

AQA A-LEVEL CHEMISTRY • 7405

CHEMISTRY



EXAM QUESTION PACK

3.2.5 TRANSITION METALS

SCORE

/276

PERCENTAGE

%

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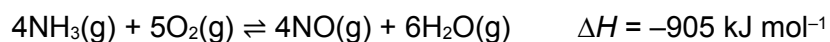
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Q1.

The equation for the reaction between ammonia and oxygen is shown.



Some standard entropies are given in the table.

Gas	$S^\circ / \text{J K}^{-1} \text{ mol}^{-1}$
$\text{NH}_3(\text{g})$	193
$\text{O}_2(\text{g})$	205
$\text{NO}(\text{g})$	211
$\text{H}_2\text{O}(\text{g})$	189

- (a) Calculate the entropy change for the reaction between ammonia and oxygen.

Entropy change _____ $\text{J K}^{-1} \text{ mol}^{-1}$

(2)

- (b) Calculate a value for the Gibbs free-energy change (ΔG), in kJ mol^{-1} , for the reaction between ammonia and oxygen at 600°C

(If you were unable to obtain an answer to part (a), you should assume that the entropy change is $211 \text{ J K}^{-1} \text{ mol}^{-1}$. This is not the correct answer.)

ΔG _____ kJ mol^{-1}

(2)

- (c) The reaction between ammonia and oxygen was carried out at a higher temperature.

Explain how this change affects the value of ΔG for the reaction.

(2)

- (d) Platinum acts as a heterogeneous catalyst in the reaction between ammonia and oxygen. It provides an alternative reaction route with a lower activation energy.

Describe the stages of this alternative route.

(3)

- (e) Deduce the change in oxidation state of nitrogen, when NH_3 is oxidised to NO

(1)

- (f) When ammonia reacts with oxygen, nitrous oxide (N_2O) can be produced instead of NO

Give an equation for this reaction.

(1)

(Total 11 marks)

Q2.

This question is about vanadium compounds and ions.

- (a) Use data from Table 4 to identify the species that can be used to reduce VO_2^+ ions to VO^{2+} in aqueous solution and no further.

Explain your answer.

Electrode half-equation	$E^\ominus / \text{V}$
$\text{VO}_2^+(\text{aq}) + 2\text{H}^+(\text{aq}) + \text{e}^- \rightarrow \text{VO}^{2+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$	+1.00
$\text{VO}^{2+}(\text{aq}) + 2\text{H}^+(\text{aq}) + \text{e}^- \rightarrow \text{V}^{3+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$	+0.34
$\text{Cl}_2(\text{aq}) + 2\text{e}^- \rightarrow 2\text{Cl}^-(\text{aq})$	+1.36
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Fe}^{2+}(\text{aq})$	+0.77
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$	-0.76

Reagent _____

Justification _____

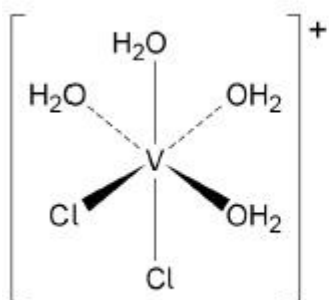
(2)

- (b) Give the oxidation state of vanadium in $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$

(1)

- (c) The $[\text{V}(\text{H}_2\text{O})_4\text{Cl}_2]^+$ ion exists as two isomers. One isomer is shown.

Draw the structure of the other isomer and state the type of isomerism.



Type of isomerism _____

(2)

- (d) Heating NH_4VO_3 produces vanadium(V) oxide, water and one other product.

Give an equation for the reaction.

(1)

- (e) Vanadium(V) oxide is the catalyst used in the manufacture of sulfur trioxide.

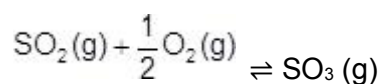
Give **two** equations to show how the catalyst is used and regenerated.

(1)

(Total 7 marks)

Q3.

An oxide of vanadium catalyses the following reaction:



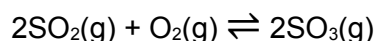
What is the formula of the vanadium-containing intermediate formed in this reaction?

