1. This paper consists of sections A, B and C.

2. Answer FIVE (5) questions including at least ONE (1) question from each of the sections A, B and C.

3. Read each question carefully.

4. Mathematical tables and calculators may be used.

5. Write your examination number on every page of your answer booklet.

6. For calculations you may use the following atomic masses.

   \[ H = 1, \quad C = 12, \quad O = 16, \quad K = 39, \quad Br = 79.9, \quad I = 127. \]
SECTION A

Answer at least ONE (1) question from this section.

1. (a) Define the following terms giving one example in each case.
   
   (i) Standard heat of atomization.
   
   (ii) Standard enthalpy of solution.
   
   (iii) An exothermic reaction. (4½ marks)

(b) State Hess’s law of constant heat summation

(c) Li_{(s)}  \rightarrow Li_{(g)} \quad \Delta H^\circ = 155.1 \text{ kJmol}^{-1}
F_{(g)} \rightarrow 2F_{(g)} \quad \Delta H^\circ = 151.0 \text{ kJmol}^{-1}
Li_{(g)} \rightarrow Li^\cdot_{(g)} + e^- \quad \Delta H^\circ = 518.3 \text{ kJmol}^{-1}
F_{(g)} + e^- \rightarrow F^-_{(g)} \quad \Delta H^\circ = -351.1 \text{ kJmol}^{-1}
Li^+_{(g)} + F^-_{(g)} \rightarrow LiF_{(s)} \quad \Delta H^\circ = -1030.0 \text{ kJmol}^{-1}

(i) From the data above draw the Born – Haber cycle for LiF_{(s)} and calculate the enthalpy of formation of LiF_{(s)} using the equation
   \[ \text{Li}_{(s)} + \frac{1}{2}F_{(g)} \rightarrow \text{LiF}_{(s)} \]

(ii) Indicate clearly whether the reaction is exothermic or endothermic. (1½ marks)

(c) Enthalpies of combustion of some substances are given below:

<table>
<thead>
<tr>
<th>Substance</th>
<th>$H_f^\circ$/kJmol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>-242</td>
</tr>
<tr>
<td>Benzene</td>
<td>-3302</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>-3746</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>-3940</td>
</tr>
</tbody>
</table>

(i) Calculate the enthalpy of hydrogenation of benzene and cyclohexene.

(ii) Comment on the differences in the enthalpies of hydrogenation of benzene and cyclohexene you have calculated in (i) with reference to the structure of the two compounds. (2½ marks)

2. (a) Define the following terms:

(i) Cathode

(ii) Anode

(iii) Standard electrode potential

(iv) Concentration cell (4 marks)

(b) (i) What is the difference between a galvanic cell and an electrolytic cell? (2 marks)

(ii) Why is it necessary to use a salt bridge in a galvanic cell? (1 mark)
(c) Standard potentials at 25 °C:
\[
\begin{align*}
\text{Cl}_2(g) + 2e^- & \rightarrow 2\text{Cl}^-(aq) \quad \varepsilon^\circ = 1.36 \text{ V} \\
\text{Ni}^{2+}(aq) + 2e^- & \rightarrow \text{Ni(s)} \quad \varepsilon^\circ = -0.23 \text{ V} \\
\text{Cr}^{3+}(aq) + e^- & \rightarrow \text{Cr}^{2+}(aq) \quad \varepsilon^\circ = -0.50 \text{ V} \\
\text{Cr}^{3+}(aq) + 3e^- & \rightarrow \text{Cr}(s) \quad \varepsilon^\circ = -0.73 \text{ V} \\
\text{Br}_2(aq) + 2e^- & \rightarrow 2\text{Br}^-(aq) \quad \varepsilon^\circ = 1.09 \text{ V} \\
2\text{SO}_3^{2-}(aq) + 2e^- & \rightarrow \text{S}_4\text{O}_6^{2-}(aq) \quad \varepsilon^\circ = 0.17 \text{ V} \\
\text{Cr}_2\text{O}_7^{2-}(aq) + 14\text{H}^+(aq) + 6e^- & \rightarrow 2\text{Cr}^{3+}(aq) + 7\text{H}_2\text{O}(l) \quad \varepsilon^\circ = 1.33 \text{ V}
\end{align*}
\]

Using the standard potentials at 25°C given above, determine the standard emf for each of the following cells.

(i) \[ \text{Ni} \left| \text{Ni}^{2+}(1\text{M}) \right| \left| \text{Br}^-(1\text{M}) \right| \left| \text{Br}_2(\text{g}) \right| \text{ Pt} \]  

(ii) \[ \text{Cr}^{3+}(1\text{M}) + \text{Cl}_2 \rightleftharpoons \text{Cr}_2\text{O}_7^{2-}(1\text{M}) + 7\text{H}_2\text{O}(l) \]  

(d) Sketch the galvanic cells based on the above reactions and identify the cathode and anode electrodes. Show the direction of electron flow.  

