Instructions

- Use black ink or ball-point pen.
- Fill in the boxes at the top of this page with your name, centre number and candidate number.
- Answer all questions.
- Answer the questions in the spaces provided – there may be more space than you need.

Information

- The total mark for this paper is 90.
- The marks for each question are shown in brackets – use this as a guide as to how much time to spend on each question.
- Questions labelled with an asterisk (*) are ones where the quality of your written communication will be assessed – you should take particular care with your spelling, punctuation and grammar, as well as the clarity of expression, on these questions.
- A Periodic Table is printed on the back cover of this paper.

Advice

- Read each question carefully before you start to answer it.
- Keep an eye on the time.
- Try to answer every question.
- Check your answers if you have time at the end.
SECTION A

Answer ALL the questions in this section. You should aim to spend no more than 20 minutes on this section. For each question, select one answer from A to D and put a cross in the box. If you change your mind, put a line through the box and then mark your new answer with a cross.

1. Name the compound below.

\[
\begin{array}{c}
\text{CH}_3 \\
\text{Cl} \\
\text{C} \\
\text{C} \\
\text{H} \\
\text{CH}_2\text{CH}_3
\end{array}
\]

☐ A E-2-chloropent-2-ene
☐ B Z-2-chloropent-3-ene
☐ C E-2-chloropent-3-ene
☐ D Z-2-chloropent-2-ene

(Total for Question 1 = 1 mark)

Use this space for any rough working. Anything you write in this space will gain no credit.
2. Which of the following compounds is **not** chiral?

- A
- B
- C
- D

(Total for Question 2 = 1 mark)

Use this space for any rough working. Anything you write in this space will gain no credit.
3. Calculate the pH of a solution of HCl, of concentration 0.25 mol dm\(^{-3}\).

- A. -0.60
- B. 0.25
- C. 0.60
- D. 1.39

(Total for Question 3 = 1 mark)

4. Which gas is the least suitable as a carrier gas in Gas-Liquid Chromatography?

- A. Argon
- B. Carbon dioxide
- C. Oxygen
- D. Nitrogen

(Total for Question 4 = 1 mark)

5. What are the units of the equilibrium constant \(K_c\) for the hypothetical reaction below?

\[2A(aq) + B(aq) \rightleftharpoons 4C(aq) + D(aq)\]

- A. mol\(^2\) dm\(^{-9}\)
- B. mol\(^{-2}\) dm\(^9\)
- C. mol\(^2\) dm\(^{-6}\)
- D. mol\(^{-2}\) dm\(^6\)

(Total for Question 5 = 1 mark)

Use this space for any rough working. Anything you write in this space will gain no credit.
6 This question is about the reversible reaction below.

\[ 2\text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g) \]

(a) A chemist investigating this reaction started with 10 moles of NO$_2$ and allowed the system to reach equilibrium. If 3 moles of N$_2$O$_4$ are formed, the number of moles of NO$_2$ at equilibrium is

- A 8.5
- B 7
- C 6
- D 4

(b) Under different conditions, 40% of the moles present at equilibrium is N$_2$O$_4$. If the total pressure of the system is 2.0 atm, the numerical value of the equilibrium constant, $K_p$, is

- A 0.56
- B 0.67
- C 1.5
- D 1.8

(Total for Question 6 = 2 marks)

Use this space for any rough working. Anything you write in this space will gain no credit.
7 Carbon monoxide and chlorine react together and reach equilibrium:

\[ \text{CO(g)} + \text{Cl}_2(g) \rightleftharpoons \text{COCl}_2(g) \]

If the pressure of the system is then **increased** at constant temperature, which of the following statements is correct?

- **A** The equilibrium moves to the left and \( K_p \) decreases.
- **B** The equilibrium moves to the right and \( K_p \) increases.
- **C** The equilibrium moves to the right, then back to the left and \( K_p \) remains the same.
- **D** The equilibrium moves to the right and \( K_p \) remains the same.