- A** V_2O ☐
- B** VO ☐
- C** V_2O_3 ☐
- D** V_2O_4 ☐

(Total 1 mark)

Q4.

In the Contact Process sulfur dioxide reacts with oxygen to form sulfur trioxide as shown in the equation.



The table shows some thermodynamic data.

	$\Delta H_f^\circ / \text{kJ mol}^{-1}$	$S^\circ / \text{J K}^{-1} \text{mol}^{-1}$
$\text{SO}_2(\text{g})$	-297	248
$\text{O}_2(\text{g})$	0	205
$\text{SO}_3(\text{g})$	-395	256

- (a) Use data from the table to calculate the standard enthalpy change for this reaction.

-
- (2)
- (b) Use data from the table to calculate the standard entropy change for this reaction.
-
-
-
-
- (2)
- (c) State what the sign of the entropy change in your answer to part (b) indicates about the product of this reaction relative to the reactants.
-
- (1)
- (d) Use your answers to parts (a) and (b) to calculate a value for the free-energy change for this reaction at 50°C.
- (If you were unable to calculate ΔH in part (a) assume a value of -250 kJ mol^{-1} .
If you were unable to calculate ΔS in part (b) assume a value of $-250 \text{ J K}^{-1} \text{ mol}^{-1}$.
These are not the correct values.)
-
-
-
-
-
-
- (3)
- (e) Use your answer to part (d) to explain whether the reaction is feasible at 50°C.
-
-
- (1)
- (f) Vanadium(V) oxide acts as a heterogeneous catalyst in the Contact Process.
- (i) State what is meant by the term heterogeneous.
-
- (1)
- (ii) Write **two** equations that show how this catalyst is involved in the Contact Process.

(2)

- (iii) Suggest why the vanadium(V) oxide is used in small pellet form rather than as large lumps.

(1)

- (iv) State why the reactants should be purified before they come into contact with the vanadium(V) oxide.

(1)

(Total 14 marks)

Q5.

A student weighed out a 2.29 g sample of impure $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ and dissolved it in water.

This solution was added to a 250 cm^3 volumetric flask and made up to 250 cm^3 with distilled water.

A 25.0 cm^3 portion was pipetted into a conical flask and an excess of acid was added. The mixture was heated to 60°C and titrated with $0.0200 \text{ mol dm}^{-3}$ KMnO_4 solution. 26.40 cm^3 of KMnO_4 solution were needed for a complete reaction.

In this titration only the $\text{C}_2\text{O}_4^{2-}$ ions react with the KMnO_4 solution.

- (a) The reaction between $\text{C}_2\text{O}_4^{2-}$ ions and MnO_4^- ions is autocatalysed.

Explain what is meant by the term autocatalysed and identify the catalyst in the reaction.

(2)

- (b) Select from the list the most suitable substance used to acidify the solution in the conical flask.

Put a tick (✓) in the correct box.

$\text{H}_2\text{C}_2\text{O}_4$

☐

H₂SO₄ ☐

HCl ☐

HNO₃ ☐

(1)

- (c) The reaction between C₂O₄²⁻ ions and MnO₄⁻ ions is very slow at first.
Explain why the reaction is initially slow.

(3)

- (d) Write an equation for the reaction between C₂O₄²⁻ ions and MnO₄⁻ ions in acidic solution.
Calculate the percentage purity of the original sample of K₃[Fe(C₂O₄)₃].3H₂O.
Give your answer to 3 significant figures.

(7)

- (e) A solution of KMnO_4 has an unknown concentration.

Describe briefly how colorimetry can be used to determine the concentration of this solution.

(3)

(Total 16 marks)

Q6.

The redox reaction, in aqueous solution, between acidified potassium manganate(VII) and sodium ethanedioate is autocatalysed.

- (a) Write an equation for this redox reaction.

Identify the species that acts as the catalyst.

Explain how the properties of the species enable it to act as a catalyst in this reaction.

(6)

- (b) Sketch a graph to show how the concentration of MnO_4^- ions varies with time in this reaction.
Explain the shape of the graph.

(4)

(Total 10 marks)

Q7.

