Centre Number						Candidate Number				
Surname										
Other Names										
Candidate Signature										

For Examiner's Use	
Examiner's Initials	
Question	Mark
1	
2	
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6	
7	
8	
TOTAL	



General Certificate of Education
Advanced Level Examination
June 2012

Chemistry CHEM5

Unit 5 Energetics, Redox and Inorganic Chemistry

Tuesday 19 June 2012 1.30 pm to 3.15 pm

For this paper you must have:
- the Periodic Table/Data Sheet provided as an insert (enclosed)
- a calculator.

Time allowed
- 1 hour 45 minutes

Instructions
- Use black ink or black ball-point pen.
- Fill in the boxes at the top of this page.
- Answer **all** questions.
- You must answer the questions in the spaces provided. Do not write outside the box around each page or on blank pages.
- All working must be shown.
- Do all rough work in this book. Cross through any work you do not want to be marked.

Information
- The marks for questions are shown in brackets.
- The maximum mark for this paper is 100.
- You are expected to use a calculator, where appropriate.
- The Periodic Table/Data Sheet is provided as an insert.
- Your answers to the questions in **Section B** should be written in continuous prose, where appropriate.
- You will be marked on your ability to:
  – use good English
  – organise information clearly
  – use accurate scientific terminology.

Advice
- You are advised to spend about 70 minutes on **Section A** and about 35 minutes on **Section B**.



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Section A

Answer **all** questions in the spaces provided.

1 White phosphorus (P_4) is a hazardous form of the element. It is stored under water.

1 (a) Suggest why white phosphorus is stored under water.

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(1 mark)

1 (b) Phosphorus(V) oxide is known as phosphorus pentoxide.
Suggest why it is usually represented by P_4O_{10} rather than by P_2O_5

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(1 mark)

1 (c) Explain why phosphorus(V) oxide has a higher melting point than sulfur(VI) oxide.

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(2 marks)

1 (d) Write an equation for the reaction of P_4O_{10} with water to form phosphoric(V) acid.
Give the approximate pH of the final solution.

Equation .....

pH .....

(2 marks)

Do not write outside the box

1 (e) A waste-water tank was contaminated by P_4O_{10}. The resulting phosphoric(V) acid solution was neutralised using an excess of magnesium oxide. The mixture produced was then disposed of in a lake.

1 (e) (i) Write an equation for the reaction between phosphoric(V) acid and magnesium oxide.

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(1 mark)

1 (e) (ii) Explain why an excess of magnesium oxide can be used for this neutralisation.

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(1 mark)

1 (e) (iii) Explain why the use of an excess of sodium hydroxide to neutralise the phosphoric(V) acid solution might lead to environmental problems in the lake.

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(1 mark)

9

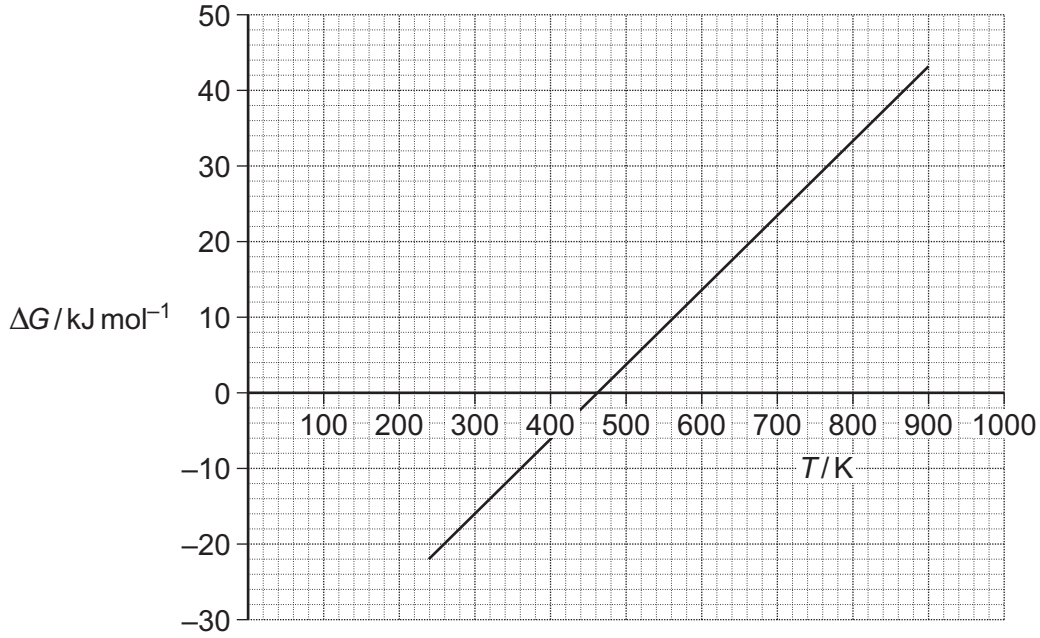
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2 The following equation shows the formation of ammonia.

