1. Manganate(VII) ions react with ethanedioate ions in acidic solution.

\[2\text{MnO}_4^-(aq) + 16\text{H}^+(aq) + 5\text{C}_2\text{O}_4^{2-}(aq) \rightarrow 2\text{Mn}^{2+}(aq) + 8\text{H}_2\text{O}(l) + 10\text{CO}_2(g)\]

(a) In a particular experiment 200 cm\(^3\) of aqueous potassium manganate(VII), KMnO\(_4\), of concentration 0.0500 mol dm\(^{-3}\) were mixed with 50.0 cm\(^3\) of ethanedioic acid, HOOCC—COOH, of concentration 0.500 mol dm\(^{-3}\), and 80 cm\(^3\) of 1.0 mol dm\(^{-3}\) sulphuric acid.

(i) Show by calculation that the starting concentration of the manganate(VII) ions was 3.03 \times 10^{-2} mol dm\(^{-3}\).

(ii) The concentration of the manganate(VII) ions was determined over a period of time.

<table>
<thead>
<tr>
<th>Time / s</th>
<th>Concentration of manganate(VII) ions/ mol dm(^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.03 \times 10^{-2}</td>
</tr>
<tr>
<td>400</td>
<td>2.98 \times 10^{-2}</td>
</tr>
<tr>
<td>800</td>
<td>2.86 \times 10^{-2}</td>
</tr>
<tr>
<td>1200</td>
<td>2.75 \times 10^{-2}</td>
</tr>
<tr>
<td>1600</td>
<td>1.90 \times 10^{-2}</td>
</tr>
<tr>
<td>2000</td>
<td>7.50 \times 10^{-3}</td>
</tr>
<tr>
<td>2400</td>
<td>2.50 \times 10^{-3}</td>
</tr>
</tbody>
</table>

Plot a graph of the concentration of manganate(VII) ions against time and from it determine the initial rate of the reaction and the rate at 1600 s.
(b) A second experiment was set up involving the same chemicals in the same concentrations as in experiment 1 but this time some solid manganese(II) sulphate was dissolved in the ethanedioic acid before the potassium manganate (VII) solution was poured in. The plot of the concentration of manganate(VII) ions against time is given below:

(i) Determine the order of the reaction with respect to manganate(VII) ions by considering the time taken for the concentration to fall by half, using the concentrations at 0, 800 and 1600 s.

(ii) Compare this graph with the one you plotted in (a) (ii) and give two pieces of evidence that manganese(II) sulphate is a catalyst for this reaction.

(c) (i) Carrying out a flame test on potassium manganate(VII) gives a lilac flame. What does this show?

(ii) Describe how aqueous sodium hydroxide solution could be used to show that manganese(II) ions had been produced in the reaction between manganate (VII) ions and ethanedioate ions in acidic solution.

(Total 14 marks)
2. (a) An alcohol, $\text{C}_3\text{H}_8\text{O}$, was analysed by low resolution NMR spectroscopy. The spectrum is given below.

![NMR spectrum](image)

The chemical shifts of some hydrogen nuclei are given in the following table (where R represents an alkyl group).

<table>
<thead>
<tr>
<th>group</th>
<th>$\delta$ / ppm</th>
<th>group</th>
<th>$\delta$ / ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_3$–R</td>
<td>0.8–1.2</td>
<td>R–OH</td>
<td>1.0–6.0</td>
</tr>
<tr>
<td>R–$\text{CH}_2$–R</td>
<td>1.1–1.5</td>
<td>R–$\text{CH}_2$–OH</td>
<td>3.3–4.0</td>
</tr>
<tr>
<td>$\text{CH}$–R$_3$</td>
<td>1.5</td>
<td>R$_2$–$\text{CH}$–OH</td>
<td>3.2–4.1</td>
</tr>
</tbody>
</table>

Show that the alcohol must be propan-2-ol.

(b) By considering the shapes of the molecules of $\text{CH}_4$ and $\text{H}_2\text{O}$ explain why a molecule of propan-2-ol has bond angles of approximately $109^\circ$ except in the bond C–O–H where the angle is approximately $107^\circ$.