When iodine molecules are dissolved in aqueous solutions containing iodide ions, they react to form triiodide ions (I_3^-).



The reaction above between I^- ions and $\text{S}_2\text{O}_8^{2-}$ ions has a high activation energy and $\text{S}_2\text{O}_8^{2-}$ ions are only reduced slowly to SO_4^{2-} ions. The reaction is catalysed by Fe^{2+} ions.

- (a) Explain why the reaction between I^- ions and $\text{S}_2\text{O}_8^{2-}$ ions is slow.

(1)

- (b) Other than having variable oxidation states, explain why Fe^{2+} ions are good catalysts for this reaction.

(1)

- (c) Write a half-equation for the reduction of $\text{S}_2\text{O}_8^{2-}$ ions to SO_4^{2-} ions.

(1)

- (d) Construct an overall equation for the reaction between $\text{S}_2\text{O}_8^{2-}$ ions and I^- ions.

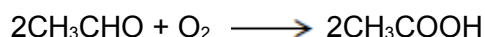
(1)

(Total 4 marks)

Q8.

This question explores some reactions and some uses of cobalt compounds.

- (a) Ethanal is oxidised to ethanoic acid by oxygen. The equation for this reaction is



This redox reaction is slow at room temperature but speeds up in the presence of cobalt compounds.

Explain why a cobalt compound is able to act as a catalyst for this process.

Illustrate your explanation with **two** equations to suggest how, in the presence of water and hydrogen ions, Co^{3+} and then Co^{2+} ions could be involved in catalysing this reaction.

(4)

- (b) In aqueous solution, the $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ion reacts with an excess of ethane-1,2-diamine to form the complex ion **Y**.

- (i) Write an equation for this reaction.

Explain, in terms of the chelate effect, why the complex ion **Y** is formed in preference to the $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ complex ion.

(3)

- (ii) Draw a diagram that shows the shape of the complex ion **Y** and shows the type of bond between the ethane-1,2-diamine molecules and the cobalt.

(3)

- (c) Compound **Z** is a complex that contains only cobalt, nitrogen, hydrogen and chlorine.

A solid sample of **Z** was prepared by reaction of 50 cm³ of 0.203 mol dm⁻³ aqueous cobalt(II) chloride with ammonia and an oxidising agent followed by hydrochloric acid.

When this sample of **Z** was reacted with an excess of silver nitrate, 4.22 g of silver chloride were obtained.

Use this information to calculate the mole ratio of chloride ions to cobalt ions in **Z**.

Give the formula of the complex cobalt compound **Z** that you would expect to be formed in the preparation described above.

Suggest **one** reason why the mole ratio of chloride ions to cobalt ions that you have calculated is different from the expected value.

(5)
(Total 15 marks)

Q9.

An equation for the decomposition of hydrogen peroxide is



- (a) The rate of reaction can be determined by collecting the oxygen formed and measuring its volume at regular intervals.

Draw a diagram to show the apparatus that you would use to collect and measure the volume of the oxygen formed.

(2)

- (b) Explain how you could use your results from the experiment in part (a) to determine the initial rate of this reaction.

(2)

- (c) The rate of decomposition of hydrogen peroxide is increased by the addition of cobalt(II) ions.

Outline the essential features of an additional experiment to show that the rate of decomposition is increased by the addition of cobalt(II) chloride. Use the same method and the same apparatus as in part (a).

(2)

(Total 6 marks)

Q10.

Transition metal compounds have a range of applications as catalysts.

- (a) State the general property of transition metals that allows the vanadium in vanadium(V) oxide to act as a catalyst in the Contact Process.

(1)

- (b) Write **two** equations to show how vanadium(V) oxide acts as a catalyst in the Contact Process.

Equation 1

Equation 2

(2)

- (c) In the Contact Process, vanadium(V) oxide acts as a heterogeneous catalyst.

- (i) Give the meaning of the term *heterogeneous*.

(1)

- (ii) Give **one** reason why impurities in the reactants can cause problems in processes that use heterogeneous catalysts.

(1)

- (d) The oxidation of $\text{C}_2\text{O}_4^{2-}$ ions by MnO_4^- ions in acidic solution is an example of a reaction that is autocatalysed.

