In addition to this paper you will require:

a calculator.

Time allowed: 1 hour 30 minutes

Instructions

• Use blue or black ink or ball-point pen.
• Fill in the boxes at the top of this page.
• Answer all questions in Section A and Section B in the spaces provided. All working must be shown.
• Do all rough work in this book. Cross through any work you do not want marked.
• The Periodic Table/Data Sheet is provided on pages 3 and 4. Detach this perforated sheet at the start of the examination.

Information

• The maximum mark for this paper is 90.
• Mark allocations are shown in brackets.
• This paper carries 15 per cent of the total marks for Advanced Level.
• You are expected to use a calculator where appropriate.
• The following data may be required.
  Gas constant $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$
• Your answers to questions in Section B should be written in continuous prose, where appropriate. You will be assessed on your ability to use an appropriate form and style of writing, to organise relevant information clearly and coherently, and to use specialist vocabulary, where appropriate.

Advice

• You are advised to spend about 1 hour on Section A and about 30 minutes on Section B.
1 The rate of the reaction between substance \textbf{A} and substance \textbf{B} was studied in a series of experiments carried out at the same temperature. In each experiment the initial rate was measured using different concentrations of \textbf{A} and \textbf{B}. These results were used to deduce the order of reaction with respect to \textbf{A} and the order of reaction with respect to \textbf{B}.

(a) What is meant by the term \textit{order of reaction} with respect to \textbf{A}?
.......................................................................................................................................................
.......................................................................................................................................................
\hspace{10cm} (1 \text{ mark})

(b) When the concentrations of \textbf{A} and \textbf{B} were both doubled, the initial rate increased by a factor of 4. Deduce the \textbf{overall} order of the reaction.
.......................................................................................................................................................
\hspace{10cm} (1 \text{ mark})

(c) In another experiment, the concentration of \textbf{A} was increased by a factor of three and the concentration of \textbf{B} was halved. This caused the initial rate to increase by a factor of nine.

(i) Deduce the order of reaction with respect to \textbf{A} and the order with respect to \textbf{B}.

\hspace{1cm} \textit{Order with respect to A} .........................................................................................
\hspace{1cm} \textit{Order with respect to B} .........................................................................................

(ii) Using your answers from part (c)(i), write a rate equation for the reaction and suggest suitable units for the rate constant.

\hspace{1cm} \textit{Rate equation} ............................................................................................................
\hspace{1cm} \textit{Units for the rate constant} ...........................................................................................

\hspace{10cm} (4 \text{ marks})
The Periodic Table of the Elements

- The atomic numbers and approximate relative atomic masses shown in the table are for use in the examination unless stated otherwise in an individual question.

<table>
<thead>
<tr>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
<th>VII</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>Hydrogen</td>
<td>6.9</td>
<td>Li</td>
<td>Lithium</td>
<td>9.0</td>
<td>Be</td>
</tr>
<tr>
<td>3</td>
<td>Li</td>
<td>Lithium</td>
<td>9.0</td>
<td>Be</td>
<td>Beryllium</td>
<td>16.0</td>
<td>C</td>
</tr>
<tr>
<td>24</td>
<td>Mg</td>
<td>Magnesium</td>
<td>12.0</td>
<td>Al</td>
<td>Aluminium</td>
<td>13.0</td>
<td>Si</td>
</tr>
<tr>
<td>39.1</td>
<td>K</td>
<td>Potassium</td>
<td>20.1</td>
<td>Ca</td>
<td>Calcium</td>
<td>21.0</td>
<td>Sc</td>
</tr>
<tr>
<td>39.5</td>
<td>Rb</td>
<td>Rubidium</td>
<td>37.0</td>
<td>Sr</td>
<td>Strontium</td>
<td>38.0</td>
<td>Y</td>
</tr>
<tr>
<td>132.9</td>
<td>Cs</td>
<td>Caesium</td>
<td>55.0</td>
<td>Ba</td>
<td>Barium</td>
<td>56.0</td>
<td>La</td>
</tr>
<tr>
<td>223.0</td>
<td>Fr</td>
<td>Francium</td>
<td>87.0</td>
<td>Ra</td>
<td>Radium</td>
<td>88.0</td>
<td>Ac</td>
</tr>
<tr>
<td>58 – 71</td>
<td>Lanthanides</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>90 – 103</td>
<td>Actinides</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Key:
- relative atomic mass
- atomic number
### Table 1
Proton n.m.r chemical shift data