$$\tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g) \longrightarrow NH_3(g)$$

The graph shows how the free-energy change for this reaction varies with temperature above 240 K.



2 (a) Write an equation to show the relationship between ΔG, ΔH and ΔS.

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(1 mark)

2 (b) Use the graph to calculate a value for the slope (gradient) of the line. Give the units of this slope and the symbol for the thermodynamic quantity that this slope represents.

Value of the slope .....

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Units .....

Symbol .....

(3 marks)

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2 (c) Explain the significance, for this reaction, of temperatures below the temperature value where the line crosses the temperature axis.

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(2 marks)

2 (d) The line is not drawn below a temperature of 240 K because its slope (gradient) changes at this point.

Suggest what happens to the ammonia at 240 K that causes the slope of the line to change.

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(1 mark)

7

Turn over for the next question

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3 Some thermodynamic data for fluorine and chlorine are shown in the table.
In the table, X represents the halogen F or Cl

	Fluorine	**Chlorine**
Electronegativity	4.0	3.0
Electron affinity / kJ mol^{-1}	–348	–364
Enthalpy of atomisation / kJ mol^{-1}	+79	+121
Enthalpy of hydration of $X^-(g)$ / kJ mol^{-1}	–506	–364

3 (a) Explain the meaning of the term *electron affinity*.

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(2 marks)

3 (b) Explain why the electronegativity of fluorine is greater than the electronegativity of chlorine.

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(2 marks)

(Extra space) .....

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3 (c) Explain why the hydration enthalpy of the fluoride ion is more negative than the hydration enthalpy of the chloride ion.

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(2 marks)

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3 (d) The enthalpy of solution for silver fluoride in water is $-20\ kJ\ mol^{-1}$.

The hydration enthalpy for silver ions is $-464\ kJ\ mol^{-1}$.

3 (d) (i) Use these data and data from the table to calculate a value for the lattice enthalpy of dissociation of silver fluoride.

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(3 marks)

3 (d) (ii) Suggest why the entropy change for dissolving silver fluoride in water has a positive value.

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(1 mark)

3 (d) (iii) Explain why the dissolving of silver fluoride in water is always a spontaneous process.

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(2 marks)

12

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4 The oxides nitrogen monoxide (NO) and nitrogen dioxide (NO_2) both contribute to atmospheric pollution.

The table gives some data for these oxides and for oxygen.

	$S^{\ominus}$ / J K^{-1} mol^{-1}	$\Delta H_f^{\ominus}$ / kJ mol^{-1}
$O_2(g)$	211	0
NO(g)	205	+90
$NO_2(g)$	240	+34

Nitrogen monoxide is formed in internal combustion engines. When nitrogen monoxide comes into contact with air, it reacts with oxygen to form nitrogen dioxide.

$$NO(g) + \tfrac{1}{2}O_2(g) \longrightarrow NO_2(g)$$

4 (a) Calculate the enthalpy change for this reaction.