- (i) Give the meaning of the term *autocatalysed*.

(1)

- (ii) Identify the autocatalyst in this reaction.

(1)

- (iii) Write **two** equations to show how the autocatalyst is involved in this oxidation of $\text{C}_2\text{O}_4^{2-}$ ions.

Equation 1

Equation 2

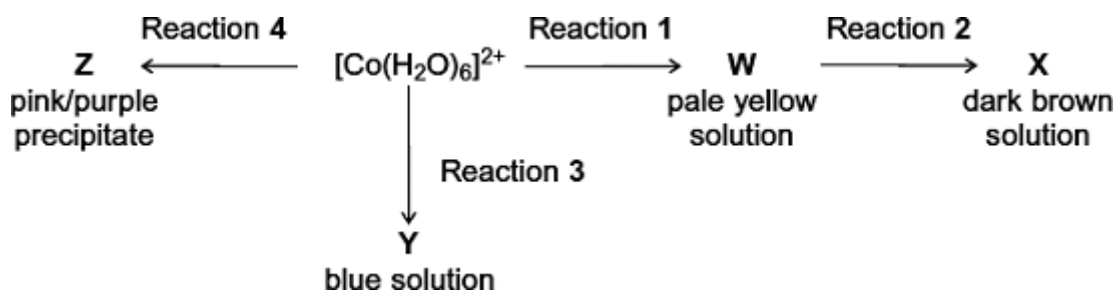
(2)

(Total 9 marks)

Q11.

This question is about cobalt chemistry.

- (a) Consider the following reaction scheme that starts from $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ 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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(12)

- (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.

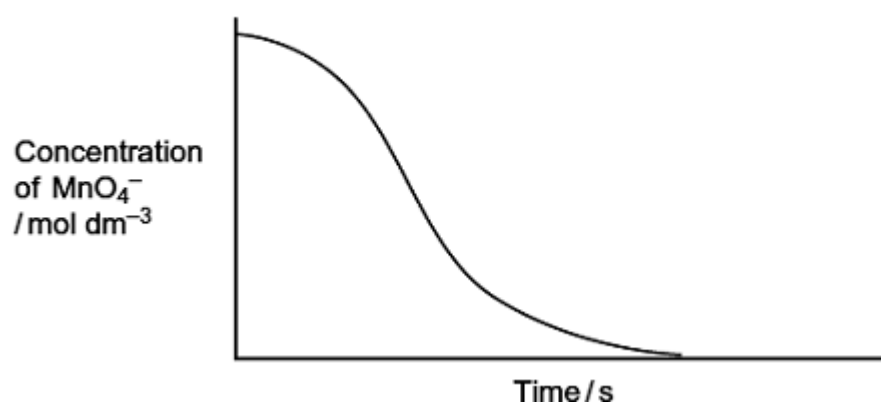
Suggest a mechanism for the catalysed reaction by writing **two** equations involving Co^{2+} and Co^{3+} ions. You will need to use H^+ ions and H_2O to balance these two equations.

(4)
(Total 16 marks)

Q12.

An acidified solution of potassium manganate(VII) was reacted with a sample of sodium ethanedioate at a constant temperature of 60 °C. The concentration of the manganate(VII) ions in the reaction mixture was determined at different times using a spectrometer to measure the light absorbed.

The following results were obtained.



- (a) Write an equation for the reaction between manganate(VII) ions and ethanedioate ions in acidic solution.

(2)

- (b) By considering the properties of the reactants and products, state why it is possible to use a spectrometer to measure the concentration of the manganate(VII) ions in this reaction mixture.

(2)

- (c) This reaction is autocatalysed. Give the meaning of the term *autocatalyst*. Explain how the above curve indicates clearly that the reaction is autocatalysed.

Meaning of *autocatalyst* _____

Explanation _____

(3)

- (d) Identify the autocatalyst in this reaction.

(1)

- (e) Write **two** equations to show how the autocatalyst is involved in this reaction.

Equation 1 _____

Equation 2 _____

(2)

(Total 10 marks)

Q13.

Iron is an important element in living systems. It is involved in redox and in acid–base reactions.

