HWA CHONG INSTITUTION
C2 Preliminary Examinations
Higher 2

CANDIDATE NAME

CT GROUP 14S

CENTRE NUMBER

INDEX NUMBER

CHEMISTRY 9647/01
Paper 1 Multiple Choice 18 September 2015

Additional Materials: Optical Mark Sheet (OMS)

Data Booklet

1 hour

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, glue or correction fluid.
Complete the information on the optical mark sheet (OMS) as shown below.

1. Enter your NAME (as in NRIC).
2. Enter the PAPER NUMBER.
3. Enter your CT GROUP.
4. Enter your NRIC NUMBER or FIN Number
5. Now SHADE the corresponding circles in the grid for EACH DIGIT or LETTER

There are forty questions on this paper. Answer all questions. For each question, there are four possible answers A, B, C and D.
Choose the one you consider correct and record your choice in soft pencil on the OMS.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this booklet.
The use of an approved scientific calculator is expected, where appropriate.
SECTION A

For each question, there are four possible answers A, B, C and D. Choose the one you consider to be correct.

1 10 cm³ of a hydrocarbon was mixed with 50 cm³ of oxygen and combusted completely. After the resulting gas mixture was cooled and passed through aqueous sodium hydroxide, the volume of the residual gas mixture was found to be ¼ the volume of the original gas mixture before combustion. All volumes were measured at room temperature and pressure.

What is the formula of the hydrocarbon?

A  C₂H₄  
B  C₂H₆  
C  C₃H₆  
D  C₃H₈

2 Equal volumes of 1 mol dm⁻³ hydrogen sulfide and sulfur dioxide (each containing a different isotope of sulfur) are mixed to precipitate sulfur according to the equations shown below:

\[ H₂^{32}S(aq) \rightarrow ^{32}S(s) + 2H^+(aq) + 2e^- \]

\[ ^{34}SO₂(aq) + 4H^+(aq) + 4e^- \rightarrow ^{34}S(s) + 2H₂O(l) \]

What is the relative atomic mass of the sulfur precipitated?

A  32.1  
B  32.7  
C  33.0  
D  33.3

3 Use of the Data Booklet is relevant to this question.

Which particle would, on losing an electron, have a half-filled set of d orbitals?

A  Cr  
B  Mn²⁺  
C  Fe³⁺  
D  Cr²⁺
4 Which of the following pairs of liquids are immiscible?

A (CH₃)₂CO and H₂O
B CH₂Cl₂ and (CH₃)₂CO
C CCl₄ and H₂O
D CCl₄ and CH₃CHO

5 A solid E has the following physical properties.
   - It is insoluble in non-polar solvents.
   - It melts at 1290 °C.
   - It conducts electricity in both aqueous and molten states.

What is the likely structure of E?

A a giant ionic structure
B a simple covalent structure
C a giant covalent structure
D a metallic structure

6 The value of $pV/RT$ is plotted against $p$ for one mole of each of the two non-ideal gases L and M, where $p$ is the pressure, $V$ is the volume and $T$ is the temperature of the gas.

Which of the following pairs of gases could be L and M?

<table>
<thead>
<tr>
<th></th>
<th>L</th>
<th>M</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>HCl</td>
<td>F₂</td>
</tr>
<tr>
<td>B</td>
<td>CH₄</td>
<td>C₂H₆</td>
</tr>
<tr>
<td>C</td>
<td>CH₃CH₂CH₃</td>
<td>CH₃Cl</td>
</tr>
<tr>
<td>D</td>
<td>N₂</td>
<td>O₂</td>
</tr>
</tbody>
</table>
7 Which of the following is involved in determining the enthalpy change of a chemical reaction?

A The number of steps involved in the chemical reaction
B The mechanism of the reaction
C The initial and final states of the reacting system
D The activation energy of the reaction

8 For which process is the enthalpy change always negative?

A Dissolving a compound in water
B Forming an ion from an atom
C Synthesizing a compound from its elements
D Burning an element in oxygen

9 The rate for the reaction $2\text{XO}(g) + \text{O}_2(g) \rightarrow 2\text{XO}_2(g)$ was investigated by varying the partial pressures of $\text{XO}$ and $\text{O}_2$. The results are shown in the table below.

| partial pressure of $\text{XO}$/ atm | 1.00 | 1.00 | 0.25 | $p$ |
| partial pressure of $\text{O}_2$/ atm | 1.00 | 0.50 | 1.00 | 0.50 |
| relative rate | 1.00 | 0.50 | 0.25 | 0.125 |

What is the value of $p$ in the table?

A 0.125  B 0.25  C 0.50  D 1.00

10 The age of a rock sample may be determined by rubidium-strontium dating, in which rubidium-87 decays to strontium-87. This radioactive decay is a first-order reaction with a half-life of $4.88 \times 10^{10}$ years.

Assuming the rock sample contained no strontium-87 initially, what is the age of the rock sample if the molar ratio of rubidium-87 to strontium-87 in the sample is now 1:7?

A $6.97 \times 10^3$ years  B $1.63 \times 10^{10}$ years  C $1.46 \times 10^{11}$ years  D $3.42 \times 10^{11}$ years
11 Which of the following statements involving the Haber process is correct?

\[ \text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}); \quad \Delta H < 0 \]

A At equilibrium, the rate constants of the forward reaction and backward reaction are the same.
B The equilibrium yield of \( \text{NH}_3 \) can be improved by using powdered iron.
C The activation energy of the forward reaction is greater than that of the backward reaction.
D The equilibrium constant decreases with increasing temperature.

12 The numerical values of the solubility products at 25 °C for \( \text{AgCl} \) and \( \text{AgI} \) are \( 1.6 \times 10^{-10} \) and \( 8.0 \times 10^{-17} \) respectively.

What is the equilibrium constant for the reaction below?

\[ \text{AgCl(s)} + \Gamma(\text{aq}) \rightleftharpoons \text{AgI(s)} + \text{Cl}^-(\text{aq}) \]

A \( 1.3 \times 10^{-26} \)
B \( 5.0 \times 10^{-7} \)
C 1400
D \( 2.0 \times 10^{6} \)

13 Which of the following solutions will form an alkaline buffer?

A 50 cm\(^3\) of 0.10 mol dm\(^{-3}\) \( \text{NaOH} \) added to 25 cm\(^3\) 0.10 mol dm\(^{-3}\) \( \text{CH}_3\text{CO}_2^-\text{Na}^+ \).
B 25 cm\(^3\) of 0.10 mol dm\(^{-3}\) \( \text{NaOH} \) added to 50 cm\(^3\) 0.10 mol dm\(^{-3}\) \( \text{CH}_3\text{CO}_2\text{H} \).
C 25 cm\(^3\) of 0.10 mol dm\(^{-3}\) \( \text{NaOH} \) added to 50 cm\(^3\) 0.10 mol dm\(^{-3}\) \( \text{CH}_3\text{NH}_2^+\text{Cl}^- \).
D 50 cm\(^3\) of 0.10 mol dm\(^{-3}\) \( \text{NaOH} \) added to 50 cm\(^3\) 0.10 mol dm\(^{-3}\) \( \text{CH}_3\text{NH}_2^+\text{Cl}^- \).

14 Two sodium chloride solutions of different concentrations were electrolyzed at 1 atm and 298 K. Which of the following correctly describes the colour of the litmus paper when placed at the respective electrodes of each solution?

<table>
<thead>
<tr>
<th></th>
<th>[NaCl(\text{aq})] = 0.001 mol dm(^{-3})</th>
<th>[NaCl(\text{aq})] = 5.0 mol dm(^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>cathode</td>
<td>anode</td>
<td>cathode</td>
</tr>
<tr>
<td>A</td>
<td>blue</td>
<td>red</td>
</tr>
<tr>
<td>B</td>
<td>blue</td>
<td>white</td>
</tr>
<tr>
<td>C</td>
<td>red</td>
<td>blue</td>
</tr>
<tr>
<td>D</td>
<td>red</td>
<td>blue</td>
</tr>
</tbody>
</table>
15. The oxide and chloride of an element \( \text{F} \) are separately mixed with water. The two resulting solutions have the same effect on litmus.

What is element \( \text{F} \)?

A. aluminium  
B. magnesium  
C. phosphorus  
D. silicon

16. A solid metal chloride with the formula, \( \text{MCI}_2 \), was analysed to yield the following results.
   - The solid is soluble in water.
   - Precipitation did not occur when \( \text{NaOH(aq)} \) is added.
   - White precipitate observed when \( \text{H}_2\text{SO}_4(aq) \) is added.

What is the identity of the cation?

A. \( \text{Mg}^{2+} \)  
B. \( \text{Pb}^{2+} \)  
C. \( \text{Zn}^{2+} \)  
D. \( \text{Ba}^{2+} \)

17. When a white solid \( \text{G} \) reacts with concentrated \( \text{H}_2\text{SO}_4 \), the products include pungent-smelling gases and a dark brown solution containing a yellow solid. When aqueous sodium thiosulfate is added, the solid remains but the dark brown colour disappears.

What is \( \text{G} \)?

A. \( \text{AgNO}_3 \)  
B. \( \text{CaCO}_3 \)  
C. \( \text{NaBr} \)  
D. \( \text{KI} \)

18. Which statement correctly defines a transition element?

A. Transition elements exhibit more than one oxidation state in their compounds.  
B. Transition elements form many coloured compounds.  
C. Transition elements have partially filled d orbitals.  
D. Transition elements or their compounds are widely used as catalysts.
19 A reaction scheme is shown below.

How can the three steps be classified?

<table>
<thead>
<tr>
<th></th>
<th>step 1</th>
<th>step 2</th>
<th>step 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>addition</td>
<td>hydrolysis</td>
<td>condensation</td>
</tr>
<tr>
<td>B</td>
<td>addition</td>
<td>oxidation</td>
<td>substitution</td>
</tr>
<tr>
<td>C</td>
<td>substitution</td>
<td>oxidation</td>
<td>substitution</td>
</tr>
<tr>
<td>D</td>
<td>reduction</td>
<td>hydrolysis</td>
<td>condensation</td>
</tr>
</tbody>
</table>

20 Which of the following compounds could be formed when dichloromethane is reacted with excess chlorine in the presence of sunlight?

A  CHCl₃ and H₂
B  CHCl₃ and CH₂ClCCl₃
C  CHCl₃ and CCl₃CHCl₂
D  CCl₃CHCl₂ and CH₂ClCCl₃

21 But-2-ene-1,4-diol is converted in two steps through an intermediate H into ketobutanedioic acid.

What could be the reagent for step 1 and the intermediate H?

<table>
<thead>
<tr>
<th></th>
<th>reagent for step 1</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>steam and concentrated H₂SO₄</td>
<td>HOCH₂CH₂CH(OH)CH₂OH</td>
</tr>
<tr>
<td>B</td>
<td>hot acidified K₂Cr₂O₇</td>
<td>HO₂CCH(OH)CH₂CO₂H</td>
</tr>
<tr>
<td>C</td>
<td>cold acidified KMnO₄</td>
<td>HOCH₂CH(OH)CH(OH)CH₂OH</td>
</tr>
<tr>
<td>D</td>
<td>warm acidified K₂Cr₂O₇</td>
<td>HO₂CCH=CHCO₂H</td>
</tr>
</tbody>
</table>
22 Compound K is first reduced with hydrogen in the presence of a platinum catalyst, and the product is oxidized by warming with acidified KMnO₄.