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(2 marks)

4 (b) Calculate the entropy change for this reaction.

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(2 marks)

Do not write outside the box

4 (c) Calculate the temperature below which this reaction is spontaneous.

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(2 marks)

4 (d) Suggest **one** reason why nitrogen dioxide is **not** formed by this reaction in an internal combustion engine.

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(1 mark)

4 (e) Write an equation to show how nitrogen monoxide is formed in an internal combustion engine.

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(1 mark)

4 (f) Use your equation from part **(e)** to explain why the free-energy change for the reaction to form nitrogen monoxide stays approximately constant at different temperatures.

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(2 marks)

10

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5 The table shows some electrode half-equations and the associated standard electrode potentials.

Equation number	Electrode half-equation	$E^{\ominus}$/V
1	$Cd(OH)_2(s) + 2e^- \rightarrow Cd(s) + 2OH^-(aq)$	–0.88
2	$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	–0.76
3	$NiO(OH)(s) + H_2O(l) + e^- \rightarrow Ni(OH)_2(s) + OH^-(aq)$	+0.52
4	$MnO_2(s) + H_2O(l) + e^- \rightarrow MnO(OH)(s) + OH^-(aq)$	+0.74
5	$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$	+1.23

5 (a) In terms of electrons, state the meaning of the term *oxidising agent*.

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(1 mark)

5 (b) Deduce the identity of the weakest oxidising agent in the table.
Explain how $E^{\ominus}$ values can be used to make this deduction.

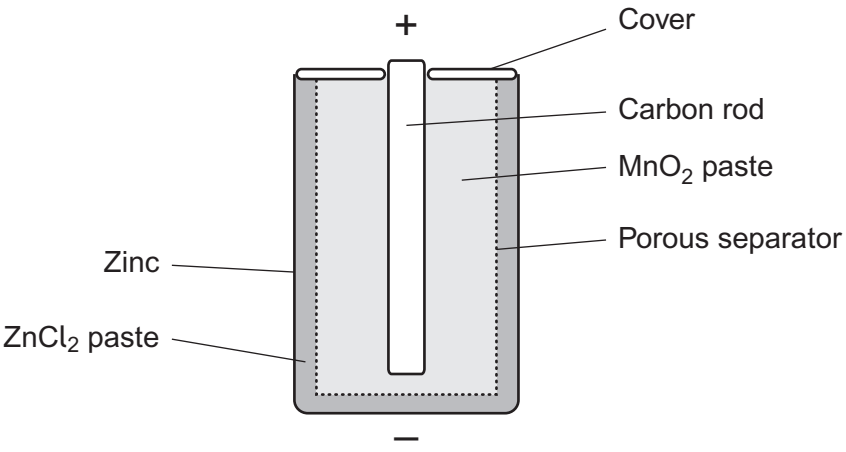
Weakest oxidising agent .....

Explanation .....

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(2 marks)

5 (c) The diagram shows a non-rechargeable cell that can be used to power electronic devices. The relevant half-equations for this cell are equations **2** and **4** in the table above.



Do not write outside the box

5 (c) (i) Calculate the e.m.f. of this cell.

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(1 mark)

5 (c) (ii) Write an equation for the overall reaction that occurs when the cell discharges.

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(1 mark)

5 (c) (iii) Deduce **one** essential property of the non-reactive porous separator labelled in the diagram.

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(1 mark)

5 (c) (iv) Suggest the function of the carbon rod in the cell.

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(1 mark)

5 (c) (v) The zinc electrode acts as a container for the cell and is protected from external damage. Suggest why a cell often leaks after being used for a long time.

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(1 mark)

Question 5 continues on the next page

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5 (d) A rechargeable nickel–cadmium cell is an alternative to the cell shown in part **(c)**. The relevant half-equations for this cell are equations **1** and **3** in the table on page 10.