- (a) Explain how and why iron ions catalyse the reaction between iodide ions and $\text{S}_2\text{O}_8^{2-}$ ions. Write equations for the reactions that occur.

(5)

- (b) Iron(II) compounds are used as moss killers because iron(II) ions are oxidised in air to form iron(III) ions that lower the pH of soil.

-
-
-
-
-

(ii) In a titration, 0.321 g of a moss killer reacted with 23.60 cm³ of acidified 0.0218 mol dm⁻³ K₂Cr₂O₇ solution.

[illegible]

(3)
(Total 16 marks)

Q14.

Three characteristic properties of transition metals are complex formation, coloured ions and catalytic activity.

- (a) State the feature of transition metals that gives rise to these characteristic properties.

(1)

- (b) State a fourth characteristic property of transition metals.

(1)

- (c) For each of the following shapes of complex, identify an appropriate example by drawing its structure.

- (i) a linear complex

(1)

- (ii) a square planar complex

(1)

- (iii) a tetrahedral complex

(1)

- (d) The chemical industry makes use of the catalytic activity of transition metal compounds. For example, vanadium(V) oxide is used as a heterogeneous catalyst in the Contact Process.

(i) Write an equation for the overall reaction in the Contact Process.

_____ (1)

(ii) Explain the meaning of the term *heterogeneous* as applied to a catalyst.

_____ (1)

(iii) Write two equations to illustrate how vanadium(V) oxide acts as a catalyst in the Contact Process.

Equation 1 _____

Equation 2 _____

(2)

(iv) Suggest what is done to a heterogeneous catalyst such as vanadium(V) oxide to maximise its efficiency and how this is achieved.

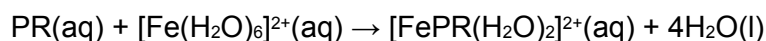
_____ (2)

- (e) The porphyrin ring is a multidentate ligand that is found in living systems complexed with iron(II) ions in haemoglobin and with cobalt(II) ions in vitamin B₁₂

(i) Give the meaning of the term *multidentate*.

_____ (1)

(ii) A porphyrin ring can be represented by the symbol PR. It reacts with aqueous iron(II) ions as shown in the equation below.
The enthalpy change for this reaction is approximately zero.



Explain why the free-energy change for this reaction is negative.

(2)

- (iii) In vitamin B₁₂ the cobalt(II) ion is co-ordinated to a porphyrin ring, a cyanide (CN⁻) ion and an additional unidentate ligand. The cyanide ion is very toxic.

Predict the co-ordination number of the cobalt ion in vitamin B₁₂
Suggest why vitamin B₁₂ is **not** toxic.

Co-ordination number _____

Reason why vitamin B₁₂ is **not** toxic

(2)

(Total 16 marks)

Q15.

Transition metal ions can act as homogeneous catalysts in redox reactions. For example, iron(II) ions catalyse the reaction between peroxodisulfate (S₂O₈²⁻) ions and iodide ions.

- (a) State the meaning of the term *homogeneous*.

(1)

- (b) Suggest why ions from s block elements do **not** usually act as catalysts.

(1)

- (c) Write an equation for the overall reaction that occurs, in aqueous solution, between S₂O₈²⁻ ions and I⁻ ions.

(1)

- (d) Give **one** reason why, in the absence of a catalyst, the activation energy for the reaction between S₂O₈²⁻ ions and I⁻ ions is high.

(1)

- (e) Write two equations to show how Fe²⁺ ions can catalyse the reaction between S₂O₈²⁻ ions and I⁻ ions. Suggest **one** reason why the activation energy for each of these reactions is low.

Equation 1 _____

Equation 2 _____

Reason _____

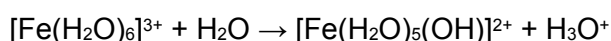
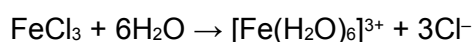
(3)

- (f) Explain why Fe^{3+} ions are as effective as Fe^{2+} ions in catalysing this reaction.

(1)
(Total 8 marks)

Q16.

When anhydrous iron(III) chloride is added to water the following reactions occur.