![compound K]

How many moles of sodium hydroxide will react with one mole of the final product?

A 0  B 1  C 2  D 3

23 Which of the following reagents and conditions can be used to distinguish between benzene and cyclohexene?

A Oxygen gas, heat
B Acidified potassium dichromate, heat
C Aqueous bromine, absence of uv light
D Hydrogen bromide, room temperature

24 Equal mass of each of the following compounds was heated with NaOH(aq), and then excess dilute HNO₃(aq) and AgNO₃(aq) were added. The precipitate was collected and shaken with aqueous ammonia.

Which compound will produce the largest mass of precipitate after shaken with excess aqueous ammonia?

A  ![A]
B  ![B]
C  ![C]
D  ![D]
25 Which of the following best describes nitrogen oxides (NO and NO₂) as atmospheric pollutants?

A NO converts carbon monoxide and unburnt hydrocarbons into harmless products in the catalytic converter.
B NO₂ is a greenhouse gas which would cause global warming.
C NO₂ catalyses the formation of acid rain from atmospheric sulfur dioxide.
D NO₂ undergoes an acid-base reaction in water to produce HNO₂ and HNO₃, which results in acid rain.

26 Pentaerythritol is used as an intermediate in the manufacture of paint.

\[
\begin{align*}
\text{HOCH}_2 & \quad \text{C} \quad \text{CH}_2\text{OH} \\
\text{HOCH}_2 & \quad \text{CH}_2\text{OH}
\end{align*}
\]

pentaerythritol

Which statement about pentaerythritol is incorrect?

A It can be dehydrated by concentrated sulfuric acid to form alkene.
B Its empirical formula and molecular formula are same.
C One mole of pentaerythritol gives two moles of hydrogen gas on reaction with excess sodium.
D It reacts with sodium bromide and concentrated sulfuric acid to form C(CH₂Br)₄.

27 Which compound has the highest \( pK_a \) value?

A \( \text{HCO}_2\text{H} \)  
B \( \text{CH}_3\text{CO}_2\text{H} \)  
C \( \text{BrCH}_2\text{CO}_2\text{H} \)  
D \( \text{C/CH}_2\text{CO}_2\text{H} \)
28 Compound \( N \), has the following features:

- Its molecular formula is \( C_8H_6O_4 \)
- 1 mole of \( N \) reacts completely with 2 moles of \( PCl_5 \) to give misty fumes
- \( N \) reacts with hot concentrated \( H_2SO_4 \) to form a compound, \( C_8H_4O_3 \)

Which of the following could be \( N \)?

- A
  ![A](image)
- B
  ![B](image)
- C
  ![C](image)
- D
  ![D](image)

29 A mixture contains the following compounds:

- \( X \) \( CH_3CH_2CH=CHCH_2CO_2H \)
- \( Y \) \( CH_3CH_2CH=CHCH_2COCH_3 \)
- \( Z \) \( CH_3CH_2CH_2CH=CHCH=CHCHO \)

If these compounds are all present in the ratio \( X : Y : Z = 2 : 2 : 1 \), and all are reduced by an excess of \( \text{LiAlH}_4 \), how many hydrogen atoms would be incorporated on average per molecule?

- A 1.2
- B 2.0
- C 3.2
- D 4.4
The earliest use of chemicals to “perm” hair was in 1938. In modern use, two different compounds are used to “perm” hair. First, compound $P$ is used as a “relaxer” to break the disulfide linkages within and between the polypeptide chains in the hair proteins:

$$R-S-S-R \rightarrow R-SH + HS-R$$

When the desired amount of curl is achieved in the hair, compound $Q$ is used as a “restorer” to reform the disulfide linkages:

$$R-SH + HS-R \rightarrow R-S-S-R$$

Which of the following shows the roles of compounds $P$ and $Q$?

<table>
<thead>
<tr>
<th></th>
<th>P</th>
<th>Q</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>acid</td>
<td>base</td>
</tr>
<tr>
<td>B</td>
<td>base</td>
<td>acid</td>
</tr>
<tr>
<td>C</td>
<td>oxidising agent</td>
<td>reducing agent</td>
</tr>
<tr>
<td>D</td>
<td>reducing agent</td>
<td>oxidising agent</td>
</tr>
</tbody>
</table>
SECTION B

For each of the questions in this section, one or more of the three numbered statements 1 to 3 may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

The responses A to D should be selected on the basis of

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1, 2 and 3 are correct</td>
<td>1 and 2 only are correct</td>
<td>2 and 3 only are correct</td>
<td>1 only is correct</td>
</tr>
</tbody>
</table>

No other combination of statements is used as a correct response.

31 In which of the following reactions is the named element undergoing a disproportionation reaction?

<table>
<thead>
<tr>
<th></th>
<th>Element</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>carbon</td>
<td>$\text{H}_2\text{C}_2\text{O}_4 \rightarrow \text{H}_2\text{O} + \text{CO} + \text{CO}_2$</td>
</tr>
<tr>
<td>2</td>
<td>copper</td>
<td>$2\text{Na(CuCl}_2) \rightarrow \text{Cu} + \text{CuCl}_2 + 2\text{NaCl}$</td>
</tr>
<tr>
<td>3</td>
<td>sulfur</td>
<td>$2\text{FeSO}_4 \rightarrow \text{Fe}_2\text{O}_3 + \text{SO}_2 + \text{SO}_3$</td>
</tr>
</tbody>
</table>

32 In which of the following pairs does the second species have a larger bond angle than the first?

1. $\text{NH}_3$ and $\text{BCl}_3$
2. $\text{SCl}_2$ and $\text{BeCl}_2$
3. $\text{SF}_6$ and $\text{XeF}_4$

33 The use of chlorine as a water disinfectant in swimming pools is now widely banned and the weak acid trichloroisocyanuric acid is used instead.

$$\text{trichloroisocyanuric acid} + \text{OH}^- \leftrightarrow \text{ClO}^- + \text{cyanuric acid}$$

The ClO$^-$ ion is the effective disinfectant.

Why is it necessary to maintain the pH of the water at 7.5?

1. At a pH of 7.5, the concentration of ClO$^-$ is at a maximum.
2. The concentration of ClO$^-$ ion depends on the pH.
3. The concentration of H$^+$ is too low for the following reaction to occur:
   $$2\text{H}^+(aq) + \text{ClO}^-(aq) + \text{Cl}^-(aq) \rightarrow \text{H}_2\text{O(l)} + \text{Cl}_2(g)$$
The responses A to D should be selected on the basis of

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
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</tbody>
</table>

No other combination of statements is used as a correct response.

34 Use of the Data Booklet is relevant to this question.

A cell is set up as shown below.

Which of the following changes would decrease the cell potential?

1. Adding sodium hydroxide to the NO$_3^-$ / NO$_2$(g) half cell
2. Adding water to the S$_4$O$_6^{2-}$ / S$_2$O$_3^{2-}$ half cell
3. Adding iodine crystals to the S$_4$O$_6^{2-}$ / S$_2$O$_3^{2-}$ half cell
The responses A to D should be selected on the basis of

<table>
<thead>
<tr>
<th></th>
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<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
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<td>1 only is correct</td>
<td></td>
</tr>
</tbody>
</table>

No other combination of statements is used as a correct response.

35 The graph below shows the variation in the melting points of eight consecutive elements in Period 2 and 3 of the Periodic Table.

Which statements are correct?

1. P and Q tend to form covalent compounds.
2. When 2 mol of dilute HCl is added to 1 mol of the oxide of W, the resulting solution is slightly acidic.
3. The ionic radius of V is larger than that of S.

36 When zinc powder was added to aqueous iron(III) chloride, effervescence was observed and the solution gradually changed colour from yellow to pale green.

Which of the following statements are correct about the reaction?

1. Fe$^{3+}$ is a stronger oxidising agent than Zn$^{2+}$.
2. Effervescence was observed as an acid-base reaction has taken place.
3. The solution is coloured as d→d transitions occur in Zn$^{2+}$. 
The responses A to D should be selected on the basis of

<table>
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<tr>
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<th>D</th>
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<td>2 and 3 only are correct</td>
<td>1 only is correct</td>
</tr>
</tbody>
</table>

No other combination of statements is used as a correct response.

37 Given that benzene undergoes bromination followed by nitration, which of the following are the major products?

1
\[
\begin{array}{c}
\text{NO}_2 \\
\end{array}
\]
\[
\begin{array}{c}
\text{Br} \\
\end{array}
\]

2
\[
\begin{array}{c}
\text{NO}_2 \\
\end{array}
\]
\[
\begin{array}{c}
\text{Br} \\
\end{array}
\]

3
\[
\begin{array}{c}
\text{Br} \\
\end{array}
\]
\[
\begin{array}{c}
\text{NO}_2 \\
\end{array}
\]

38 An account in a student’s notebook read:

“An excess of aqueous bromine was added to aqueous phenol in a test-tube. 2,4,6-tribromophenol was produced as a creamy-white precipitate suspended in a yellow alkaline solution.”

Which statements in this account are correct?

1 2,4,6-tribromophenol was produced as a creamy-white precipitate.
2 The resultant solution is yellow.
3 The resultant solution is alkaline.
The responses A to D should be selected on the basis of

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
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<td>2 and 3 only are correct</td>
<td>1 only is correct</td>
</tr>
</tbody>
</table>

No other combination of statements is used as a correct response.

39 Which of the following compounds will give a yellow precipitate with alkaline aqueous iodine?

1

![image]

2

![image]

3

![image]

40 An organic compound Z is sparingly soluble in water, but readily dissolves in cold dilute sulfuric acid. Evaporation of this solution formed yields a crystalline solid.

Which of the following compounds could Z be?

1

![image]

2

![image]

3

![image]
<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>11</th>
<th>D</th>
<th>21</th>
<th>A</th>
<th>31</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>B</td>
<td>12</td>
<td>D</td>
<td>22</td>
<td>B</td>
<td>32</td>
<td>B</td>
</tr>
<tr>
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<td>A</td>
<td>13</td>
<td>C</td>
<td>23</td>
<td>C</td>
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<td>C</td>
</tr>
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<td>C</td>
<td>14</td>
<td>A</td>
<td>24</td>
<td>D</td>
<td>34</td>
<td>A</td>
</tr>
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<td>5</td>
<td>A</td>
<td>15</td>
<td>C</td>
<td>25</td>
<td>C</td>
<td>35</td>
<td>B</td>
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<td>26</td>
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<td>D</td>
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<td>A</td>
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<td>B</td>
</tr>
<tr>
<td>9</td>
<td>B</td>
<td>19</td>
<td>A</td>
<td>29</td>
<td>B</td>
<td>39</td>
<td>B</td>
</tr>
<tr>
<td>10</td>
<td>C</td>
<td>20</td>
<td>C</td>
<td>30</td>
<td>D</td>
<td>40</td>
<td>D</td>
</tr>
</tbody>
</table>
INSTRUCTIONS TO CANDIDATES

1) Write your name, CT group, centre number and index number clearly in the spaces at the top of this page.