<table>
<thead>
<tr>
<th>Type of proton</th>
<th>δ/ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>RCH₃</td>
<td>0.7–1.2</td>
</tr>
<tr>
<td>R₂CH₂</td>
<td>1.2–1.4</td>
</tr>
<tr>
<td>R₃CH</td>
<td>1.4–1.6</td>
</tr>
<tr>
<td>RCOCH₃</td>
<td>2.1–2.6</td>
</tr>
<tr>
<td>ROCH₃</td>
<td>3.1–3.9</td>
</tr>
<tr>
<td>RCOOCH₃</td>
<td>3.7–4.1</td>
</tr>
<tr>
<td>ROH</td>
<td>0.5–5.0</td>
</tr>
</tbody>
</table>

### Table 2
Infra-red absorption data

<table>
<thead>
<tr>
<th>Bond</th>
<th>Wavenumber/cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>C—H</td>
<td>2850–3300</td>
</tr>
<tr>
<td>C—C</td>
<td>750–1100</td>
</tr>
<tr>
<td>C=C</td>
<td>1620–1680</td>
</tr>
<tr>
<td>C=O</td>
<td>1680–1750</td>
</tr>
<tr>
<td>C—O</td>
<td>1000–1300</td>
</tr>
<tr>
<td>O—H (alcohols)</td>
<td>3230–3550</td>
</tr>
<tr>
<td>O—H (acids)</td>
<td>2500–3000</td>
</tr>
</tbody>
</table>
2 When a mixture of 0.345 mol of PCl₃ and 0.268 mol of Cl₂ was heated in a vessel of fixed volume to a constant temperature, the following reaction reached equilibrium.

\[ \text{PCl}_3(g) + \text{Cl}_2(g) \rightleftharpoons \text{PCl}_5(g) \quad \Delta H^\circ = -93 \text{ kJ mol}^{-1} \]

At equilibrium, 0.166 mol of PCl₅ had been formed and the total pressure was 225 kPa.

(a) (i) Calculate the number of moles of PCl₃ and of Cl₂ in the equilibrium mixture.

Moles of PCl₃ ....................................................................................................................

Moles of Cl₂ ......................................................................................................................

(ii) Calculate the total number of moles of gas in the equilibrium mixture.

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

(3 marks)

(b) Calculate the mole fraction and the partial pressure of PCl₃ in the equilibrium mixture.

Mole fraction of PCl₃ ........................................................................................................

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

Partial pressure of PCl₃ ......................................................................................................

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

(3 marks)

(c) (i) Write an expression for the equilibrium constant, \( K_p \), for this equilibrium.

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

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

(ii) The partial pressures of Cl₂ and PCl₅ in the equilibrium mixture were 51.3 kPa and 83.6 kPa, respectively, and the total pressure remained at 225 kPa. Calculate the value of \( K_p \) at this temperature and state its units.

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

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

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

(4 marks)

(d) State the effect on the mole fraction of PCl₃ in the equilibrium mixture if

(i) the volume of the vessel were to be increased at a constant temperature,

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

(ii) the temperature were to be increased at constant volume.

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

(2 marks)
3 (a) At 50°C, the ionic product of water, $K_w$, has the value $5.48 \times 10^{-14}$ mol$^2$ dm$^{-6}$.

(i) Define the term $K_w$
.............................................................................................................................................

(ii) Define the term pH
.............................................................................................................................................

(iii) Calculate the pH of pure water at 50°C. Explain why pure water at 50°C is still neutral even though its pH is not 7.

 Calculation .....................................................................................................................................
.......................................................................................................................................................
.......................................................................................................................................................

 Explanation .....................................................................................................................................
.......................................................................................................................................................
.......................................................................................................................................................

(5 marks)

(b) At 25°C, $K_w$ has the value $1.00 \times 10^{-14}$ mol$^2$ dm$^{-6}$. Calculate the pH at 25°C of

(i) a 0.150 mol dm$^{-3}$ solution of sodium hydroxide,
.............................................................................................................................................
.......................................................................................................................................................
.......................................................................................................................................................
.......................................................................................................................................................
.......................................................................................................................................................
.......................................................................................................................................................
.......................................................................................................................................................

(ii) the solution formed when 35.0 cm$^3$ of this solution of sodium hydroxide is mixed with 40.0 cm$^3$ of a 0.120 mol dm$^{-3}$ solution of hydrochloric acid.
.............................................................................................................................................
.......................................................................................................................................................
.......................................................................................................................................................
.......................................................................................................................................................
.......................................................................................................................................................
.......................................................................................................................................................
.......................................................................................................................................................