- (a) State the type of acidity shown by FeCl_3 and by $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ in these reactions. Explain your answers.

(4)

- (b) Explain why the pH of a solution of iron(II) chloride is higher than that of a solution of iron(III) chloride of the same concentration.

(2)

- (c) Transition metals have variable oxidation states. This is an important factor in their ability to act as heterogeneous and homogeneous catalysts.

- (i) Vanadium(V) oxide acts as a heterogeneous catalyst in the Contact Process.

Write equations to show the role of vanadium(V) oxide in this process.

(2)

- (ii) In aqueous solution, Fe^{2+} ions act as a homogeneous catalyst in the reaction between I^- and $\text{S}_2\text{O}_8^{2-}$ ions. Give one reason why the reaction is slow in the absence of a catalyst. Write equations to show how Fe^{2+} ions act as a catalyst for this reaction.

(5)

(Total 13 marks)

Q17.

This question is about the use of transition metals as catalysts.

- (a) State how a catalyst speeds up a chemical reaction.

(2)

- (b) State the characteristic property of transition metals that enables them to act as catalysts in redox reactions.

(1)

- (c) In the Contact Process for the conversion of sulfur dioxide into sulfur trioxide, vanadium(V) oxide acts as a heterogeneous catalyst.

- (i) Write **two** equations to show how the catalyst is involved in this reaction.

Equation 1 _____

Equation 2 _____

(2)

- (ii) Suggest **one** reason why poisoning reduces the effectiveness of a heterogeneous catalyst.

(1)

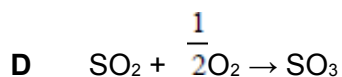
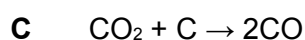
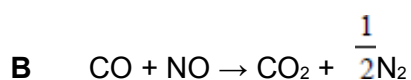
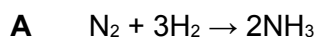
- (iii) Suggest how poisoning of a catalyst, used in an industrial process, can be minimised.

(1)

(Total 7 marks)

Q18.

In which one of the following reactions is a heterogeneous catalyst **not** used?



(Total 1 mark)

Q19.

- (a) State and explain the effect of a catalyst on the rate and on the equilibrium yield in a reversible reaction.

(5)

- (b) Explain the terms *heterogeneous* and *active sites* as applied to a catalyst. Give **two** reasons why a ceramic support is used for the catalyst in catalytic converters in cars. Explain how lead poisons this catalyst.

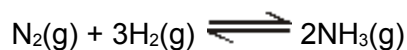
(7)

- (c) In aqueous solution, Fe^{2+} ions act as a homogeneous catalyst in the reaction between I^- and $\text{S}_2\text{O}_8^{2-}$ ions. Give **one** reason why the reaction is slow in the absence of a catalyst. Write equations to show how Fe^{2+} ions act as a catalyst for this reaction.

(5)
(Total 17 marks)

Q20.

- (a) In the Haber Process for the manufacture of ammonia, the following equilibrium is established in the presence of a heterogeneous catalyst.



Identify the heterogeneous catalyst used in this process and state what is meant by the term *heterogeneous*.

A heterogeneous catalyst can become poisoned by impurities in the reactants. Give one substance which poisons the heterogeneous catalyst used in the Haber Process and explain how this substance poisons the catalyst.

(5)

- (b) State what is observed when an excess of aqueous ammonia reacts with an aqueous iron(II) salt. Write an equation for this reaction.

Q21.

- (a) State what is meant by the term *homogeneous* as applied to a catalyst.

(1)

- (b) (i) State what is meant by the term *autocatalysis*.

- (ii) Identify the species which acts as an autocatalyst in the reaction between ethanedioate ions and manganate(VII) ions in acidic solution.

(2)

- (c) When petrol is burned in a car engine, carbon monoxide, carbon dioxide, oxides of nitrogen and water are produced. Catalytic converters are used as part of car exhaust systems so that the emission of toxic gases is greatly reduced.

- (i) Write an equation for a reaction which occurs in a catalytic converter between two of the toxic gases. Identify the reducing agent in this reaction.