(e) For the oxidation-reduction reaction
\[ \text{S}_4\text{O}_6^{2-}(aq) + \text{Cr}^{3+}(aq) \rightleftharpoons \text{Cr}^{2+}(aq) + 2\text{SO}_3^{2-}(aq) \]
calculate

(i) \[ \varepsilon^\circ \] for the cell
(ii) the equilibrium constant \( K \) at 25°C

given the Nernst equation \[ \varepsilon = \varepsilon^\circ - 0.0592 \log Q \]

3. (a) Define the following terms:

(i) Allotropy  (ii) Enantiotropy

(b) Explain the difference between

(i) allotropy and isotropy.  (ii) polymorphs and allotropes.

(c) With the aid of a well labelled diagram derive the Bragg’s equation.

(d) X-rays from copper X-ray tube (\( \lambda = 1.54 \text{ Å} \)) were diffracted at an angle \( \theta = 19.5^\circ \) by a crystal silicon. Assuming first order diffraction (\( n = 1 \)) calculate the distance between the plane of atoms producing this diffraction in silicon.
4. (a) Define the following.  

(i) Order of reaction  

(ii) Molecularity  

(b) A gaseous reaction  

\[ 2 \text{A} + \text{B} \rightarrow \text{A}_2\text{B} \]  

\[ \text{A} + \text{B} \rightarrow \text{AB} \]  

\[ \text{AB} + \text{A} \rightarrow \text{A}_2\text{B} \]  

It was observed that when the concentration of B was kept constant while that of A doubled, the rate of reaction doubled. When the concentration of A was kept constant while the concentration of B tripled, the rate of reaction was tripled.

(i) Out of the two steps of reaction (1) and (2) above, which one is the rate determinant step?  

(ii) Write an expression representing the rate law for this gaseous reaction.  

(c) For the reaction between G and F the following initial rates were measured at 25°C.

<table>
<thead>
<tr>
<th>S/N</th>
<th>Initial rate (mol dm(^{-3}) s(^{-1}))</th>
<th>G (mol dm(^{-3}))</th>
<th>F (mol dm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>3.10 \times 10^{-3}</td>
<td>2.0</td>
<td>3.0</td>
</tr>
<tr>
<td>2.</td>
<td>7.75 \times 10^{-4}</td>
<td>1.0</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Calculate the overall order of reaction between G and F if the rate constant is 3.44 \times 10^{-4} dm\(^3\) mol\(^{-1}\) sec\(^{-1}\).  

SECTION B

Answer at least ONE (1) question from this section.

5. (a) What is meant by  

(i) resonance energy  

(ii) lattice energy  

(iii) disproportionation reaction  

(iv) inert pair effect?  

(4 marks)
(b) Complete and balance the following equations.

(i) \( \text{Li}_2\text{N}_3 + \text{HCl}_\text{aq} \rightarrow \)

(ii) \( \text{Rb}_2\text{O}_3 + \text{H}_2\text{O}_\text{aq} \rightarrow \)

(iii) \( \text{NaH}_4 + \text{H}_2\text{O}_\text{aq} \rightarrow \)

(iv) \( \text{Cs}_2\text{O}_{20} + \text{H}_2\text{O}_\text{aq} \rightarrow \)  

(6 marks)

(c) (i) Arrange the following ions in the order of decreasing size.

\[ \text{Br}^-, \text{Se}^{2-}, \text{Rb}^+ \text{ and } \text{Sr}^{2+} \]

(2 marks)

(iii) Arrange the following bonds according to polarity.

\[ \text{H} - \text{H}, \text{O} - \text{H}, \text{Cl} - \text{H}, \text{S} - \text{H} \text{ and } \text{F} - \text{H}. \]

(2 marks)

(c) The element magnesium (Mg) has three stable isotopes with the following masses and abundances.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Mass (amu)</th>
<th>Abundance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^{24}\text{Mg} )</td>
<td>23.9850</td>
<td>78.99</td>
</tr>
<tr>
<td>( ^{25}\text{Mg} )</td>
<td>24.9858</td>
<td>10.00</td>
</tr>
<tr>
<td>( ^{26}\text{Mg} )</td>
<td>25.9826</td>
<td>11.01</td>
</tr>
</tbody>
</table>

Calculate the average atomic mass of magnesium from this data. Give your answer to 2 decimal places.  

(6 marks)

6. (a) Comment, with the help of chemical equations where necessary, on the following concepts.