(Total for Question 7 = 1 mark)

8 The table shows some data about metal ions, non-metal ions and their compounds.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Enthalpy change of hydration / kJ mol(^{-1})</th>
<th>Compound</th>
<th>Lattice energy / kJ mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(^{2+})(g)</td>
<td>–1921</td>
<td>MgCl(_2)(s)</td>
<td>–2526</td>
</tr>
<tr>
<td>Cl(^–)(g)</td>
<td>–340</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cs(^+)(g)</td>
<td>–276</td>
<td>CsF(s)</td>
<td>–747</td>
</tr>
<tr>
<td>F(^–)(g)</td>
<td>–483</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Use the data to calculate

(a) the standard enthalpy change, in kJ mol\(^{-1}\), for the following process.

\[ \text{Mg}^{2+}(g) + 2\text{Cl}^–(g) \rightarrow \text{Mg}^{2+}(aq) + 2\text{Cl}^–(aq) \]

(1)

- **A** –1241
- **B** –1581
- **C** –2261
- **D** –2601
(b) the standard enthalpy change of solution, in kJ mol\(^{-1}\), of caesium fluoride, CsF.

\[
\begin{array}{c}
\text{A} & -12 \\
\text{B} & +12 \\
\text{C} & -1506 \\
\text{D} & +1506
\end{array}
\]

(Total for Question 8 = 2 marks)

9 Which of these solvents is most likely to be warmed by microwave radiation?

\[
\begin{array}{c}
\text{A} & \text{Hexane} \\
\text{B} & \text{Cyclohexane} \\
\text{C} & \text{Cyclohexanol} \\
\text{D} & \text{Cyclohexene}
\end{array}
\]

(Total for Question 9 = 1 mark)

Use this space for any rough working. Anything you write in this space will gain no credit.
Some chemical tests are described below.

A Warm with Fehling’s (or Benedict’s) solution
B Warm with acidified potassium dichromate(VI) solution
C Add sodium carbonate solution
D Add 2,4-dinitrophenylhydrazine solution

(a) Which test always gives a positive result with carbonyl compounds?

☐ A
☐ B
☐ C
☐ D

(b) Which test would give a positive result with ethane-1,2-diol?

☐ A
☐ B
☐ C
☐ D

(c) Which test would result in effervescence with ethanoic acid?

☐ A
☐ B
☐ C
☐ D

(Total for Question 10 = 3 marks)

Use this space for any rough working. Anything you write in this space will gain no credit.
Consider the four compounds shown below.

A \( \text{CH}_3\text{COOCH}_3 \)

B \( \text{CH}_3\text{COOH} \)

C \( \text{CH}_3\text{CONHCH}_2\text{CH}_3 \)

D \( \text{CH}_3\text{COCl} \)

Which of these compounds

(a) will react most vigorously with water?

☐ A

☐ B

☐ C

☐ D

(b) forms methanol when refluxed with aqueous sodium hydroxide?

☐ A

☐ B

☐ C

☐ D

(c) has at least one triplet in its high resolution proton nmr spectrum?

☐ A

☐ B

☐ C

☐ D

(Total for Question 11 = 3 marks)

Use this space for any rough working. Anything you write in this space will gain no credit.
The diagram below shows part of the mechanism for the nucleophilic addition of hydrogen cyanide to butanone.

Step 1: Intermediate X

Step 2: Organic Products

(a) The formula of the intermediate X is

☐ A

☐ B

☐ C

☐ D
(b) Consider the dissociation of the weak acid, HCN.

\[
\text{HCN}(aq) \rightleftharpoons \text{H}^+(aq) + \text{CN}^-(aq)
\]

Which of the following reagents would shift the position of the equilibrium towards formation of the nucleophile, \( \text{CN}^- \)?

- [ ] A. KOH
- [ ] B. KCN
- [ ] C. \( \text{H}_2\text{SO}_4 \)
- [ ] D. \( \text{CH}_3\text{COOH} \)

(c) Which statement about the mixture of organic products formed is not correct?

- [ ] A. The mixture contains products with chiral molecules.
- [ ] B. The mixture rotates the plane of plane-polarized light.
- [ ] C. The mixture contains products with the nitrile functional group.
- [ ] D. The mixture contains products each of which has four carbon atoms in a straight chain.

(Total for Question 12 = 3 marks)

TOTAL FOR SECTION A = 20 MARKS
A student carried out a titration by adding 0.032 mol dm$^{-3}$ potassium hydroxide solution to 25.0 cm$^3$ of 0.024 mol dm$^{-3}$ propanoic acid. A sketch graph of pH against volume of potassium hydroxide solution added is shown below.

(a) *(i) Describe and explain the behaviour of the solution formed in the region circled on the sketch graph. (3)
*(ii) Explain why the pH at the equivalence point of this titration is greater than 7.

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(iii) By considering the amount of excess alkali remaining, calculate the pH of the solution formed when 40 cm$^3$ of 0.032 mol dm$^{-3}$ potassium hydroxide solution has been added to 25.0 cm$^3$ of 0.024 mol dm$^{-3}$ propanoic acid.

\[ K_w = 1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6} \text{ at } 298 \text{ K} \]
(b) The student made the following statement:

‘The pH of pure water is always 7.0’

Is the student correct? Use the following information to justify your answer.