Equation _____

Reducing agent _____

- (ii) Identify a transition metal used in catalytic converters and state how the converter is constructed to maximise the effect of the catalyst.

Transition metal _____

How effect is maximised _____

(5)

- (d) The strength of the adsorption of reactants and products onto the surface of a transition metal helps to determine its activity as a heterogeneous catalyst.

- (i) Explain why transition metals which adsorb strongly are not usually good catalysts.

- (ii) Explain why transition metals which adsorb weakly are not usually good catalysts.

(Total 10 marks)

Q22.

- (a) Vanadium(V) oxide is used as a heterogeneous catalyst in the Contact Process.

Explain what is meant by the terms *heterogeneous* and *catalyst* and state, in general terms, how a catalyst works.

State the essential feature of vanadium chemistry which enables vanadium(V) oxide to function as a catalyst and, by means of equations, suggest how it might be involved in the Contact Process.

[illegible]

(7)

- (b) The following method was used to determine the percentage by mass of vanadium in a sample of ammonium vanadate(V).

A solution was made up by dissolving 0.160 g of ammonium vanadate(V) in dilute sulphuric acid. The ammonium vanadate(V) formed VO_2^+ ions in this solution. When an excess of zinc was added to this solution, the VO_2^+ ions were reduced to V^{2+} ions and the zinc was oxidised to Zn^{2+} ions.

After the unreacted zinc had been removed, the solution was titrated against a $0.0200 \text{ mol dm}^{-3}$ solution of potassium manganate(VII). In the titration, 38.5 cm^3 of

Using half-equations, construct an overall equation for the reduction of VO_2^+ to V^{2+} by zinc in acidic solution.

This image shows a blank sheet of white paper with horizontal ruling lines. The lines are evenly spaced and extend across the width of the page. There are no margins, text, or other markings on the paper.

(Total 15 marks)

(a) The ion $\text{C}_2\text{O}_4^{2-}$ can act as a bidentate ligand.

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(5)

- (b) Explain the meaning of the term *chelate effect*.

(2)

- (c) The chloride ion can act as a monodentate ligand.

- (i) Deduce the formula of the linear complex formed when an excess of concentrated hydrochloric acid is added to silver chloride.

- (ii) Explain why metal(II) ions do not usually form octahedral complexes when chloride ions are the only ligands.

(2)

- (d) The concentration of $\text{C}_2\text{O}_4^{2-}$ ions can be determined by titration in acidic solution using a standard solution of potassium manganate(VII). At room temperature, the reaction proceeds very slowly at first but becomes faster after some of the manganate(VII) ions have reacted.

- (i) Suggest why this reaction is very slow at first.

- (ii) This is an example of an autocatalytic reaction. State the meaning of the term *autocatalytic* and identify the catalyst.

Meaning of the term *autocatalytic* _____

Catalyst _____

- (iii) Suggest how this catalyst might be involved in the reaction.

(5)

Q24.

- (a) "The strength of adsorption onto the active sites on the surface of a heterogeneous catalyst helps to determine the activity of the catalyst."

Explain how heterogeneous catalysts work, give **one** example of a reaction catalysed in this way and discuss why different catalysts have different activities.

(8)

- (b) Outline a plan of an experiment to determine the percentage of iron present as iron(III) in a solution containing $\text{Fe}^{3+}(\text{aq})$ and $\text{Fe}^{2+}(\text{aq})$ ions. You are provided with zinc, a standard solution of potassium dichromate(VI) and dilute sulphuric acid. Zinc can reduce $\text{Fe}^{3+}(\text{aq})$ to $\text{Fe}^{2+}(\text{aq})$.

Write equations for all the reactions that occur. Explain how you would use the zinc and how you would calculate the final answer.

(7)
(Total 15 marks)

(a) The reaction between aqueous persulphate ions, $\text{S}_2\text{O}_8^{2-}(\text{aq})$, and iodide ions, $\text{I}^-(\text{aq})$, is catalysed by $\text{Fe}^{2+}(\text{aq})$ ions. Suggest why this reaction has a high activation energy.
Write equations to explain the catalytic action of $\text{Fe}^{2+}(\text{aq})$ ions.
Suggest why $\text{V}^{3+}(\text{aq})$ ions will also act as a catalyst for this reaction but $\text{Mg}^{2+}(\text{aq})$ ions will not.