5 (d) (i) Deduce the oxidation state of the nickel in this cell after recharging is complete. Write an equation for the overall reaction that occurs when the cell is **recharged**.

Oxidation state .....

Equation .....

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(3 marks)

5 (d) (ii) State **one** environmental advantage of this rechargeable cell compared with the non-rechargeable cell described in part **(c)**.

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(1 mark)

5 (e) An ethanol–oxygen fuel cell may be an alternative to a hydrogen–oxygen fuel cell. When the cell operates, all of the carbon atoms in the ethanol molecules are converted into carbon dioxide.

5 (e) (i) Deduce the equation for the overall reaction that occurs in the ethanol–oxygen fuel cell.

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(1 mark)

5 (e) (ii) Deduce a half-equation for the reaction at the ethanol electrode. In this half-equation, ethanol reacts with water to form carbon dioxide and hydrogen ions.

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(1 mark)

5 (e) (iii) The e.m.f. of an ethanol–oxygen fuel cell is 1.00 V. Use data from the table on page 10 to calculate a value for the electrode potential of the ethanol electrode.

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(1 mark)

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5 (e) (iv) Suggest why ethanol can be considered to be a carbon-neutral fuel.

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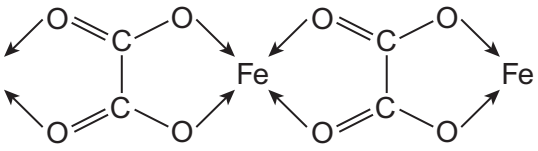
(2 marks)

17

Turn over for the next question

Do not write outside the box

6 Solid iron(II) ethanedioate dihydrate ($FeC_2O_4.2H_2O$) has a polymeric structure. Two repeating units in the polymer chain are shown.



Each iron ion is also bonded to two water molecules. These are **not** shown in the diagram.

6 (a) Name the type of bond that is represented by the arrows.

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(1 mark)

6 (b) In terms of electrons explain how the water molecules, **not** shown in the diagram, form bonds to the iron.

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(2 marks)

6 (c) Predict the value of the bond angle between the two bonds to iron that are formed by these two water molecules.

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(1 mark)

Do not write outside the box

6 (d) Iron(II) ethanedioate dihydrate can be analysed by titration using potassium manganate(VII) in acidic solution. In this reaction, manganate(VII) ions oxidise iron(II) ions and ethanedioate ions.

A 1.381 g sample of impure $FeC_2O_4.2H_2O$ was dissolved in an excess of dilute sulfuric acid and made up to 250 cm^3 of solution.
25.0 cm^3 of this solution decolourised 22.35 cm^3 of a 0.0193 mol dm^{-3} solution of potassium manganate(VII).

6 (d) (i) Use the half-equations given below to calculate the reacting ratio of moles of manganate(VII) ions to moles of iron(II) ethanedioate.

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$
$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$
$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$$

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(1 mark)

6 (d) (ii) Calculate the percentage by mass of $FeC_2O_4.2H_2O$ in the original sample.

(If you have been unable to answer part **(d) (i)** you may assume that three moles of manganate(VII) ions react with seven moles of iron(II) ethanedioate. This is **not** the correct ratio.)

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(5 marks)

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Section B

Answer **all** questions in the spaces provided.

7 You may find the following electrode potential data helpful when answering this question.

Electrode half-equation	$E^{\ominus}$/V
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	+1.33
$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$	+1.23
$Cr^{3+}(aq) + e^- \longrightarrow Cr^{2+}(aq)$	–0.44
$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	–0.76
$Cr^{2+}(aq) + 2e^- \longrightarrow Cr(s)$	–0.91

7 (a) Describe the colour changes that you would observe when an excess of zinc is added to an acidified solution of potassium dichromate(VI) in the absence of air.