(i) Iron (II) chloride cannot be prepared by heating iron filings in a steam of chlorine gas.  

(2 marks)

(ii) Hydrochloric acid cannot be used as an acidic medium during redox titration of potassium permanganate against iron (II) sulphate.  

(2 marks)

(iii) Solid aluminium hydroxide is soluble in aqueous solution of sodium hydroxide.  

(2 marks)

(iv) When acidified potassium dichromate reacts with sodium chloride, green colouration is observed.  

(2 marks)

(b) Write down the electronic configuration of

(i) cobalt atom.  

(1 mark)

(ii) cobalt (III) ion.  

(1 mark)

(c) Use the configuration of the 3d electrons in cobalt (III) ions to explain why \([\text{CoF}_6]^{3-}\) is paramagnetic, while \([\text{Co(CN)}_6]^{3-}\) is not paramagnetic?  

(10 marks)
7. (a) (i) Define the term “melting point” of a substance. (3 marks)
(ii) State the modern periodic law. (3 marks)
(iii) What are the two factors that helped the classification of elements in the periodic table? (3 marks)

(b) Below is a table of elements of period 3 and their melting points.

<table>
<thead>
<tr>
<th>Element</th>
<th>Na</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point °C</td>
<td>98</td>
<td>650</td>
<td>660</td>
<td>1423</td>
<td>44</td>
<td>120</td>
<td>-101</td>
</tr>
</tbody>
</table>

Account for the following:

(i) The melting point of magnesium is very high compared to that of sodium. (2 marks)
(ii) Although aluminium is on the right handside, across period 3, its melting point is too close to that of magnesium. (3 marks)
(iii) Silicon has got the highest melting point of all elements in period 3. (2 marks)
(iv) The melting point of sulphur is higher than that of phosphorus. (2 marks)
(v) The melting point of chlorine is very low. (2 marks)

SECTION C
Answer at least ONE (1) question from this section.

8. (a) Using one appropriate example in each case explain what is meant by the following terms.

(i) Hoffmann’s degradation
(ii) Aööl condensation
(iii) Condensation polymer
(iv) Ortho and para director
(v) Electrophilic substitution. (10 marks)

(b) Show how the compound \( \text{H}_2\text{N} - \text{CHO} \) reacts with each of the following reagents.

(i) A cold mixture of sodium nitrite and concentrated hydrochloric acid.

(ii) 2, 4 - dinitrophenylhydrazine.

(iii) Excess mixture of sodium hydroxide and iodine.

(iv) Hydrogen cyanide followed by lithium aluminium hydride.

In each case you should give a balanced equation for the reaction and state the reaction condition(s) where necessary. (8 marks)

(c) What is the IUPAC name for the compound in (b) above? (2 marks)
9. (a) A phenolic acid C₆H₅O₃ (K) exists in two isomeric forms. Both rapidly decolourizes permanganate and on moderate oxidation yield salicylic and oxalic acids as the only organic products.

\[ K \xrightarrow{\text{oxidation}} \text{salicylic acid} + \text{oxalic acid} \]

One isomer of K easily loses water when heated, to yield C₆H₅O₂ while the other fails to dehydrate under the same conditions. Suggest structural formulae for the isomers. (7 marks)

(b) Give equations that illustrate a good method to synthesize each of the following acids.

(i) Butanoic acid from 1-butanol.
(ii) Butanoic acid from n-propyl alcohol (two ways).
(iii) Para-chlorobenzoic acid from para-chlorotoluene.
(iv) Cyclopentane carboxylic acid from cyclopentane. (10 marks)

(c) Name each of the following compounds.

(i) \[
\begin{array}{c}
\text{CO₂H} \\
\text{NO₂} \\
\end{array}
\]

(ii) \[
\begin{array}{c}
\text{CO₂H} \\
\end{array}
\]

(iii) \[
\begin{array}{c}
\text{CH₃} \\
\text{CH - CO₂H} \\
\text{C₆H₅} \\
\end{array}
\]

(3 marks)

10. 4.1 g of a bromoalkane was reacted with excess sodium hydroxide solution. The resulting solution was acidified with excess nitric acid and diluted to exactly 250 cm³. 25 cm³ of this solution required 33.28 cm³ of 0.1M silver nitrate solution for complete precipitation of silver bromide.

(a) Calculate the relative formula mass of the bromoalkane. (6 marks)

(b) From your answer to (a) deduce the molecular formula of the bromoalkane. (4 marks)

(c) Write the structural formulae of the possible isomers of the bromoalkane. (4 marks)

(d) Explain the difference in the reactivity of one of the bromoalkanes you have given in (c) and bromobenzene with sodium hydroxide. (6 marks)