- \( \text{H}_2\text{O}(l) \rightleftharpoons \text{H}^+(aq) + \text{OH}^-(aq) \)
- \( K_w = 1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6} \) at 298 K
- \( \Delta H \) is positive for the forward reaction in the equilibrium.

(Total for Question 13 = 14 marks)
The kinetics of the fast reaction below were investigated in a series of experiments.

\[ \text{A} + \text{B} \xrightarrow{\text{catalyst X}} \text{C} + \text{D} \quad \Delta H \text{ is negative} \]

(a) Outline a titrimetric method that could be used to measure the change in concentration of compound A with time. Compound A is an alkali, whereas compounds B, C and D are neutral.
(b) The rate of the reaction was measured at several different concentrations of A, in the presence of a large excess of compound B and a constant amount of catalyst X, to find the order of reaction with respect to A. The results are shown on the graph below.

![Graph showing rate vs. [A]](image)

(i) Explain how the graph confirms that the reaction is first order with respect to A.

(ii) Suggest an explanation, other than human error, for the two anomalous results circled on the graph.
(c) In a second series of experiments, further data were collected using an initial rates method. These results are summarised in the table below.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Initial concentration / mol dm(^{-3})</th>
<th>Initial rate / mol dm(^{-3}) s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABX</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.020</td>
<td>0.005</td>
</tr>
<tr>
<td></td>
<td>0.500</td>
<td>2.1 \times 10^{-3}</td>
</tr>
<tr>
<td>2</td>
<td>0.040</td>
<td>0.005</td>
</tr>
<tr>
<td></td>
<td>0.500</td>
<td>4.2 \times 10^{-3}</td>
</tr>
<tr>
<td>3</td>
<td>0.060</td>
<td>0.010</td>
</tr>
<tr>
<td></td>
<td>0.500</td>
<td>6.3 \times 10^{-3}</td>
</tr>
<tr>
<td>4</td>
<td>0.080</td>
<td>0.010</td>
</tr>
<tr>
<td></td>
<td>0.250</td>
<td>4.2 \times 10^{-3}</td>
</tr>
</tbody>
</table>

(i) Give one reason why obtaining these further data may be considered useful. (1)
(ii) Deduce the rate equation for this reaction, explaining how you arrived at your answer. 

(iii) Use your answer from (c)(ii), and appropriate data from Experiment 4, to calculate the value of the rate constant, \( k \). Include units in your answer.
(d) A student carried out a similar investigation into the kinetics of the reaction between 2-bromomethylpropane and hydroxide ions. A summary of the student’s findings is shown below.

Kinetics Investigation - Summary of Key Findings

Reaction is first order with respect to 2-bromomethylpropane

Suggested Mechanism

$S_{n2}$ - as two steps in process

Use your knowledge of the mechanism of nucleophilic substitution reactions to suggest one feature of the summary, including the student’s mechanism, that you agree with and two features you think are incorrect.

One feature you agree with.

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

Two features you think are incorrect.

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

(Total for Question 14 = 18 marks)
Aspirin can be manufactured from sodium phenoxide using the process shown below.

\[ \text{ONa} \quad (s) + \text{CO}_2 \quad (g) \rightarrow \text{COONa} \quad (s) \]

Step 1

Step 2

Step 3

Overall yield for process = 79%

(a) Explain one effect of an increase in pressure on the reaction in Step 1.

(b) The overall yield for this process is 79%.

Calculate the mass, in tonnes, of aspirin that would be formed from 2.5 tonnes of sodium phenoxide. Give your answer to two significant figures.

[Molar masses / g mol⁻¹: sodium phenoxide = 116; aspirin = 180]

(c) Classify the reaction type in Step 3 and suggest a suitable reagent.

(Total for Question 15 = 7 marks)
Fresh coffee is made by adding hot water to ground coffee beans. Chemists at the University of Nevada have produced bio-diesel fuel from used coffee grounds. The grounds contain approximately 10–15% oil by mass. This oil can be extracted, using standard chemical techniques, and then converted to bio-diesel by the reaction with methanol in the presence of a suitable catalyst.

(a) (i) A solvent is added to the solid coffee grounds to dissolve the oil. Suggest how the oil is then obtained from this mixture.

(ii) Complete the equation below for the formation of a bio-diesel from the reaction of an oil with methanol.

\[ 3\text{CH}_3\text{OH} + \text{CH}_2\text{OOCR'} \rightarrow \text{CH}_3\text{OOCR''} + \text{CH}_2\text{OOCR'''} \]

(iii) Suggest a suitable catalyst for the reaction in (a)(ii).
*(b) Another source of oil for bio-diesel production is palm oil, obtained from the fruit of palm trees grown on large plantations across many tropical regions.