2) Answer all questions in the spaces provided in this Question Paper.

INFORMATION FOR CANDIDATES

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

A Data Booklet is provided.

Do not use staples, paper clips, highlighters, glue or correction fluid.

You may use a calculator.

You are reminded of the need for good English and clear presentation in your answers.

<table>
<thead>
<tr>
<th>For Examiner’s Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<tr>
<td>2</td>
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<tr>
<td>3</td>
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<tr>
<td>4</td>
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<tr>
<td>5</td>
</tr>
<tr>
<td>6</td>
</tr>
</tbody>
</table>

Deductions

Total / 72

Calculator Model:
1 Planning (P)

When excess ammonia is added to an aqueous solution containing transition metal ion $M^{2+}$, a complex ion $[M(NH_3)_n]^{2+}$, where $n$ has a maximum value of 6, is formed.

When this solution is shaken with trichloromethane ($\text{density} = 1.49 \text{ g cm}^{-3}$), an equilibrium mixture consisting of two immiscible layers is obtained. The aqueous layer contains the complex ion and uncomplexed ‘free’ ammonia while the organic layer contains only ‘free’ ammonia.

The ratio of the concentrations of ‘free’ ammonia in the two immiscible layers at equilibrium is a constant, known as the partition ratio, $K$.

\[
\text{NH}_3(\text{aq}) \rightleftharpoons \text{NH}_3(\text{trichloromethane}) \quad K = \frac{[\text{NH}_3(\text{trichloromethane})]}{[\text{NH}_3(\text{aq})]} = 0.4
\]

To determine the value of $n$ in $[M(NH_3)_n]^{2+}$, the equilibrium mixture is prepared. A sample is withdrawn from the organic layer and the ‘free’ ammonia is titrated with standard hydrochloric acid. As the aqueous acid is unable to dissolve in the organic layer, an equal volume of water is added to the organic layer before titration so that the ‘free’ ammonia can be neutralised by the acid.

The titration results can be used to determine the concentration of ‘free’ ammonia in the organic and aqueous layers. The amount of ammonia used to form the complex ion and hence the value of $n$ can then be determined.

(a) Explain why the value of the partition ratio, $K$, of ammonia between trichloromethane and water is less than 1.

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

..............................................................................................................................................................................................[1]

(b) With the aid of an equation, explain why the concentration of ‘free’ ammonia in the aqueous layer cannot be determined by titrating the aqueous layer with standard hydrochloric acid.

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..............................................................................................................................................................................................[2]
(c) You are required to write a plan to determine the formula of the complex ion, \([M(NH_3)_n]^{2+}\).

You are provided with:
- aqueous ammonia, of concentration 1.0 mol dm\(^{-3}\)
- aqueous M\(^{2+}\), of concentration 0.10 mol dm\(^{-3}\)
- hydrochloric acid, of concentration 0.050 mol dm\(^{-3}\)
- trichloromethane
- the apparatus and chemicals normally found in a school or college laboratory.

Your plan should give details of:
- the preparation of the equilibrium mixture containing the complex ion using 50.0 cm\(^3\) of 0.10 mol dm\(^{-3}\) M\(^{2+}\) and appropriate volumes of aqueous ammonia and trichloromethane;
- withdrawal of sample(s) from the organic layer;
- the titration of the ‘free’ ammonia in the organic layer.
(d) In one experiment, an equilibrium mixture was prepared using 1 dm$^3$ of 1.0 mol dm$^{-3}$ aqueous ammonia, 1 dm$^3$ of 0.10 mol dm$^{-3}$ aqueous M$^{2+}$ and 1 dm$^3$ of trichloromethane. The concentration of ‘free’ ammonia in the organic layer was found to be $x$ mol dm$^{-3}$.

Express the concentration of ‘free’ ammonia in the aqueous layer and the value of $n$ in terms of $x$. 

[2]

[Total: 12]
This question is about the chemistry of Kuro Tamago (lit. "black eggs"), a local specialty of egg hard-boiled in the hot springs of Owankundai, Japan.

When raw eggs are boiled in hot spring water of Owankundai (pH = 9.2), a chemical reaction between aqueous iron(II) and sulfide ions (from hydrogen sulfide, H₂S), produces a black solid, FeS, that adheres to the porous egg shells.

Iron sulfide is precipitated by the following reaction.

reaction 1: \( \text{Fe}^{2+}(\text{aq}) + \text{S}^{2-}(\text{aq}) \rightarrow \text{FeS}(s) \quad \Delta H_{\text{ppt}}^\circ \)

Hydrogen sulfide gas from volcanic systems is released into the hot spring water and behaves as a dibasic (diprotic) weak acid.

\[ \text{H}_2\text{S}(g) + \text{aq} \rightleftharpoons 2\text{H}^+(\text{aq}) + \text{S}^{2-}(\text{aq}) \]

In a saturated solution of hydrogen sulfide,

\[ [\text{H}^+]^2[\text{S}^{2-}] = 1.0 \times 10^{-23} \text{ mol}^3 \text{ dm}^{-9} \]

(a) (i) Calculate the maximum concentration of sulfide ions present in hot spring water.

(ii) Hence, calculate the minimum concentration of \( \text{Fe}^{2+} \) present in hot spring water in order for precipitation to occur.

\( (K_{\text{sp}} \text{ of FeS} = 4.9 \times 10^{-18} \text{ mol}^2 \text{ dm}^{-6}) \)
(b) Use the following data, together with relevant data from the *Data Booklet*, to calculate the $\Delta H^\circ_{\text{ppt}}$ for reaction 1.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Energy (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard enthalpy change of formation of FeS(s)</td>
<td>-102</td>
</tr>
<tr>
<td>Standard enthalpy change of atomisation of Fe(s)</td>
<td>+415</td>
</tr>
<tr>
<td>Standard enthalpy change of atomisation of S(s)</td>
<td>+279</td>
</tr>
<tr>
<td>Sum of first two electron affinities of sulfur</td>
<td>+337</td>
</tr>
<tr>
<td>Enthalpy change of hydration of Fe$^{2+}$(g)</td>
<td>-1981</td>
</tr>
<tr>
<td>Enthalpy change of hydration of S$^{2-}$(g)</td>
<td>-1372</td>
</tr>
</tbody>
</table>

(c) When a precipitate is formed, $\Delta G^\phi_{\text{ppt}}$, in J mol$^{-1}$, is given by the following expression.

$$\Delta G^\phi_{\text{ppt}} = 2.303RT \log K_{\text{sp}}$$

(i) Use the data given in (a)(ii) to calculate $\Delta G^\phi_{\text{ppt}}$, in kJ mol$^{-1}$, for FeS.
(ii) Use your answer in (b) and (c)(i) to calculate $\Delta S_{\text{ppt}}^\circ$, in J mol$^{-1}$ K$^{-1}$, for the formation of the precipitate FeS(s) at 298 K.

\[ \text{[2]} \]

(iii) Explain the significance of the sign of your answer in (c)(ii).

\[ \text{[2]} \]

[Total: 10]
A student synthesised compound R using the following scheme.

(a) Given that each step gave a yield of 50.0%, determine the mass of compound P required to produce 1.00 g of compound R.

(b) State the reagents and conditions for step I.

(c) MnO₂ was used as an oxidising agent in step II.
   (i) State the oxidation state of Mn in MnO₂.
(ii) At the end of the reaction in step II, \( \text{MnO}_2 \) was converted to \( \text{Mn}^{2+} \).

State the full electronic configuration of \( \text{Mn}^{2+} \).

………………………………………………………………………………………………………………………………………………..[1]

(iii) The oxidation states of Mn in \( \text{MnO}_2 \) and \( \text{Mn}^{2+} \) are different.

Explain briefly why Mn exhibits variable oxidation states.

………………………………………………………………………………………………………………………………………………..[1]

(iv) \( \text{KMnO}_4 \) cannot be used as the oxidising agent in step II in place of \( \text{MnO}_2 \).

Explain the above statement, supporting your answer with relevant values from the Data Booklet.

………………………………………………………………………………………………………………………………………………..[2]

(v) Suggest another set of reagents and conditions that could be used in step II.

………………………………………………………………………………………………………………………………………………..[1]

(d) (i) Given that the mechanism in step IV is a nucleophilic substitution, draw the mechanism, showing clearly any curly arrows, charges, dipoles and lone pairs where relevant.
(ii) No significant reaction was detected when step IV was carried out at room temperature. The student observed that the increase in temperature increased the rate of reaction in step IV.

With the aid of a sketch of the Boltzmann distribution, explain these observations.

………………………………………………………………………………………………
………………………………………………………………………………………………
………………………………………………………………………………………………[4]

(iii) Predict the effect on the rate of reaction when BrCH₂CH₂C≡CH was used in place of ClCH₂CH₂C≡CH in step IV. Explain your answer.

………………………………………………………………………………………………
………………………………………………………………………………………………[1]

(e) The student found the addition of K₂CO₃ in step IV reduced the amount of time required for the reaction.

(i) Given that K₂CO₃ reacted with compound Q in an acid–base reaction, write an ionic equation for this reaction.

………………………………………………………………………………………………[1]

(ii) It was known that the nature of the nucleophile affected the rate of the reaction in step IV.

Based on your answer for (e)(i), explain how the addition of K₂CO₃ in step IV increased the rate of reaction.

………………………………………………………………………………………………[1]

[Total: 17]
A zinc-air battery uses oxygen gas in the air as an oxidising agent and zinc metal as a reducing agent. Zinc is oxidised to a soluble zincate, \( \text{Zn(OH)}_4^{2-} \). The electrolyte circulated through the battery is NaOH(aq).

(i) Give the equation for the reactions which occur at the anode and cathode respectively.

Anode: \……………………………………………………………………………………………………

Cathode: \………………………………………………………………………………………………

(ii) Given that the standard cell potential is +1.65V, calculate the standard electrode potential, \( E^{\circ}_{\text{Zn(OH)}_4^{2-} / \text{Zn}} \).
(iii) Professor Kamata from Gakugei University studied the volume of oxygen consumed by the zinc-air battery using the set-up below. The experiment was conducted under room temperature and pressure.

When the switch was closed, the drop of ethanol began to move from $a_1$ to $a_2$.

The following data was collected during the experiment:

- Cross sectional area of glass tube = 0.0314 cm$^2$
- Initial glass tube reading, $a_1$ = 1.00 cm
- Current produced, $I$ = 0.0384 A
- Time taken for the ethanol to travel from $a_1$ to $a_2$, $t$ = 50 s

Calculate the final glass tube reading $a_2$, in the experiment.

(b) If present in sufficient concentration in the air, carbon dioxide can cause the formation of zinc carbonate, which can clog the electrode and add resistance to the zinc-air battery. Zinc carbonate and barium carbonate decompose when heated to give similar products.