For each colour change, identify the coloured ions responsible and write an equation for each reaction that occurs with zinc.
In the equations, you should represent the ions in their simplest form, for example Cr^{3+}

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7 (b) Describe what you would observe when dilute aqueous sodium hydroxide is added, dropwise until in excess, to a dilute aqueous solution containing chromium(III) ions.

Write **two** equations to illustrate your observations.
In these equations you should give the full formula of each of the complexes, for example $[Cr(H_2O)_6]^{3+}$

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7 (c) When an aqueous solution containing $[Cr(H_2O)_6]^{3+}$ ions is warmed in the presence of Cl^- ions, $[Cr(H_2O)_5Cl]^{2+}$ ions are formed and the colour of the solution changes.

Name this type of reaction.

Suggest, in terms of electrons, why the colours of the complex ions are different.

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(3 marks)

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Question 7 continues on the next page

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7 (d) The chromium(II) ion $[Cr(H_2O)_6]^{2+}$ has different properties from the $[Cr(H_2O)_6]^{3+}$ ion.

Use data from the table on page 16 to explain why, in an open container, $[Cr(H_2O)_6]^{2+}$(aq) ions change into $[Cr(H_2O)_6]^{3+}$(aq) ions.

Suggest the identity of the products formed in each case when sodium carbonate solution is added to separate solutions containing $[Cr(H_2O)_6]^{2+}$(aq) ions and $[Cr(H_2O)_6]^{3+}$(aq) ions.

Explain why the $[Cr(H_2O)_6]^{3+}$(aq) ions behave differently from the $[Cr(H_2O)_6]^{2+}$(aq) ions.

In your answer to this part of the question, equations are **not** required.

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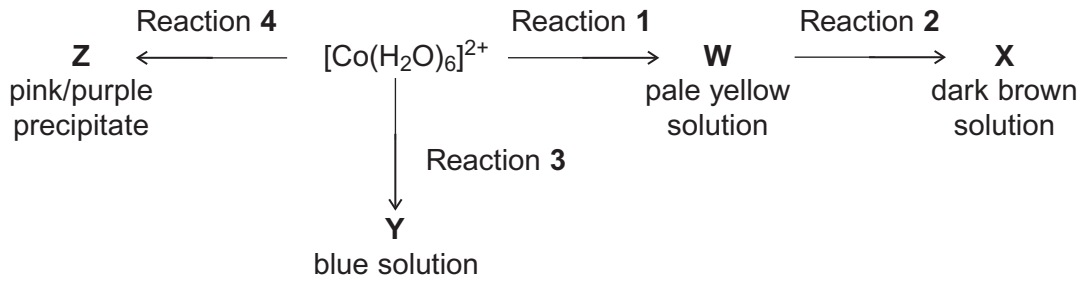
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19

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8 This question is about cobalt chemistry.

8 (a) Consider the following reaction scheme that starts from $[Co(H_2O)_6]^{2+}$ ions.
W, **X** and **Y** are ions and **Z** is a compound.



For each of the reactions **1** to **4**, identify a suitable reagent.

Identify **W**, **X**, **Y** and **Z** and write an equation for each of reactions **1** to **4**.

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Question 8 continues on the next page

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8 (b) A flue-gas desulfurisation process involves the oxidation, by oxygen, of aqueous sulfate(IV) ions (SO_3^{2-}) into aqueous sulfate(VI) ions (SO_4^{2-}). This reaction is catalysed by Co^{2+} ions in an acidic aqueous solution.

Write an equation for the overall reaction of sulfate(IV) ions with oxygen to form sulfate(VI) ions.

Suggest why this overall reaction is faster in the presence of Co^{2+} ions.

Suggest a mechanism for the catalysed reaction by writing **two** equations involving Co^{2+} and Co^{3+} ions. You will need to use H^+ ions and H_2O to balance these two equations.

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(4 marks)

16

END OF QUESTIONS

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