(c) Propan-2-ol can be oxidised by an aqueous solution of potassium dichromate(VI) acidified with dilute sulphuric acid. The two half-equations for the reactions involved are:

$$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+ (\text{aq}) + 6\text{e}^- \rightleftharpoons 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(l)$$

$$\text{C}_3\text{H}_6\text{O}(\text{aq}) + 2\text{H}^+ (\text{aq}) + 2\text{e}^- \rightleftharpoons \text{C}_3\text{H}_7\text{OH}(\text{aq})$$

(i) Oxidation of the alcohol takes place. Explain what this indicates about the standard electrode potentials of the two half reactions. Write the equation for the reaction.

(ii) An aqueous solution of chromium(III) ions is coloured. Explain the cause of this colour.
(iii) What would you see if the organic product of the oxidation reaction reacts with iodine in alkaline solution? Write the equation for the reaction. (3)

(d) (i) State the name of the organic product if propan-2-ol is heated with concentrated sulphuric acid and classify the type of reaction occurring. (2)

(ii) Draw the structural formula of the organic product that results from heating propan-2-ol with a mixture of sodium bromide and 50% sulphuric acid. (1)

(Total 18 marks)

3. (a) Magnesium sulphate is soluble in water whereas barium sulphate is almost insoluble. Draw an enthalpy level cycle for a Group 2 sulphate to show how the lattice enthalpy and enthalpy of hydration can be used to explain the difference in the solubilities of magnesium sulphate and barium sulphate. (4)

(b) Solid magnesium sulphate contains water of crystallisation, \( \text{MgSO}_4 \cdot x\text{H}_2\text{O} \). 1.23 g of magnesium sulphate crystals was dissolved in distilled water and excess barium nitrate solution was added. The white precipitate of barium sulphate was filtered off, dried and weighed. 1.16 g of anhydrous barium sulphate was formed. Calculate \( x \). (4)

(c) State how the thermal stability of magnesium carbonate differs from that of barium carbonate. Account for the difference in terms of the sizes and charges on the cations involved and their polarising power. (4)

(d) (i) Suggest which \( d \)-block element is most similar to magnesium. Give a reason for your choice. (3)

(ii) \( d \)-block elements and their compounds are often used in industry as catalysts. Give an example of an industrial process catalysed by a compound of \( d \)-block metal. Explain why \( d \)-block metal compounds have this ability whereas magnesium compounds do not. (3)

(Total 18 marks)
4. A compound \( \text{D}, \text{CH}_3\text{CH(OH)COOH} \), may be prepared from \( \text{C}_3\text{H}_7\text{OH} \) by the following series of reactions.

\[
\text{C}_3\text{H}_7\text{OH} \xrightarrow{\text{K}_2\text{Cr}_2\text{O}_7\text{(aq)}/\text{H}_2\text{SO}_4\text{(aq)}} \text{C}_2\text{H}_6\text{O}_2
\]

\[
\text{C}_3\text{H}_7\text{OH} \xrightarrow{(\text{i}) \text{NaOH(aq)}} \text{D} \xrightarrow{(\text{ii}) \text{HCl(aq)}} \text{C}_3\text{H}_5\text{O}_2\text{Cl}
\]

(a) (i) Identify compounds \( \text{A}, \text{B} \) and \( \text{C} \).

(ii) Classify the reaction with chlorine.

(iii) \( \text{D} \) has a boiling temperature of 186°C whereas \( \text{C}, \text{C}_3\text{H}_5\text{O}_2\text{Cl} \), boils at 122°C. Draw a boiling temperature/composition diagram applicable to a mixture of \( \text{C} \) and \( \text{D} \) and use it to show how fractional distillation of a mixture of the two compounds could produce a sample of \( \text{D} \).

(b) Assuming the percentage yield for each step in sequence to be 80%, calculate the mass of \( \text{D} \) that could be made from 60 g of \( \text{C}_3\text{H}_7\text{OH} \).

(c) An aqueous solution of \( \text{D} \) of concentration 0.100 mol dm\(^{-3}\) has a pH value of 2.04.

(i) Calculate the value of the dissociation constant, \( K_a \), for \( \text{D} \).

(ii) Suggest, with reasoning, whether \( \text{D} \) or propanoic acid, \( \text{CH}_3\text{CH}_2\text{COOH} \), \( K_a = 1.3 \times 10^{-5} \text{ mol dm}^{-3} \), would be more exothermic in reaction with aqueous sodium hydroxide solution of concentration 0.1 mol dm\(^{-3}\).