By quoting appropriate data from the Data Booklet, deduce whether zinc carbonate would decompose at a higher or lower temperature than barium carbonate. Explain your answer.

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[3]

[Total: 9]
Thyroliberin and tyrocidine are molecules consisting of amino acids joined together.

(a) The hormone thyroliberin is a tripeptide made up of proline (pro), pyroglutamic acid (pyr) and histidine (his). Interestingly, there are no free carboxylic acid or amine groups at the carbon and nitrogen termini.

(i) Identify the residue (proline, pyroglutamic acid or histidine) at the carbon terminus.

(ii) Draw the structure of all nitrogen-containing products when thyroliberin is subjected to prolonged heating with sodium hydroxide.
(b) Tyrocidine is an antibacterial drug. It was discovered more than 60 years ago.

(i) It is suggested that each tyrocidine molecule is folded into a beta-pleated sheet-like structure. In the diagram above, draw and fully annotate an example of the stabilising interaction in the interior of the molecule.

(ii) A drug designer proposes to alter the structure of the tyrocidine molecule by incorporating residues of azetidine-2-carboxylic acid (aze) in place of all phenylalanine residues (phe).

\[
\text{azetidine-2-carboxylic acid (aze)}
\]

\[
\text{phenylalanine (phe)}
\]

By considering your answer in (b)(i), explain the likely effect that this change will have on the stability of the folded structure.

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(iii) Tyrocidine works by diffusing into the hydrophobic bacterial cell membrane, thus disrupting the membrane’s integrity. In the diagram on the previous page, circle one R group of the molecule which will interact with the membrane to make the disruption possible. State the type of interaction occurring.

Type of interaction: ………………………………………………………………………………………………………[2]

[Total: 9]
Compound **Z** is an important starting material in the synthesis of antibiotics.

**Z** could be made from 3-bromopropene and compound **Y** via the Grignard reaction through the following scheme.

For Examiner's use

(a) The carbon atom bonded to Br in 3-bromopropene is electrophilic in nature. After reacting with Mg in step I to form **X**, it becomes nucleophilic in nature.

Explain why the carbon atom becomes nucleophilic after reacting with Mg in step I.

…………………………………………………………………………………………………………………………[1]

(b) Suggest the type of reaction which occurs in steps II and III.

Step II: ...........................................................................................................................................

Step III: ...........................................................................................................................................

[2]

(c) A small amount of 3-bromopropene, **Y** and **Z** was introduced into three separate test tubes. Describe a simple chemical test you could carry out to distinguish **Z** from the other two compounds. State what you would observe.

…………………………………………………………………………………………………………………………...

…………………………………………………………………………………………………………………………[2]
The experimental set-up in the synthesis of Z is shown below.

(d) (i) Fill in the boxes near the reflux condenser with the following two terms:
- water in
- water out

(ii) A student suggested replacing the calcium chloride drying tube with a stopper cap. Explain briefly whether this is a wise suggestion.

.................................................................................................................................................................................................................................................................[1]
(e) Compounds \( V \) and \( W \) are structural isomers of \( Z \).

The table below shows the results of tests being carried out on \( V \) and \( W \).

<table>
<thead>
<tr>
<th>Test</th>
<th>Reagents and conditions</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fehling’s solution</td>
<td>Brick red precipitate formed</td>
</tr>
<tr>
<td>2</td>
<td>Aqueous bromine</td>
<td>Orange solution remained</td>
</tr>
</tbody>
</table>

When \( V \) and \( W \) were separately subjected to chlorine in the presence of sunlight, the number of monochlorinated products (not including stereoisomers) was found to be three and two respectively.

Suggest a possible structure for \( V \) and \( W \) in the boxes below.
The above reaction takes around 60 min for completion. When zinc is used instead of indium, a much longer reaction time under more vigorous conditions is required.

(f) (i) It was postulated that the rate-determining step of the reaction involved the transfer of an electron from the metal surface to 3-bromopropene.

Given that the first ionisation energy of indium is 558 kJ mol\(^{-1}\) and together with relevant data from the *Data Booklet*, suggest why a more vigorous reaction condition is required when zinc is used.

........................................................................................................................................
........................................................................................................................................[1]

(ii) A student suggested using sodium metal as the alternative source of metal for the Barbier reaction since its first ionisation energy is close to that of indium. Explain whether the suggestion is feasible.

........................................................................................................................................
........................................................................................................................................[1]
(iii) The reactive intermediate in the Barbier reaction is thought to have the structure shown below. The carbon atoms have been numbered.

\[
\begin{align*}
&\text{Br} \\
&\text{In} \\
&\text{Br} \\
&\text{2} \\
&\text{1} \\
&\text{3}
\end{align*}
\]

In an attempt to locate the nucleophilic carbon, a $^{13}$C isotopic labeling experiment was performed with the following results:

Based on the above results, suggest which carbon (1, 2 or 3) in the intermediate is the nucleophilic carbon.

\[\text{[1]}\]

(iv) The reaction scheme below shows a three-step synthesis of compound \( \text{N} \) from compounds \( \text{L} \) and \( \text{M} \).

\[
\text{L} + \text{M} \xrightarrow{\text{indium}, \text{H}_2\text{O}} \text{HO-} \xrightarrow{\text{PBr}_3} \text{Br-} \xrightarrow{\text{LiAlH}_4, \text{dry ether}} \text{N} \tag{C_{12}H_{15}N}
\]

Suggest the structures of \( \text{L} \), \( \text{M} \) and \( \text{N} \) in the boxes below.

\[
\begin{array}{ccc}
\text{L} & \text{M} & \text{N} \\
\end{array}
\]

\[\text{[3]}\]

[Total: 15]
Ammonia is more soluble in water than it is in trichloromethane as the molecules are able to form hydrogen bonds with water molecules. Hence, \([\text{NH}_3(\text{aq})]\) is higher than \([\text{NH}_3(\text{trichloromethane})]\). [1]

\[
\text{M}^{2+}(\text{aq}) + n\text{NH}_3(\text{aq}) \rightleftharpoons [\text{M(NH}_3]_n^{2+}(\text{aq}) \quad [1]
\]
or
\[
[\text{M(H}_2\text{O}]_3^{2+}(\text{aq}) + n\text{NH}_3(\text{aq}) \rightleftharpoons [\text{M(NH}_3]_n^{2+}(\text{aq}) + 6\text{H}_2\text{O(}l) \quad [1]
\]

Addition of acid (to the aqueous layer) removes the ‘free’ ammonia. Position of equilibrium shifts to the left. The titration results will give the total amount of ammonia (‘free’ plus complexed) in the aqueous layer. [1]

1) Using separate burettes, place 50.0 cm\(^3\) of aqueous \(\text{M}^{2+}\), 50.0 cm\(^3\) of aqueous ammonia and 100.0 cm\(^3\) of trichloromethane into a stoppered bottle.

2) Stopper the bottle and shake vigorously for about 5 minutes before leaving to equilibrate to room conditions.

3) Use a dry pipette to transfer 25.0 cm\(^3\) of the bottom organic layer into a conical flask.

   (Place a finger over the top of pipette or fit the pipette filler before lowering into the bottom layer. This will minimise the amount of top aqueous layer that enters the pipette.)

4) Add an equal volume of water and 2 drops of methyl orange indicator.

5) Fill a burette with hydrochloric acid. Record the initial burette reading.

6) Titrate the ammonia with hydrochloric acid (shaking between each addition) until the indicator changes colour from yellow to orange. Record the final burette reading.

7) Repeat the titration until titres are within 0.10 cm\(^3\) of one another.

\[
\eta(\text{NH}_3) = 1.0 \text{ mol}
\]

Total ‘free’ ammonia = \(x + (2.5x)(2) = 6x\) mol

\(\eta(\text{M}^{2+}) = 0.1 \text{ mol}\)

\(\eta(\text{NH}_3)\) complexed = \(1 - 6x\) mol

\[
\frac{\eta(\text{NH}_3)\text{complexed}}{\eta(\text{M}^{2+})} = 10 (1 - 6x) \quad [1]
\]
2 (a) (i) \([H^+] = \times 10^{-9.2}\)
\[= 6.31 \times 10^{-10} \text{ mol dm}^{-3}\] \[\text{[1]}\]
\([S^{2-}] = \frac{1.0 \times 10^{23}}{(6.31 \times 10^{10})^2} = 2.51 \times 10^{-5} \text{ mol dm}^{-3}\] \[\text{[1]}\]
(ii) \(K_{sp} = [\text{Fe}^{2+}][S^{2-}]\)
\([\text{Fe}^{2+}] = \frac{4.9 \times 10^{18}}{2.51 \times 10^5} = 1.95 \times 10^{-13} \text{ mol dm}^{-3}\] \[\text{[1]}\]
(b) \(-102 = 415 + 279 + 337 + 762 + 1560 - 1981 - 1372 + \Delta H_{ppt}^{\phi}\] \[\Delta H_{ppt}^{\phi} = -102 \text{ kJ mol}^{-1}\] \[\text{[1]}\]
(c) (i) \(\Delta G_{ppt}^{\phi} = 2.303 \times 8.31 \times 298 \times \lg(4.9 \times 10^{-18})\)
\[= -98.7 \text{ kJ mol}^{-1}\] \[\text{[1]}\]
(ii) \(\Delta G_{ppt}^{\phi} = \Delta H_{ppt}^{\phi} - T \Delta S_{ppt}^{\phi}\)
\[-98.7 = -102 - 298 \Delta S_{ppt}^{\phi}\]
\[\Delta S_{ppt}^{\phi} = \frac{102 + 98.7}{298} \text{ J mol}^{-1} \text{ K}^{-1}\] \[\text{[1]}\]
(iii) entropy decreases \[\text{[1]}\] as the ppt forms because ions in the aqueous form are converted to ions held in the solid lattice (decrease in disorder) and there are fewer ways of distributing the energy / arranging the particles. \[\text{[1]}\]

3 (a) \(\eta(\text{compound R}) = \eta(\text{compound P}) = (1.00 / 327.1) = 0.003057 \text{ mol}\)
Mass of compound P = 0.003057 \(\times 137.0 \times (100/50)^4 = 6.70 \text{ g}\) \[\text{[1]}\]
(b) LiA/H₄ in dry ether \[\text{[1]}\]
(c) (i) +4 \[\text{[1]}\]
(ii) \(1s^22s^22p^63s^23p^6\) \[\text{[1]}\]
(iii) 4s and 3d subshells are close in energy level, once 4s electrons are removed, some or all 3d electrons may be removed without requiring significantly more energy. \[\text{[1]}\]
(iv) $E^\circ$ of MnO$_4^-$/Mn$^{2+}$ (i.e. +1.52 V) is more positive than $E^\circ$ of MnO$_2$/Mn$^{2+}$ (i.e. +1.23 V), or $E^\circ$ of MnO$_4^-$/MnO$_2$ (i.e. +1.67 V) is more positive than $E^\circ$ of MnO$_2$/Mn$^{2+}$ (i.e. +1.23 V), hence KMnO$_4$ is a stronger oxidising agent than MnO$_2$. [1] If KMnO$_4$ is used, product would be a carboxylic acid instead of an aldehyde. [1]

