Class | Adm No

Candidate Name: _____

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]

(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**.

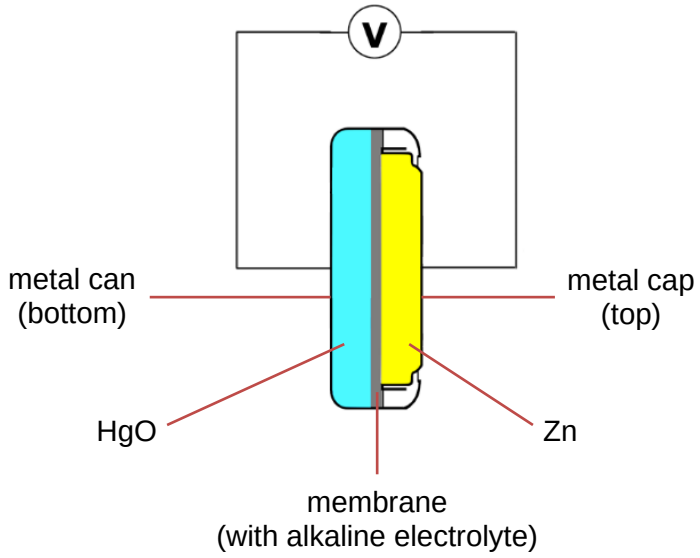


Fig 1.1

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

	charge	anode or cathode
metal cap		
metal can		

[2]

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

(iv) Suggest the function of the membrane.

……[1]

(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]

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

……

……

……

……

……

……[2]

(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]

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

……

……

……

…… [2]

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

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g) \qquad \textbf{equation 1.2}$$

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]

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

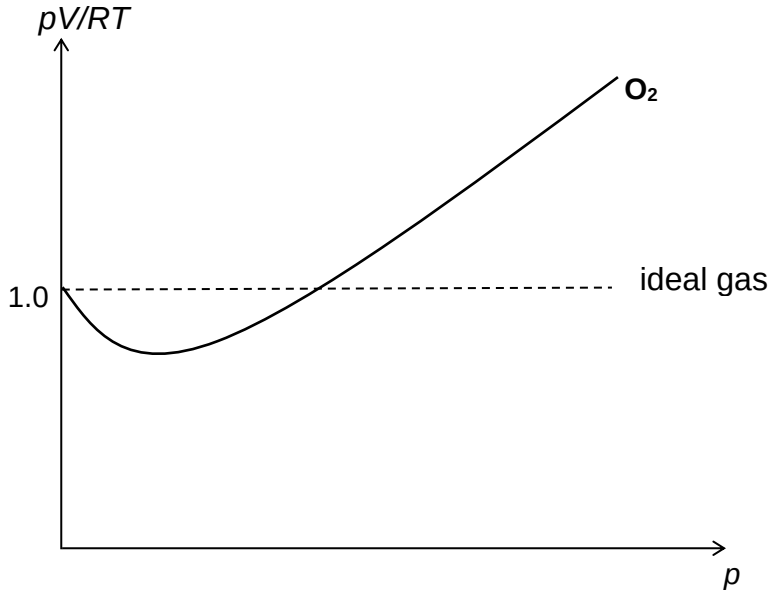


Fig 1.2

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

……

……

……[2]

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

……

……

……[1]

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

……

……

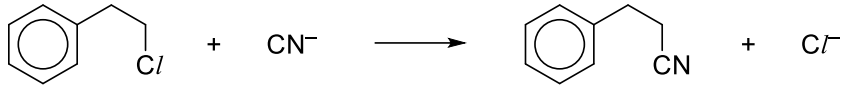
……

……[2]

[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:

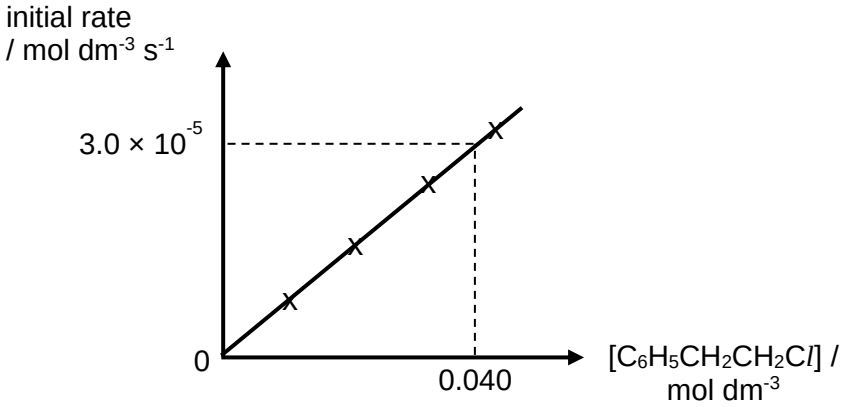


Fig 2.1

(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]

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

……

……[1]

(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]

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

……

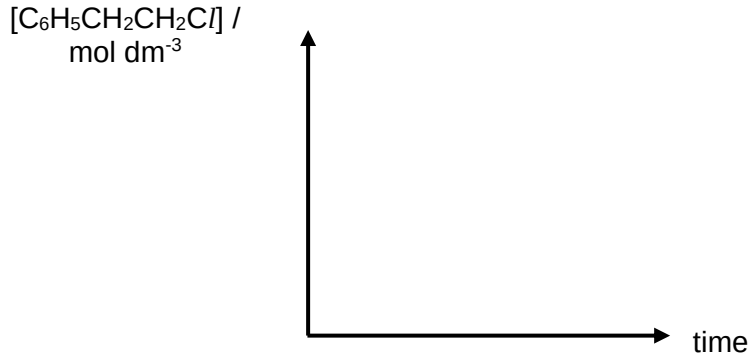
……

……

……

……[2]

(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]

(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]

(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]

[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]

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

……

……

……

……

……[2]

(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]

(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]

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

……

……

……

……

……[2]

(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]

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

[1]

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

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

……

……

……

……

……

…….. [2]

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

……

……

……

…….... [2]

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

Calculate the concentration of pure water.

