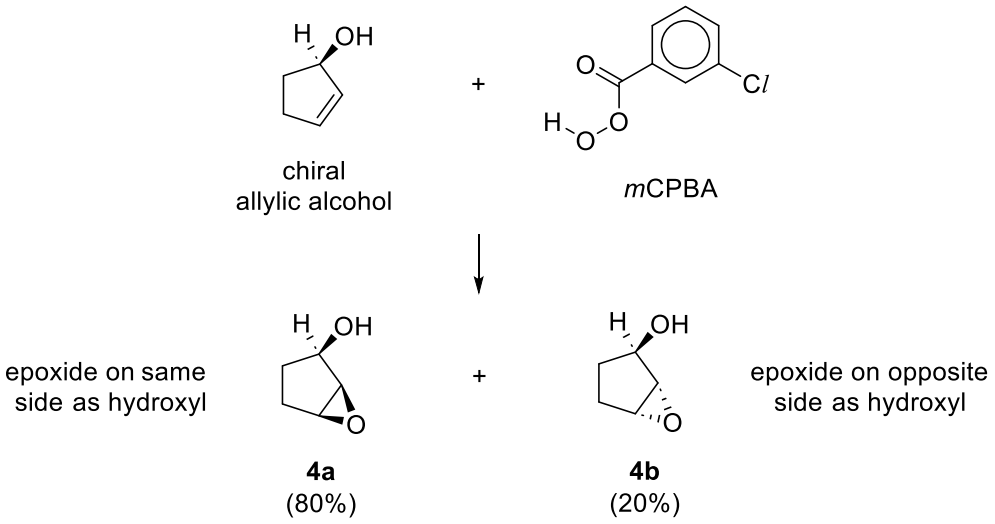
$[H_2O] = \frac{0.05555}{1\times10^{-3}}$
= 55.6 mol dm^{-3} ;

[Total: 20]

For Examiners' Use

4 Enantioselective synthesis is a form of chemical synthesis that favours the formation of specific enantiomers or diastereomers. It is a key process in modern chemistry and is particularly important in the field of pharmaceuticals.

An example of enantioselective synthesis is the epoxidation of chiral allylic alcohols using meta-chloroperoxybenzoic acid (*m*CPBA), where the epoxide functional group (O) is selectively formed on the same side as the hydroxyl group.



In this reaction, the epoxide products are formed in the ratio of 80:20. This reaction is said to have a *diastereomeric excess* (%*de*) of 60%, favouring the formation of epoxide **4a**.

(a) **(i)** Suggest why enantioselective synthesis is particularly important in the field of pharmaceuticals.

……

…… [1]

Chiral compounds exhibit different biological properties. / Chiral compounds are needed to interact with chiral receptors in the body. ; *OWTTE*

In the best case scenario, the other enantiomer is inactive. In the worst case scenario, the other enantiomer is toxic (refer to Thalidomide example).

(ii) The epoxide products, **4a** and **4b**, are stereoisomers of one another, but they are not considered enantiomers.

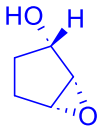
Explain why **4a** and **4b** are not enantiomers.

…… [1]

They are not mirror images of one another. ;

(iii) Draw the enantiomer of **4a**.

[1]

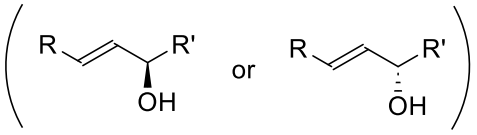


mark leniently, mirror plane not required

(iv) Deduce how the value for %*de* of 60% was calculated.

[1]

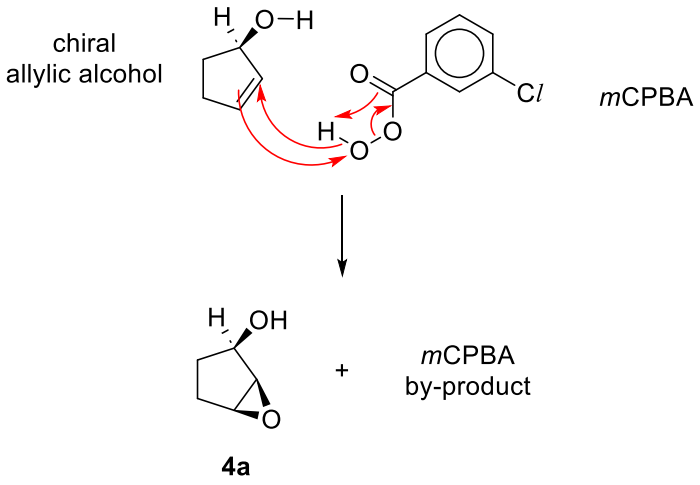
%*de* = 80 - 20
= 60% (shown) ;

(b) Allylic alcohols consist of a hydroxyl group that is bonded to a carbon atom adjacent to a C=C 

.