(v) K$_2$Cr$_2$O$_7$, dilute H$_2$SO$_4$, heat with immediate distillation [1]

(d) (i)

[Diagram]

(ii)

[Diagram]

At room temperatures, the proportion of molecules with kinetic energy greater than or equal to the activation energy is low hence there is no significant reaction. [1]

At higher temperatures, the proportion of molecules with kinetic energy greater than or equal to the activation energy increases. [1] Thus, the frequency of effective collisions increases, and reaction rate increases. [1]

(iii) Less energy is required to break weaker C–Br bond than C–C' bond, rate of reaction using BrCH$_2$CH$_2$C≡CH will be faster than that of using C/CH$_2$CH$_2$C≡CH. [1]
(e) (i) 

\[ \text{CHO} + \text{CO}_3^{2-} \rightarrow \text{CHO} + \text{HCO}_3^- \]

OR

\[ 2\text{CHO} + \text{CO}_3^{2-} \rightarrow 2\text{CHO} + \text{H}_2\text{O} + \text{CO}_2 \]

(ii) \( K_2\text{CO}_3 \) acts as base to deprotonate \( \text{H} \) on amine group in compound \( \mathbf{Q} \), making the deprotonated amine a stronger nucleophile than compound \( \mathbf{Q} \). [1]

4 (a) (i) 

Anode: \[ \text{Zn} + 4\text{OH}^- \rightleftharpoons [\text{Zn(OH)}_4]^{2-} + 2\text{e}^- \]
Cathode: \[ \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightleftharpoons 4\text{OH}^- \]

(ii) \( E^\circ_{\text{Zn(OH)}_4^{2-}/\text{Zn}} = 0.40 - 1.65 = -1.25 \) V [1]

(iii) \( Q = It = nF \)
\( n_\text{Zn} = (0.0384)(50) / 96500 = 1.99 \times 10^{-5} \) mol [1]
\( n_{\text{O}_2} = 1.99 \times 10^{-5} / 4 = 4.97 \times 10^{-6} \) mol
\( \text{Vol}_{\text{O}_2} = 4.97 \times 10^{-6} \times 24000 = 0.119 \) cm\(^3\) [1]
\( \text{Vol}_{\text{O}_2} = \) cross sectional area of glass tube \( \times (a_2 - a_1) \)
\( 0.119 = 0.0314 \times (a_2 - 1.00) \)
\( a_2 = 4.80 \) cm [1]

(b) • Zn\(^{2+} \) ionic radius (0.074 nm) is smaller than Ba\(^{2+} \) (0.135nm) while the charge remains the same.
• Charge density of Zn\(^{2+} \) is higher than Ba\(^{2+} \).
• Zn\(^{2+} \) has a higher polarizing power than Ba\(^{2+} \) and can thus better distort the electron cloud of CO\(_3^{2-} \), weakening the covalent bond in CO\(_3^{2-} \) to a bigger extent.
• This result in a greater ease of decomposition for ZnCO\(_3 \). Hence, decomposition temperature of ZnCO\(_3 \) is lower than BaCO\(_3 \). [3]

5 (a) (i) Proline [1]

(ii) 

4 structures: [3]

(b) (i) Hydrogen bond between oxygen of C=O in a peptide bond with the –CONH– hydrogen from another peptide bond across the interior of the molecule with the following indicated: lone pair on oxygen, dipoles on polar N–H bond, label. [1]
(ii) The N at the aze residues will not have a H bonded to it after the peptide linkage is formed. [1] Therefore there will be fewer stabilising internal hydrogen bonds possible. Thus the stability of the folded structure will be weakened. [1]

(iii) Circle phenyl or benzyl group of phe, isopropyl group of val, isobutyl group of leu, alkyl group of pro (any one) [1] Type of interaction: Dispersion forces / van der Waals forces / instantaneous dipole-induced dipole [1]

6 (a) As magnesium is less electronegative than carbon, it will take on a partial negative charge, making it an electron rich site. [1]

(b) Step II: Nucleophilic addition [1] Step III: Acidic hydrolysis [1]

(c) PCl₅ or SOCl₂ [1] White fumes of HCl observed, confirming the presence of the alcohol functional group present in Z (which is absent in X and 3-bromoprop-1-ene). [1] or Na [1]. Effervescence of colourless gas (H₂) observed. [1]

(d) (i) Top box: water out
Bottom box: water in [1]

(ii) Not a wise decision. Replacing it with a stopper cap will result in a closed system; as reflux is involved, pressure might build up, leading to unwanted consequences. [1]

(e) V: [1]
W: [1]

(f) (i) 1ˢᵗ IE of Zn (908 kJ mol⁻¹) is higher than that of indium, suggesting more energy required for the electron transfer from the metal to 3-bromopropene. [1]

(ii) This is a bad choice as sodium will react with water explosively to produce hydrogen gas. [1]

(iii) C3 [1]

(iv) L: [1]  
M: [1]  
N: [1]  
Answer for L and M can be interchangeable
INSTRUCTIONS TO CANDIDATES

Write your name and class on all the work you hand in.
Write in dark blue or black pen.
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 any four questions.

Begin each question on a new piece of paper.

A Data Booklet is provided.

You are reminded of the need for good English and clear presentation in your answers.

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

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

Circle the question numbers for the questions that you have attempted on the cover page provided.
Answer any four questions.

1. Margarine was first created in 1869 as a response to a challenge from the French emperor Louis Napoleon III to make a cheap substitute for butter for the army and lower classes. Today, margarine is made by passing hydrogen gas over unsaturated vegetable oils in the presence of a nickel catalyst.

A representative reaction may be written as given below:

\[
\text{CH}_2\text{CH}_3 \quad \text{H} \quad \text{Ni} \quad \text{H}_2 \quad \text{CH}_2\text{CH}_3 \quad \text{H} \quad \text{CH}_3 \quad \text{C} \quad \text{C} \quad \text{CH}_2\text{CH}_2\text{CH}_3
\]

(a) (i) State the type of catalysis that this hydrogenation reaction undergoes. [1]

(ii) State the type of isomerism that the product displays and draw diagrams to illustrate the isomerism. [2]

(iii) In this type of catalysis, one side (bottom face) of the planar alkene molecule is adsorbed to the surface of the catalyst. Both the hydrogen atoms will be added to the same side of the alkene which is adsorbed to the catalyst and not the other side (top face).

The diagram below illustrates how the alkene molecule may be adsorbed to the surface of the catalyst.

In the light of this information and your answer to (a)(ii), explain why the product mixture does not rotate plane-polarised light. The use of a diagram may aid in the clarity of your explanation. [3]

(b) (i) Using appropriate data from the Data Booklet, calculate the standard enthalpy change of reaction for the reaction given above. [2]

(ii) Based on your answer for (b)(i), under what conditions would you expect the hydrogenation reaction to be spontaneous? [2]

(iii) Hence explain why a catalyst is still required for the hydrogenation. [2]
(c) A much more effective rhodium-based catalyst for the hydrogenation of alkenes was discovered in 1965. Wilkinson’s catalyst, Rh(PPh₃)₃Cl, is added to the alkene dissolved in benzene and then stirred at ambient temperature with hydrogen gas being passed through the solution at atmospheric pressure. The hydrogenation was found to occur within minutes of stirring.

The diagram below shows the proposed mode of action for Wilkinson’s catalyst for the hydrogenation of propene.

(i) Wilkinson’s catalyst is one of the earliest examples of a transition metal complex behaving as a *homogeneous* catalyst. Explain what is meant by the word in italics.  

(ii) The oxidation state of Rh in Wilkinson’s catalyst is +1. The phosphine ligands (PPh₃) are neutral ligands while the hydrogen atoms in compound 2 act as hydride ligands. Hence calculate the oxidation number of Rh in compound 2.

(iii) Explain what is meant by the term *coordination number* and state the coordination number of Rh in Wilkinson’s catalyst and in compound 3.

(iv) Based on your answers for (c)(ii) and (iii), state two properties of Rh that allows Rh(PPh₃)₃Cl, to behave as a homogeneous catalyst. Use the proposed mode of action above to illustrate your answers.
2 (a) Describe the appearance of chlorine, bromine and iodine at room temperature and explain how the volatility of these elements varies down the group.

(b) A sample aqueous solution could contain either the chloride or bromide ion. Describe reactions you would carry out to confirm the identity of the ion, and write equations for reactions that occur, including state symbols.

Brominated organic compounds have found uses in drugs and fire retardants. They can be synthesized by reacting bromine with alkenes and arenes. Chemists have studied several alternative methods of bromination to avoid handling bromine directly.

An alternative bromine source is pyridinium tribromide, an ionic salt which produces bromine in the reaction mixture via the following equilibrium:

```
pyridinium tribromide = pyridinium bromide + Br₂
```

(c) (i) Explain one advantage of using pyridinium tribromide instead of bromine in organic synthesis reactions.

(ii) Draw the structure of the tribromide ion, Br₃⁻, showing its shape.

Pyridinium tribromide can be used in the synthesis of mono-brominated anilide. There are two potential routes to this synthesis starting from phenylamine.

In the diagram below, the line connecting Br to the benzene ring indicates that Br is attached to one of the carbons in the benzene ring.

Route 1:

Route 2:

(iii) What types of reaction are Step 1 and Step 2 of Route 1?

(iv) Route 1 is the preferred route for the synthesis because it produced mostly mono-brominated anilide while Route 2 produced mostly multi-brominated anilide. Explain this observation as fully as you can. You may assume pyridinium tribromide in polar solvent has the same reactivity as aqueous bromine.
(v) 4-bromoanilide is obtained from Step 2 of Route 1 at 88% yield. Suggest why it is the major product in this step instead of 2-bromoanilide. [1]

(vi) Describe and explain the relative basicities of the three nitrogen-containing compounds in Route 2. [3]

(d) Equilibrium systems involving tribromide have been studied extensively, one of which is shown below.

\[ \text{Br}_2 + \text{Br}^- \rightleftharpoons \text{Br}_3^- \]

At 25 °C, the \( K_C \) value for the above equilibrium is 100. When 16.0 mg of liquid bromine was dissolved in 150 cm\(^3\) of a 0.500 mol dm\(^{-3}\) solution of sodium bromide, the reaction is “virtually complete”.

(i) Calculate the initial concentration of \( \text{Br}_2 \) added and, together with the information given, explain why the reaction is “virtually complete”. [2]

(ii) Using your answer in (d)(i), estimate the concentrations of bromide and tribromide in the mixture at equilibrium. [1]

(iii) Hence, deduce the concentration of \( \text{Br}_2 \) in the mixture at equilibrium, without solving quadratic equations. [1]

[Total: 20]
3 This question is about reactions of Period 3 elements or their compounds.

(a) Sodium iodate, NaIO₄ \((M_r = 214)\), is a powerful oxidising agent that can be used to oxidise thioethers into sulfoxides with excellent yield.