Consider one advantage and one disadvantage of each source to decide which oil may provide a potentially greener and more sustainable supply of bio-diesel.

(Total for Question 16 = 9 marks)

(Total for Section B = 48 MARKS)
17  Adipic acid, HOOC(CH₂)₆COOH, is a dicarboxylic acid used in the production of polymers. It can be made by the reaction of buta-1,3-diene with carbon monoxide and water.

\[ \text{CH}_2\text{CHCHCH}_2(g) + 2\text{CO}(g) + 2\text{H}_2\text{O}(l) \rightarrow \text{HOOC(CH}_2\text{)_6COOH}(s) \]

(a) (i) Use the Data Booklet to complete the table below.

<table>
<thead>
<tr>
<th></th>
<th>CH₂CHCHCH₂(g)</th>
<th>CO(g)</th>
<th>H₂O(l)</th>
<th>HOOC(CH₂)₆COOH(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta H_f )</td>
<td>+109.9</td>
<td></td>
<td></td>
<td>–994.3</td>
</tr>
<tr>
<td>( S_f )</td>
<td>278.7</td>
<td></td>
<td></td>
<td>250.0</td>
</tr>
</tbody>
</table>

(ii) Use data from the table to calculate the standard enthalpy change, in kJ mol⁻¹, when adipic acid is formed from buta-1,3-diene, carbon monoxide and water.

(iii) Use data from the table to calculate the standard entropy change of the system, in J mol⁻¹ K⁻¹, when adipic acid is formed from buta-1,3-diene, carbon monoxide and water.
(iv) Use your answers to (a)(ii) and (a)(iii) to calculate $\Delta S_{\text{surroundings}}$ and $\Delta S_{\text{total}}$ for the reaction at 298 K.

(3)

(v) It was suggested that decreasing the temperature of the reaction to less than 298 K would produce a greater yield of adipic acid.

Explain, in terms of the effect on $\Delta S_{\text{system}}$, $\Delta S_{\text{surroundings}}$ and hence $\Delta S_{\text{total}}$, whether this would be the case.

(3)

(b) Infrared spectroscopy can be used to follow the progress of reactions. During the reaction to produce adipic acid, suggest one peak which diminishes and one peak which appears.

Use information from the Data Booklet to identify two such possible peaks, giving their wave numbers and the bonds involved.

(2)
(c) Adipic acid is used as an additive in some fruit jellies. Suggest what effect the adipic acid will have on the flavour of the jelly.

(1)

(d) An organic compound, Q, is found to contain 49.3% carbon and 6.8% hydrogen by mass.

(i) Use these data to confirm its empirical formula is C₃H₅O₂.

(3)
(ii) The structure of Q is shown below.

The table below summarises some information about parts of the nmr spectrum of compound Q.

Use the Data Booklet, and your knowledge of splitting patterns, to complete the table with respect to the features of compound Q shown in bold.

<table>
<thead>
<tr>
<th>Feature of compound Q</th>
<th>Chemical shift / ppm</th>
<th>Splitting pattern</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃</td>
<td>0.1 – 1.9</td>
<td></td>
</tr>
<tr>
<td>CH₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>COOH</td>
<td></td>
<td>singlet</td>
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(Total for Question 17 = 22 marks)
<table>
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<th>(9)</th>
<th>(10)</th>
<th>(11)</th>
<th>(12)</th>
</tr>
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<tbody>
<tr>
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<td>B</td>
<td>C</td>
<td>N</td>
<td>O</td>
<td>F</td>
<td>Ne</td>
<td>Na</td>
<td>Mg</td>
<td>Al</td>
<td>Si</td>
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<td>12</td>
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<td>Ti</td>
<td>V</td>
<td>Cr</td>
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<tr>
<td>Cs</td>
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<td>La*</td>
<td>Hf</td>
<td>Ta</td>
<td>W</td>
<td>Re</td>
<td>Os</td>
<td>Ir</td>
<td>Pt</td>
<td>Au</td>
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<tr>
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<td>Ra</td>
<td>Ac*</td>
<td>Rc</td>
<td>Ds</td>
<td>Rf</td>
<td>Db</td>
<td>Sg</td>
<td>Bh</td>
<td>Hs</td>
<td>Mt</td>
<td>Ds</td>
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<td>108</td>
<td>109</td>
<td>110</td>
<td>111</td>
<td>140</td>
</tr>
</tbody>
</table>

* Lanthanide series
* Actinide series

Elements with atomic numbers 112–116 have been reported but not fully authenticated.