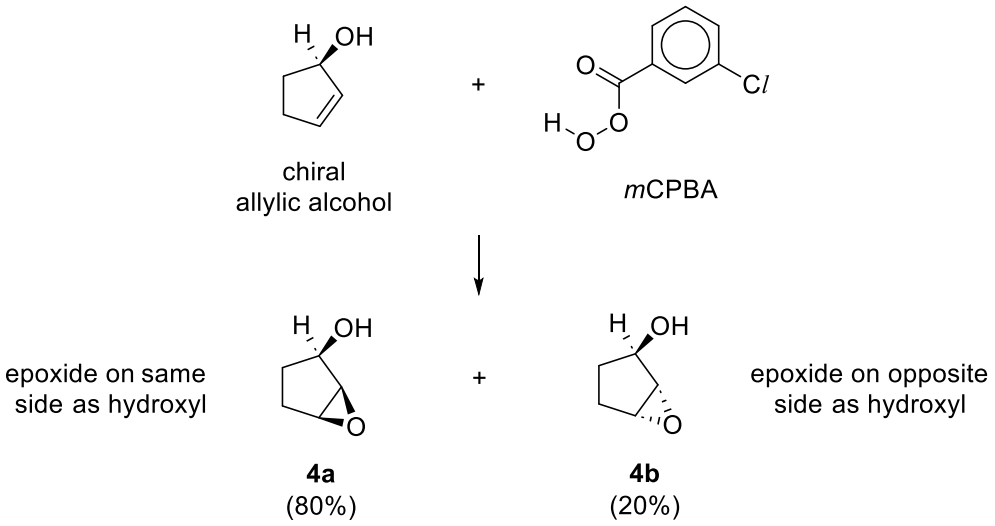
[2]

[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 ( ) 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]

(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.

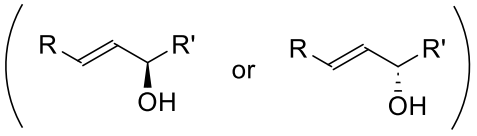
……[1]

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

[1]

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

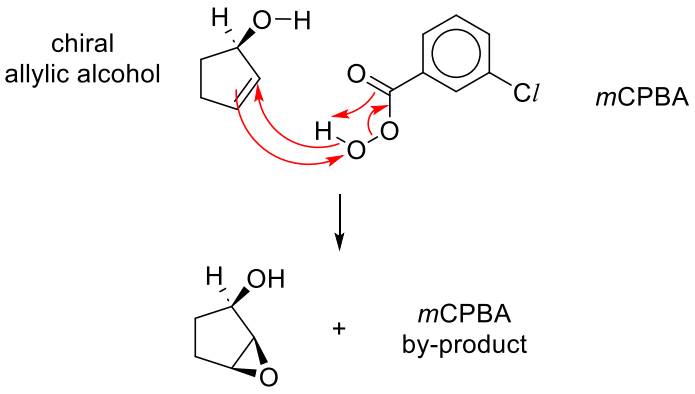
[1]

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

.

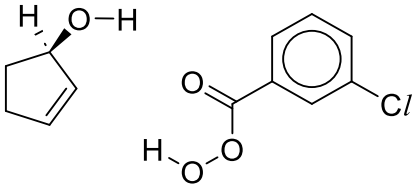
In the epoxidation of chiral allylic alcohols using *m*CPBA, the enantioselective property of the reaction arises as a result of the intermolecular forces of attraction between the hydroxyl group of the allylic alcohol and the C=O oxygen atom of *m*CPBA.

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]

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

……

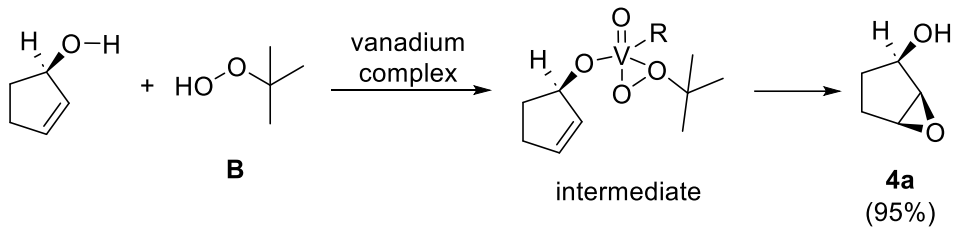
……

…… [2]

(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]

(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]

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

…… [1]

(iv) Identify the type of catalysis taking place.

…… [1]

(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]

(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]

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

……

……

……

……[2]

[Total: 21]

BLANK PAGE