Thioanisole \((M_r = 124.1)\) is a thioether. In a reaction between thioanisole and 0.500 mol dm\(^{-3}\) solution of sodium iodate, it was found that the reaction yielded 9.82 g of the corresponding methyl phenyl sulfoxide. The percentage yield of the reaction was determined to be 91.3%.

\[
\text{thioanisole} \xrightarrow{\text{NaIO}_4} \text{methyl phenyl sulfoxide}
\]

(i) Calculate the mass of thioanisole that was used in the above reaction. \[2\]

The oxidation state of iodine in the product was +5, and the reacting mole ratio of thioanisole to sodium iodate was 1:1.

(ii) Determine the volume of sodium iodate, in cm\(^3\), that was used in the above reaction. \[1\]

(iii) Explain why the reacting mole ratio is 1:1. \[1\]

(b) Thioethers can be synthesised by the reaction of a thiol (containing the \(-\text{SH}\) functional group) with an alkene. When methanethiol, CH\(_3\)SH, is reacted with ethene, the thioether ethyl methyl sulfide is obtained.

\[
\text{CH}_2=\text{CH}_2 \xrightarrow{\text{CH}_3\text{SH}} \text{CH}_3\text{CH}_2\text{SCH}_3
\]

(i) Name the type of reaction that occurs when synthesising thioethers in this way. \[1\]

(ii) Suggest a mechanism for this reaction, showing all charges and using curly arrows to show the movement of electron pairs, and clearly indicating the rate-determining step. \[2\]

(iii) Draw the structure of the major product obtained when the starting alkene is replaced by propene. \[1\]
(c) Benzenesulfonic acid, C₆H₅SO₃H, was once widely used in the production of phenol. The process simply required heating the benzenesulfonic acid with aqueous sodium hydroxide, replacing the –SO₃H group with –OH.

Suggest the reagents and conditions you would use in a three-step synthesis of 3-aminophenol starting from benzenesulfonic acid, identifying F and G. The reactivity of the –SO₃H group and its influence as a side-chain of benzene is similar to that of a –NO₂ group.

\[
\begin{align*}
\text{C}_6\text{H}_5\text{SO}_3\text{H} & \quad \text{step 1} \quad \rightarrow \quad F \quad \text{step 2} \quad \rightarrow \quad G \quad \text{step 3} \quad \rightarrow \quad \text{3-aminophenol} \\
\end{align*}
\]

(d) The chlorides of the elements from sodium to phosphorus (each in their highest possible oxidation state) are separately added to water. Sketch a graph to show the trend in pH of the resulting mixtures. Label your graph with the full formula of each of the relevant chlorides.

(e) The Bayer process, outlined below, involves extracting aluminium oxide from bauxite, which also contains the metal oxide titanium dioxide, TiO₂, and compounds of iron(III) as impurities.

\[
\begin{align*}
\text{NaOH(aq)} & \quad \rightarrow \quad \text{reaction mixture} \\
& \quad \rightarrow \quad 180 \degree \text{C} \\
& \quad \rightarrow \quad \text{filtering} \\
& \quad \rightarrow \quad \text{cooling and filtration} \\
& \quad \rightarrow \quad \text{crystallisation of white solid} \\
& \quad \rightarrow \quad \text{aluminium oxide} \\
\end{align*}
\]

(i) State the identity of solution J.

(ii) Explain, in terms of the nature of the oxides, how the addition of aqueous sodium hydroxide is able to separate the aluminium oxide from the titanium dioxide impurity. Write equations with state symbols for the reactions you describe.

(iii) Suggest the identity of the compound responsible for the colour of the ‘red mud’.

(iv) Upon cooling, solution J forms a white solid and sodium hydroxide solution as the only products. Aluminium oxide is then recovered via step A. Suggest the reagents and/or conditions required to carry out step A, giving an equation for the reaction.

[Total: 20]
4 (a) Sulfur dioxide and oxygen are used in the manufacture of sulfuric acid. In an experimental set-up, two sealed 30 dm$^3$ cylinders containing sulfur dioxide and oxygen separately at 450 °C, have a pressure of 4.0 atm and 2.0 atm respectively. The cylinders are combined and the two gases are allowed to react according to the equation

$$2\text{SO}_2 (g) + \text{O}_2 (g) \rightleftharpoons 2\text{SO}_3 (g)$$

At equilibrium at 450 °C, 90% of the SO$_2$ is converted into SO$_3$.

(i) For the mixture at equilibrium, calculate:
   I the total pressure;
   II the mole fraction of oxygen; and
   III the number of moles of gas.

(ii) State and explain how you would expect the actual total pressure to be different from your answer in (a)(i).

(b) When antimony(V) fluoride, SbF$_5$, dissolves in hydrogen fluoride HF, the following reaction occurs

$$2\text{HF} + \text{SbF}_5 \rightarrow \text{H}_2\text{F}^+ + \text{SbF}_6^-$$

In H$_2$F$^+$, the proton is extremely weakly bound, making H$_2$F$^+$ a stronger acid than pure sulfuric acid, and is therefore called a superacid.

(i) Use VSEPR theory to predict the shape of the H$_2$F$^+$ ion.

(ii) Identify the Brønsted acid and Brønsted base in the HF/SbF$_5$ reaction.

(iii) The Lewis classification of acids and bases is broader and encompasses many more substances than the Brønsted-Lowry theory. A Lewis acid is an electron pair acceptor, while a Lewis base is an electron pair donor. Identify the Lewis acid and Lewis base in the HF/SbF$_5$ reaction.

(c) Thioglycolic acid is a sulfur-containing organic acid used to break disulfide bonds during hair perms. It has the structure shown below.

```
\begin{center}
\begin{tikzpicture}
\draw[thick] (0,0) -- (0.5,0) -- (0.5,0.5) -- (0,0.5) -- cycle;
\draw[thick] (0.5,0) -- (1,0) -- (1,0.5) -- (0.5,0.5) -- cycle;
\draw[thick] (0,0.5) -- (1,0.5);
\draw[thick] (0,0.25) -- (1,0.25);
\draw[thick] (0,0.5) -- (0.25,0.75);
\draw[thick] (0.75,0.75) -- (1,0.5);
\node at (0.25,0.75) {O};
\node at (0.5,0.75) {SH};
\node at (0.5,0) {HO};
\node at (0.5,0.5) {thioglycolic acid};
\end{tikzpicture}
\end{center}
```

The successive $pK_a$ values of thioglycolic acid are 3.67 and 10.31, and sulfur has almost the same electronegativity as carbon.

(i) Draw the predominant form of thioglycolic acid present in aqueous solution at pH 7.

(ii) Suggest a reason why the second $pK_a$ of thioglycolic acid is higher than the first $pK_a$. You may use the symbol H$_2$A to represent thioglycolic acid.
(iii) Calculate the ratio of concentrations of the di-anion, \( A^{2-} \), and mono-anion, \( HA^- \), of thioglycolic acid present at pH 9.3. You may assume that these are the only two sulfur-containing species present at this pH.

[1]

(iv) Explain whether the solution in (c)(iii) is an effective buffer solution.

[1]

(v) The \( pK_a \) of phenolphthalein is 9.3. Explain whether phenolphthalein is a suitable indicator for detecting the second equivalence point of the titration of thioglycolic acid with aqueous sodium hydroxide.

[1]

(d) For all its health benefits, the effect of eating asparagus on the odour of urine has long been observed. It was once thought that the compound responsible for the smell in so-called ‘asparagus-pee’ was methanethiol, \( \text{CH}_3\text{SH} \). In a more recent study, two other sulfur-containing compounds, \( A \) and \( B \), were detected in ‘asparagus-pee’, rather than methanethiol itself.

(i) When hydrolysed in water, \( A \) releases propenoic acid and methanethiol, hence the earlier suspicion of this compound.

\[
\begin{align*}
A & \quad + \quad \text{H}_2\text{O} \quad \rightarrow \quad \text{propenoic acid} \quad \text{+} \quad \text{CH}_3\text{SH} \\
\end{align*}
\]

Draw the displayed formula of \( A \).

[1]

(ii) \( B \) can be prepared in the laboratory from propenoic acid by the following route.

\[
\text{Step 1} \quad \begin{align*}
\text{propenoic acid} & \quad + \quad \text{H}_2\text{S} \quad \rightarrow \quad X
\end{align*}
\]

\[
\text{Step 2} \quad X & \quad + \quad \text{CH}_3\text{I} \quad \rightarrow \quad Y
\]

\[
\text{Step 3} \quad Y & \quad + \quad \text{CH}_3\text{SH} \quad \text{condensation} \quad \rightarrow \quad B \quad + \quad \text{H}_2\text{O}
\]

\( X \), \( Y \), and \( B \) do not contain any chiral carbon. Only \( X \) and \( Y \) produce effervescence with \( \text{Na}_2\text{CO}_3 \), but not \( B \).

Suggest structures for \( X \), \( Y \), and \( B \), and state the type of reaction occurring in Step 1 and Step 2.

[5]

[Total: 20]
5 (a) Ruthenium and strontium are elements in the fifth period of the Periodic Table.

<table>
<thead>
<tr>
<th>Element</th>
<th>Ruthenium</th>
<th>Strontium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronic configuration</td>
<td>1s²2s²2p⁶3s²3p⁶3d¹⁰4s²4p⁶5s¹</td>
<td>1s²2s²2p⁶3s²3p⁶3d¹⁰4s²4p⁶5s²</td>
</tr>
<tr>
<td>Melting point/°C</td>
<td>2334</td>
<td>777</td>
</tr>
</tbody>
</table>

(i) Explain the difference in the melting points of ruthenium and strontium. [2]

(ii) Sketch the trend of the successive ionisation energies of the first 10 electrons of a strontium atom and explain the trend observed. [3]

(b) The standard electrode potential for the reduction of Ru³⁺ to Ru²⁺ is shown below.

\[ \text{Ru}^{3+}(aq) + e^- \rightleftharpoons \text{Ru}^{2+}(aq) \quad E^\circ = +0.23 \text{ V} \]

(i) What do you understand by the term standard electrode potential of a half-cell? [1]

(ii) By using relevant \( E^\circ \) values from the Data Booklet, show that the reaction between \( \text{Ru}^{3+}(aq) \) and \( \text{Zn}(s) \) is feasible. Construct a balanced equation, including state symbols, for the reaction. [2]

(iii) When aqueous ruthenium(III) chloride is treated with zinc and aqueous ammonia, orange crystals of a complex of ruthenium are formed. The crystals contain 36.9% of ruthenium by mass, the remainder consisting of hydrogen, nitrogen and chlorine. Suggest a formula for the orange crystals. [2]

(c) Aldehydes and ketones can react with alcohols to form hemiacetals in the presence of an acid catalyst via nucleophilic addition.

\[
\begin{align*}
\text{R}_1\text{C}=\text{O} & + \quad \text{R}_3\text{OH} \quad \text{HA} \quad \text{R}_1\text{C}(-\text{O})\text{R}_3 \\
\text{hemiacetal} & 
\end{align*}
\]

The mechanism for the reaction of benzaldehyde with methanol is thought to proceed as described below:
- The oxygen of the carbonyl group is first protonated by HA catalyst via an acid-base reaction to activate the carbonyl group.
- The alcohol is then added to the activated carbonyl group.
- Lastly, deprotonation gives the hemiacetal and regenerates the catalyst.