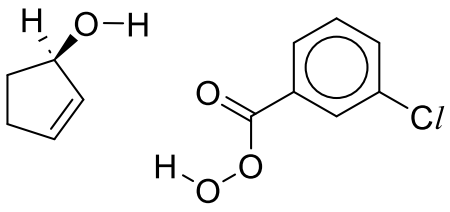
In the epoxidation of chiral allylic alcohols using *m*CPBA, the enantioselective property of the reaction arises as a result of the intermolecular forces of attraction between the hydroxyl group of the allylic alcohol and the C=O oxygen atom of *m*CPBA.

The reaction mechanism (with curly arrows) is as follows:



4a

(i) Illustrate on the diagram below the intermolecular forces of attraction between the hydroxyl group of the allylic alcohol and the C=O oxygen atom of *m*CPBA.



[2]

<ans>

(ii) Hence, explain why the epoxide functional group is selectively formed on the same side as the hydroxyl group, favouring the epoxide **4a** product.

……

……

……[2]

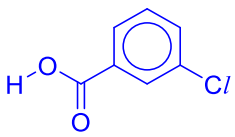
The interaction (H-bonding) tethers the *m*CPBA on the side of the alkene closer to the hydroxyl group, / brings the C=C and O atom of *m*CPBA involved into close proximity, ;

introducing the epoxide O atom there. ;

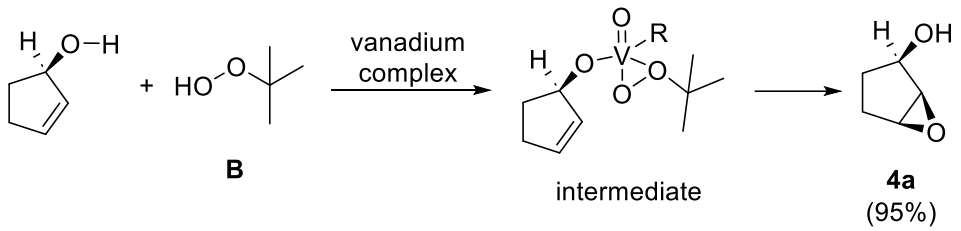
OWTTE, ecf for interaction

(iii) Draw the structure of the *m*CPBA by-product.

[1]



(c) The same enantioselective epoxidation reaction can also be carried out using a vanadium complex, which acts as a catalyst. A small quantity of this soluble catalyst is added to a solution containing a 1:1 mixture of the chiral allylic alcohol and compound **B**.



B intermediate **4a** (95%)

The reaction proceeds with ligand exchange, followed by the transfer of an oxygen atom to the allylic alcohol to form epoxide **4a** with 95% yield.

(i) Define the term *complex*.

……

…… [1]

A complex contains a central metal atom or ion datively bonded to one or more surrounding molecules or ions (called ligands). ;

(ii) Compound **B** is said to be acting as a *bidentate ligand* in the intermediate.

Explain the term bidentate, and how compound **B** is able to act as a bidentate ligand.

……

……

…… [2]

A bidentate ligand is one that can form 2 dative bonds to the central metal atom or ion. ;

A single molecule of compound **B** comprises of two O atoms with lone pairs of electrons available for donation. ; *OWTTE*

(iii) Suggest the role of compound **B**, other than it acting as a ligand.

…… [1]

Oxidising agent / source of epoxide O atom ;

(iv) Identify the type of catalysis taking place.

…… [1]

Homogeneous catalysis ;

(v) 3d block transition metal ions have smaller ionic radii and higher charge densities compared to their 4d block counterparts of similar oxidation state.

Suggest how changing the catalyst to its counterpart 4d block complex could affect the yield of the reaction.

……

……

……

……[2]

Decrease:
Larger ionic radii causes **B** to be too far from allylic alcohol for successful reaction.
Lower charge density causes ligands to not bond well to central metal atom for any reaction to even take place.

OR

Increase:
Larger ionic radii allows for more ligands to be bonded to central metal atom, facilitating reaction.
Lower charge density causes ligands to be less strongly bonded to central metal atom, facilitating ease of ligand exchange and hence reaction.

any combination of 1 ionic radii and 1 charge density, award mark for any other logical answer

(d) **(i)** The catalytic hydrogenation of alkenes using hydrogen gas with nickel is an example of heterogeneous catalysis.

Outline the mode of action of this heterogeneous catalysis, clearly illustrating your answer with suitable diagrams.

[3]

Adsorption – reactant molecules stick to the surface of the nickel catalyst

Reaction – the H atoms are added onto the alkene molecule

Desorption – products leave from surface of nickel catalyst

(ii) Briefly explain how this heterogeneous catalysis increases the rate of reaction.

……

……

……

……[2]

Partial bonds formed between the reactants and catalyst weakens the bonds within the reactants, lowering activation energy of reaction. ;

When reactants are adsorbed onto the catalyst surface, they are brought to closer proximity / [reactants] on surface of catalyst increases, leading to increased frequency of effective collisions. ;

[Total: 21]

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