(8 marks)
(c) In a 0.150 mol dm\(^{-3}\) solution of a weak acid HX at 25\(^\circ\)C, 1.80\% of the acid molecules are dissociated into ions.

(i) Write an expression for \(K_a\) for the acid HX.

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

(ii) Calculate the value of \(K_a\) for the acid HX at this temperature and state its units.

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

\((5\text{ marks})\)

TURN OVER FOR THE NEXT QUESTION
4 (a) Outline a mechanism for the reaction of CH$_3$CH$_2$CH$_2$CHO with HCN and name the product.

*Mechanism*

*Name of product* .................................................................

(5 marks)

(b) Outline a mechanism for the reaction of CH$_3$OH with CH$_3$CH$_2$COCl and name the organic product.

*Mechanism*

*Name of organic product* ..................................................

(5 marks)
(c) An equation for the formation of phenylethanone is shown below. In this reaction a reactive intermediate is formed from ethanoyl chloride. This intermediate then reacts with benzene.

\[
\text{Ph} + \text{CH}_3\text{COCl} \xrightarrow{\text{AlCl}_3} \text{PhCOCH}_3 + \text{HCl}
\]

(i) Give the formula of the reactive intermediate.

(ii) Outline a mechanism for the reaction of this intermediate with benzene to form phenylethanone.
5 (a) The hydrocarbon M has the structure shown below.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2 \text{C} = \text{CH}_2 \\
\text{CH}_3
\end{align*}
\]

(i) Name hydrocarbon M.

(ii) Draw the repeating unit of the polymer which can be formed from M. State the type of polymerisation occurring in this reaction.

Repeating unit

Type of polymerisation ........................................................................................................................................

(iii) The reaction between M and benzene in the presence of HCl and AlCl₃ is similar to the reaction between ethene and benzene under the same conditions. Name the type of mechanism involved and draw the structure of the major product formed in the reaction between M and benzene.

Name of mechanism ........................................................................................................................................

Major product

(iv) Draw a structural isomer of M which shows geometrical isomerism.

(6 marks)

(b) Draw the repeating unit of the polymer formed by the reaction between butanedioic acid and hexane-1,6-diamine. State the type of polymerisation occurring in this reaction and give a name for the linkage between the monomer units in this polymer.

Repeating unit

Type of polymerisation ........................................................................................................................................

Name of linkage ..................................................................................................................................................

(4 marks)
Use the data given on the back of the Periodic Table on page 3 of this booklet to help you answer this question.

Compounds A to G are all isomers with the molecular formula C₆H₁₂O₂

(a) Isomer A, C₆H₁₂O₂, is a neutral compound and is formed by the reaction between compounds X and Y in the presence of a small amount of concentrated sulphuric acid. X and Y can both be formed from propanal by different redox reactions. X has an absorption in its infra-red spectrum at 1750 cm⁻¹. Deduce the structural formulae of A, X and Y. Give suitable reagents, in each case, for the formation of X and Y from propanal and state the role of concentrated sulphuric acid in the formation of A. (7 marks)

(b) Isomers B, C, D and E all react with aqueous sodium carbonate to produce carbon dioxide. Deduce the structural formulae of the three isomers that contain an asymmetric carbon atom. The fourth isomer has only three singlet peaks in its proton n.m.r. spectrum. Deduce the structural formula of this isomer and label it E. (4 marks)

(c) Isomer F, C₆H₁₂O₂, has the structural formula shown below, on which some of the protons have been labelled.

\[
\begin{align*}
\text{CH₃} & \quad \text{CH₂} & \quad \text{O} & \quad \text{CH₂} & \quad \text{CH₂} & \quad \text{CH} \\
\end{align*}
\]

A proton n.m.r. spectrum is obtained for F. Using Table 1 on page 4 of this booklet, predict a value of δ for the protons labelled a and also for those labelled b. State and account for the splitting patterns of the peaks assigned to the protons a and b. (6 marks)

(d) Isomer G, C₆H₁₂O₂, contains six carbon atoms in a ring. It has an absorption in its infra-red spectrum at 3270 cm⁻¹ and shows only three different proton environments in its proton n.m.r. spectrum. Deduce a structural formula for G. (2 marks)
7 (a) Outline a mechanism for the formation of ethylamine from bromoethane. State why the ethylamine formed is contaminated with other amines. Suggest how the reaction conditions could be modified to minimise this contamination. (6 marks)

(b) Suggest one reason why phenylamine cannot be prepared from bromobenzene in a similar way. Outline a synthesis of phenylamine from benzene. In your answer you should give reagents and conditions for each step, but equations and mechanisms are not required. (5 marks)

END OF QUESTIONS