(i) Suggest a mechanism for this reaction, showing all charges and using curly arrows to show the movement of electron pairs. [3]
(ii) Hemiacetal \( \textbf{R} \) can be formed from the reaction of \( \textbf{P}, \text{C}_9\text{H}_8\text{O}_3 \), with acidified ethanol.

Both \( \textbf{P} \) and \( \textbf{R} \) yield a colourless gas which forms a white precipitate with limewater when warmed with aqueous sodium carbonate.

With alkaline aqueous iodine, \( \textbf{P} \) gives a yellow precipitate. Treating \( \textbf{P} \) with methanolic sodium borohydride yields compound \( \textbf{Q}, \text{C}_9\text{H}_{10}\text{O}_3 \). \( \textbf{Q} \) reacts with aqueous sodium hydroxide to yield compound \( \textbf{S} \).

Use the information above to deduce the structures of compounds \( \textbf{P}, \textbf{Q}, \textbf{R} \) and \( \textbf{S} \), explaining all the reactions involved.

[7]
[Total: 20]
1 (a) (i) Heterogeneous catalysis [1]

(ii) Optical isomerism [1]

(iii) The addition of \( \text{H}_2 \) to one side (bottom face) of the planar alkene molecule creates a chiral alkane molecule. [1]

When the opposite side (top face) of the alkene is now adsorbed to the surface of the Ni catalyst, the addition of \( \text{H}_2 \) produces a chiral alkane molecule which is the non-superimposable mirror image of the product formed at the bottom face. [1]

As there is 50% chance for each side (face) of the alkene to bind to the surface of the catalyst, the two enantiomers are produced in a 1:1 ratio resulting in a racemic mixture. Hence the product mixture does not rotate the plane of plane-polarised light. [1]

If a diagram is used, it will substitute the 1st two marks:
Show opposite faces adsorbed to the catalyst surface [1]
Indicate which carbon forms the chiral alkane and the corresponding enantiomer. [1]

(b) (i) \[ \Delta H_{\text{reaction}} = \Sigma (\text{B.E. of Bonds Broken}) - \Sigma (\text{B.E. of Bonds Formed}) \]
\[ = \Sigma [\text{B.E. (C = C)} + \text{B.E. (H – H)}] - \Sigma [\text{B.E. (C – C)} + \text{B.E. (C – H)} \times 2] \]
\[ = (610 + 436) - (350 + 410 \times 2) \]
\[ = -124 \text{ kJ mol}^{-1} \]

Correct bond energies used [1]
Correct equation and answer [1]
(ii) $\Delta H_{\text{reaction}}^\circ$ is exothermic. $\Delta S_{\text{reaction}}^\circ$ is negative as there is a decrease in the number of moles of gas in the reaction. [1]

Given that $\Delta G_{\text{reaction}}^\circ = \Delta H_{\text{reaction}}^\circ - T\Delta S_{\text{reaction}}^\circ$

$\Delta G_{\text{reaction}}^\circ$ is expected to be negative only at low temperatures and so the reaction would be spontaneous only at low temperatures. [1]

(iii) Although the reaction is energetically feasible, the activation energy is very high. Or as the low temperatures are necessary for the reaction to be feasible, the rate of reaction may be very slow. [1]

Hence the catalyst provides an alternative pathway with a lower activation energy and the reaction speeds up. [1]

(d) (i) A homogeneous catalyst acts in the same phase as the reactants. [1]

(ii) Oxidation number of Rh in compound 2: +3 [1]

$x + (-1) + [(-1) \times 2] = 0$

$x = +3$

(workings is not required)

(iii) The coordination number indicates the number of dative bonds about the central atom or ion. [1]

Wilkinson’s catalyst: coordination number = 4
Compound 3: coordination number = 6

[½] for each correct coordination number

(iv) Rh is able to exhibit variable oxidation states. [1]

The proposed mechanism requires the addition of $\text{H}_2$ to Rh in the form of two hydride ligands, which causes the oxidation state of Rh to increase from +1 to +3. [1]

Rh is able to form complexes of variable coordination numbers. [1]

The proposed mechanism requires the alkene and $\text{H}_2$ to bind to Rh as ligands before the addition reaction occurs. Or coordination number changes from 4 to 6 from Wilkinson’s catalyst to Compound 3. [1]

2 (a) Chlorine is a greenish yellow gas. Bromine is a reddish-brown liquid. Iodine is a black solid. [1]

Down the group, the volatility decreases as the number of electrons in the halogen molecule increases. The size of the electron cloud increases, making the electron cloud more polarizable and hence giving rise to stronger dispersion forces. Thus more energy is required to overcome the stronger dispersion forces between the molecules for them to vaporize. [2]

(b) Add a few drops of aqueous $\text{AgNO}_3$ to the sample solution, followed by dilute aqueous ammonia.
If a white ppt forms which dissolves in dilute aqueous ammonia, the sample contains Cl⁻ ion.

\[ \text{Ag}^+ (aq) + \text{Cl}^- (aq) \rightarrow \text{AgCl} (s) \quad \text{--- white ppt} \]

\[ \text{AgCl} (s) + 2\text{NH}_3 (aq) \rightarrow \text{Ag(NH}_3)_2^+ (aq) + \text{Cl}^- (aq) \]

If a cream ppt forms which is insoluble in dilute aqueous ammonia, the sample contains Br⁻ ion.

\[ \text{Ag}^+ (aq) + \text{Br}^- (aq) \rightarrow \text{AgBr} (s) \quad \text{--- cream ppt} \]

\( \{\text{AgBr} (s) + 2\text{NH}_3 (aq) \rightarrow \text{Ag(NH}_3)_2^+ (aq) + \text{Br}^- (aq)\} \) – this reaction occurs as well but does not decrease the [Ag⁺] sufficiently to make AgBr dissolve completely since \( K_{sp}(\text{AgBr}) \) is lower than \( K_{sp}(\text{AgCl}) \).

1) for correct reagents
1) for equation for AgX precipitation and colours of ppt
1) for equation with ammonia and correct observation of solubility

OR

Add a few drops of \( \text{Cl}_2(aq) \) into the sample solution.

If the solution turns from colorless to yellow-orange, the sample contains Br⁻ ion.

\[ \text{Cl}_2(aq) + 2\text{Br}^- (aq) \rightarrow \text{Br}_2(aq) + 2\text{Cl}^- (aq) \]

If the solution does not turn yellow-orange (OR remains colourless), the sample contains Cl⁻ ion.

1) for correct reagents
1) for correct observations for both ions
1) for redox equation

(c) (i) Pyridinium tribromide is a solid and is less volatile, hence it is safer to use compared to bromine which is a fuming liquid and gives off toxic bromine fumes. [1]

OR Pyridinium tribromide is a solid, hence it is easier to weigh and use compared to bromine which is a fuming liquid.

Pyridinium tribromide is given as an ionic salt, hence students can deduce it is a solid and will be less volatile compared to bromine which is fuming and toxic, and relate its advantage to safety and ease of use.

(ii) \[ \text{Br}-\text{Br}^-\text{Br} \quad [1] \]

(iii) Step 1: condensation [1]

OR nucleophilic (acyl) substitution or addition-elimination

Step 2: electrophilic substitution [1]

(iv) In Route 2, the Br₂ reacts with phenylamine. The lone pair on NH₂ delocalises into the benzene ring and increases electron density in the ring. The ring is highly activated towards electrophilic attack, hence it is able to undergo further brominations to give multi-brominated products. [1]

In Route 1, the anilide is not as activated as phenylamine as the –NHCOR group is less electron-donating due to the delocalization of the nitrogen lone pair into the –C=O group as well. [1]
The bulky –NHCOR group sterically hinders the approach of the electrophile towards the 2\textsuperscript{nd} carbon. Hence substitution occurs mainly on the 4\textsuperscript{th} position. [1]

Phenylamine is the most basic of the three, followed by bromophenylamine and then bromoanilide. [1]

Bromoanilide is the least basic. In the amide group, the lone pair on N is delocalized into the C=O group (as well as into the benzene ring) and least (or not) available for protonation.

In bromophenylamine and phenylamine, the lone pair on N delocalizes into the benzene ring. However, bromophenylamine is less basic because its Br substituent is electron-withdrawing and decreases the electron density on the benzene ring. Hence the lone pair on N delocalizes into the benzene ring to a greater extent and is less available for protonation, compared to phenylamine. [1]

(d) (i) amount of Br₂ = 16.0 x 10\textsuperscript{-3} / (79.9 x 2) = 1.00 x 10\textsuperscript{-4} mol

\[ [\text{Br}_2] = 1.00 \times 10^{-4} / (150/1000) = 6.67 \times 10^{-4} \text{ mol dm}^{-3} \quad [1] \]

The value of \( K_C >1 \) shows that the equilibrium is product favoured. The concentration of Br\(^-\) is 0.5/6.67 x 10\textsuperscript{-4} = 750 times more than that of Br₂. The large excess of Br\(^-\) will push the equilibrium position very much to the right, such that the reaction is almost complete. [1]

(ii) Assuming the reaction is complete,

\[ [\text{Br}_3^{-}] \text{ at eqm} = 6.67 \times 10^{-4} \text{ mol dm}^{-3} \]

\[ [\text{Br}^{-}] \text{ at eqm} = 0.5 - 6.67 \times 10^{-4} = 0.499 \text{ mol dm}^{-3} \quad [1] \]

(iii) \( K_C = [\text{Br}_3^{-}] / ([\text{Br}_2][\text{Br}^{-}]) \)

\[ 100 = 6.67 \times 10^{-4} / ([\text{Br}_2] (0.499)) \]

\[ [\text{Br}_2] = 1.34 \times 10^{-5} \text{ mol dm}^{-3} \quad [1] \]

3 (a) (i) No. of moles of sulfoxide recovered = 91.3\% of theoretical no. of moles

\[ \therefore \text{ no of moles of thioanisole used} = \text{theoretical no of moles of sulfoxide} \]

\[ = (9.82/(124.1 + 16.0))/(91.3/100) \]

\[ = (9.82/140.1)/(91.3/100) \]

\[ = 0.07677 \text{ mol} \quad [1] \]

Correct substitution of \( M_t \) and % yield

\[ \therefore \text{ mass of thioanisole used} = 0.07677 \times 124.1 = 9.53 \text{ g} \quad \text{(must be 3 s.f.)} \quad [1] \]

(ii) Since IO\textsubscript{4}\textsuperscript{-} and thioanisole react in a 1:1 ratio,

\[ \Rightarrow \text{ no of moles of IO}_4\textsuperscript{-} \text{ required} = 0.07677 \text{ mol (from (i))} \]

\[ \therefore \text{ volume of sodium iodate solution required} = 0.07677/0.500 \times 1000 \]

\[ = 154 \text{ cm}^3 \quad [1] \]

(allow ecf from no of moles of thioanisole in (i))
(iii) Oxidation state of iodine in IO₄⁻ = +7
∴ change in oxidation state of iodine = (+5) – (+7) = −2

By observing the structure of thioether and sulfoxide product, the sulfur atom changes its oxidation state by +2 (due to new double-bond formation with the more electronegative oxygen atom)

As such, IO₄⁻ and thioanisole should react in a 1:1 ratio.

(b) (i) Electrophilic addition [1]

(ii)

[Note: not necessary to show all 3 lone pairs on S atom in 2nd step (only 1 is necessary)]

(iii) Isopropyl methyl sulfide

S

\[ \text{S} \quad \text{CH}_3 \quad \text{CH} \quad \text{CH}_3 \]

(accept other unambiguous ways of drawing the structure)

(c)

3-nitrobenzenesulfonic acid

\[
\begin{align*}
\text{F} & : \quad \text{NO}_2 \\
\text{G} & : \quad \text{NH}_3^+ \text{Cl}^-
\end{align*}
\]

[Step 1: conc. HNO₃, conc. H₂SO₄, >55 °C [1] (since –SO₃H is deactivating)]

Step 2: Sn, excess conc. HCl, heat [1] (no need to follow with NaOH since we add it in the next step anyway)

Step 3: heat with NaOH(aq) [1]

OR Inverse Steps 2 and 3, then G will be as follows (all others remain unchanged):
(d) 3-nitrophenoxide

Formula of each chloride must be correctly written [1]

Trend must be correct: [1]
- pH 7 must be clearly indicated on axis (if not, this mark is lost)
- trend in pH must be correct (neutral for NaCl, slightly below neutral for MgCl₂ (accept 6-6.5), lower for AlCl₃, and lowest for SiCl₄ and PCl₅ (accept if PCl₅ is at lower pH than SiCl₄)

(e) (i) J contains NaAl(OH)₄ or Al(OH)₄⁻ [1]

(ii) Al₂O₃ is amphoteric, and so it is dissolves in NaOH(aq) [½]

\[ \text{Al}_2\text{O}_3(s) + 2\text{NaOH}(aq) + 3\text{H}_2\text{O}(l) \rightarrow 2\text{NaAl(OH)}_4(aq) \] [1]

Accept: ionic equation (without Na⁺ spectator ion)

TiO₂ is basic in nature, and does not dissolve in NaOH, hence it remains as a solid and can be separated from the solution (filtered out) [½]

(iii) Fe(OH)₃ OR Fe₂O₃ [1]
Accept: iron(III) hydroxide OR iron(III) oxide (oxidation state of iron must be stated)

(iv) Step A requires heating to decompose the hydroxide.

\[ 2\text{Al(OH)}_3 \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O} \] [1]
4 (a) (i) \[2\text{SO}_2 (g) + \text{O}_2 (g) \rightleftharpoons 2\text{SO}_3 (g)\]

Initial P / atm \[\tfrac{1}{2} \times 4 \quad \tfrac{1}{2} \times 2 \quad 0 \quad \text{(from doubling of volume)} \quad [1]\]
Change \[-1.8 \quad -0.9 \quad +1.8 \quad \text{(from 90\% conversion of \text{SO}_2)}\]
At eqm / atm \[0.2 \quad 0.1 \quad 1.8 \quad \text{[1]}\]

I. Total P = 0.2 + 0.1 + 1.8 = 2.1 atm \quad [1]

II. \[x(\text{O}_2) = \frac{0.1}{2.1} = 0.0476 \quad [1]\]

III. \[n = \frac{(2.1 \times 1.01 \times 10^5) \times (60 \times 10^{-3})}{8.31 \times (450 + 273)} = 2.12 \text{ mol} \quad [1]\]

(ii) The actual total pressure will be smaller than in (a)(i) because the gases (are not ideal, and) have non-negligible intermolecular forces which reduce the pressure on the container. \quad [1]

(b) (i) The F atom in H$_2$F$^+$ has two lone pairs and two bond pairs, hence, bent / V-shaped \quad [1]
Accept a diagram leading to a statement of ‘bent / V-shaped’.

(ii) Brønsted acid: HF \[\tfrac{1}{2}\] and Brønsted base: HF \[\tfrac{1}{2}\]

(iii) Lewis acid: SbF$_5$ \[\tfrac{1}{2}\] and Lewis base: F$^- \quad [\tfrac{1}{2}]$

(c) (i) \[\text{[1]}\]

(ii) It is harder to remove a positively charged H$^+$ from the negatively charged thioglycolate anion HA$^-$ due to the attraction of opposite charges compared to the loss of H$^+$ from an uncharged thioglycolic acid molecule H$_2$A. \quad [1]
This results in HA$^-$ being a weaker acid compared to H$_2$A and hence larger pK$_a$. \quad [1]

Accept: The —CO$_2$H group in H$_2$A is a stronger acid than —SH group because the —CO$_2^-$ is stabilized by resonance (the negative charge on the carboxylate ion is delocalized over two highly electronegative oxygen atoms), while the —S$^-$ ion is not similarly stabilized.

(iii) \[K_a = \frac{[H^+][A^{2-}]}{[HA^-]} \quad [\text{[1]}\]
\[\frac{[A^{2-}]}{[HA^-]} = \frac{K_a}{[H^+]} \quad 10^{-10.31} = 0.098 \quad [\text{[1]}\]

\[\text{OR}\]
\[\text{pK}_a = \text{pH} - \log \frac{[A^{2-}]}{[HA^-]}\]
\[10.31 = 9.3 - \log \frac{[A^{2-}]}{[HA^-]}\]
\[\log \frac{[A^{2-}]}{[HA^-]} = -1.01\]
\[\frac{[A^{2-}]}{[HA^-]} = 0.098\]
(iv) Not an effective buffer because ratio of concentrations of $\text{HA}^-$ and $\text{A}^{2-}$ is too small / not close to 1 / the reservoir of $\text{A}^{2-}$ is too low compared to $\text{HA}^-$, (and therefore $\text{HA}^-$ will be used up very quickly when $H^+$ is added). [1]

(v) Not suitable because the working range of phenolphthalein is $9.3 \pm 1$, but at pH 9.3, thioglycolic acid has not reached its second equivalence point, $[\frac{1}{2}]$ which occurs only after 10.31 $[\frac{1}{2}]$.

(d) (i) \[\text{[1] deduct } \frac{1}{2} \text{ mark if not fully displayed.}\]

(ii) $X$ \[\text{HS--CO--OH}\] $Y$ \[\text{S--CO--OH}\]

$B$ \[\text{S--CO--S}\]

$X, Y, B$ [3] (1 mark for each compound)
Step 1: electrophilic addition [1]
Step 2: nucleophilic substitution [1]
In Step 1, $H_2S$ adds across the $\text{C}=$C double bond; the absence of chiral carbon in $X$ rules out the Markovnikov product.
In Step 2, the $\text{─SH}$ group acts as a nucleophile for substituting $I$ in $\text{CH}_3I$, and loses its H as a proton.
During the condensation in Step 3, $H_2O$ is lost between the $\text{─CO}_2\text{H}$ group and $\text{CH}_3\text{SH}$ to form $\text{─C─S─CH}_3$.

5 (a) (i) The melting point of Ru is higher than that of Sr. In Sr, only the 5s electrons are involved in metallic bonding. In Ru, both 5s and 4d electrons are involved in metallic bonding due to their proximities in energies [1]. More energy is required to overcome the stronger metallic bonding in Ru compared to Sr [1].
The IE increases as more electrons are removed. As more electrons are removed, the number of protons is more than the number of electrons and there are stronger electrostatic forces of attraction on the remaining electrons [1]. More energy is needed to remove another electron from the increasingly positively charged ion. There is a big increase in IE between the 2nd to the 3rd electrons removed. The 3rd electron is removed from an inner quantum shell \[\frac{1}{2}\].

There is a small increase in IE between the 8th and 9th electrons removed. The 9th electron removed is from 4s subshell which is closer to the nucleus compared to 4p subshell \[\frac{1}{2}\].

(b) (i) The standard electrode potential of a half-cell is the potential associated with a given half-reaction when all components are in their standard states (temperature of 298 K, pressure of any gas at 1 atm, and concentration of any ion at 1 mol dm\(^{-3}\)), measured relative to the standard hydrogen electrode. [1]

\[ E_{\text{cell}}^\circ = +0.23 - (-0.76) = +0.99 \text{ V} > 0 \text{ [1]} \]

\[ 2\text{Ru}^{3+}(aq) + \text{Zn}(s) \rightarrow 2\text{Ru}^{2+}(aq) + \text{Zn}^{2+}(aq) \text{ [1]} \]

(iii) \( A \) of Ru = 101, \( M \) of orange crystal = 101/0.369 = 273.7
To balance the charges, \( \text{Ru}^{2+} : \text{Cl}^- \) is 1:2 [1]
\( M \) of NH\(_3\) ligands = 273.7 – 101 – 2(35.5) = 101.7
Number of NH\(_3\) ligands = 101.7/(14.0 + 3.0) \( \approx 6 \)
Formula for orange crystals: \([\text{Ru(NH}_3)_6]\text{Cl}_2\) [1]
(c) (i)

[Diagrams of chemical reactions]

[1] for each of the 3 steps
Accept protonation using just H⁺ in first step and deprotonation without using A⁻ in last step

(ii)

<table>
<thead>
<tr>
<th>Test/Observation</th>
<th>Deduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>P reacts with acidified ethanol to yield compound R.</td>
<td>P undergoes nucleophilic addition with acidified ethanol to produce a hemiacetal. φ P contains aldehyde/ketone functional group.</td>
</tr>
<tr>
<td>Both P and R yield a colourless gas which forms a white precipitate with limewater when warmed with aqueous sodium carbonate.</td>
<td>P and R undergoes acid-base reaction with Na₂CO₃ to give CO₂ gas. φ P and R contain carboxylic acid functional group [1]</td>
</tr>
<tr>
<td>With alkaline aqueous iodine, P gives a yellow precipitate</td>
<td>P reacts with alkaline aqueous iodine to give CHI₃ ppt. φ P contains CH₃CH(OH)- or CH₃CO- group [1]</td>
</tr>
<tr>
<td>Treating P with methanolic sodium borohydride yields compound Q, C₉H₁₀O₃.</td>
<td>Carboxylic acid in P cannot be reduced by methanolic NaBH₄. P contains ketone group which undergoes reduction [1]</td>
</tr>
</tbody>
</table>
| Q | \[
\begin{array}{c}
\text{CO}_2\text{H} \\
\text{CH(OH)CH}_3
\end{array}
\] Q [1] |
|---|---|
| R | \[
\begin{array}{c}
\text{CO}_2\text{H} \\
\text{CH}_3
\text{C} \\
\text{OH} \\
\text{OCH}_2\text{CH}_3
\end{array}
\] R [1] |
| S | \[
\begin{array}{c}
\text{CO}_2\text{Na}^+ \\
\text{CH(OH)CH}_3
\end{array}
\] S [1] |

Q reacts with aqueous sodium hydroxide yields S

Q undergoes **acid-base/neutralisation** reaction

[1] for each correct structure (accept 1,2 or 1,3 or 1,4 di-substituted structures)

[1] for each correct deduction, max 3 out of 4 available