(6)

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[illegible]

(Total 15 marks)

Summarised directions for recording responses to multiple completion questions			
A (i), (ii) and (iii) only	B (i) and (iii) only	C (ii) and (iv) only	D (iv) alone

(i) It speeds up the forward reaction and slows down the reverse action.

- (iii) It increases the proportion of molecules with higher energies.
- (iii) A homogeneous catalyst usually acts in the solid state.
- (iv) It does not alter the value of the equilibrium constant.

(Total 1 mark)

Mark schemes

Q1.

(a) $(\Delta S = \Sigma(S_{\text{products}}) - \Sigma(S_{\text{reactants}}))$
 $= [(4 \times 211) + (6 \times 189)] - [(4 \times 193) + (5 \times 205)] = (1978 - 1797)$

1

181 (J K⁻¹ mol⁻¹)

1

(b) $(\Delta G = \Delta H - T\Delta S) = -905 - (600 + 273) \times 181 \times 10^{-3}$
If answer to (a) is incorrect, mark consequentially:
 $-905 - (873 \times (a) \times 10^{-3})$

1

$\Delta G = -1063 / -1060$ (kJ mol⁻¹)

If alternative value of $\Delta S = 211$ used, answer = -1089 (kJ mol⁻¹)

1

(c) ΔG becomes more negative/less positive
Ignore increase/decrease/larger/smaller ΔG

1

The entropy change / ΔS is positive / $T\Delta S$ gets bigger / $-T\Delta S$ gets more negative.

Consequential on wrong (a)

If candidate does a calculation in (a) to produce ΔS negative then allow ΔG becomes less negative or more positive

1

(d) Reactant(s) adsorbed onto the (platinum surface) / (platinum) provides a surface / active sites

1

Reaction (on the surface) or bond breaking(weakening) / bond making occurs (on the surface)

1

Desorption (of the product) or wtte

1

(e) (Oxidation state changes from) -3 to +2 OR (+) 5

1

(f) $2\text{NH}_3 + 2\text{O}_2 \rightarrow \text{N}_2\text{O} + 3\text{H}_2\text{O}$
Allow multiples
Ignore state symbols

1

[11]

Q2.

(a) Fe²⁺

Accept any Fe(II) compound – correct formula or name

1

$$E^\ominus \text{VO}_2^+(/ \text{VO}^{2+}) > E^\ominus \text{Fe}^{3+}(/ \text{Fe}^{2+}) > E^\ominus \text{VO}^{2+}(/ \text{V}^{3+})$$

If calculations of EMF are provided producing EMFs = 0.23(V) and -0.43(V), with a comment, allow M2

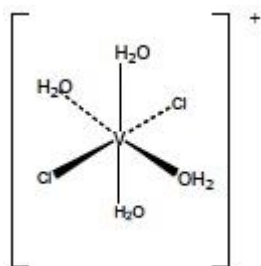
allow $E^\ominus \text{Fe}^{3+}(/ \text{Fe}^{2+})$ value of +0.77 is between the $E^\ominus$ values for the electrode half-equations containing the V species or wtte

1

(b) (+) 4

IV or four

1



(c)

Ignore absence of charge

Wedges, dotted lines and [] not required

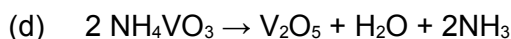
Do not penalise bond from H to V (in water ligands)

1

Cis/trans

allow E/Z, geometric and stereo(isomerism)

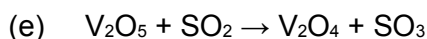
1



Accept multiples

Ignore state symbols

1



Both equations needed for 1 mark in this order

Allow multiples

1

[7]

Q3.

D

[1]

Q4.

(a) $\Delta H^\ominus = \sum \Delta H_f^\ominus \text{ products} - \sum \Delta H_f^\ominus \text{ reactants}$

1

or $(2 \times -395) - (2 \times -297)$

$$= -196 \text{ (kJ mol}^{-1}\text{)}$$

Penalise incorrect units, ignore missing units

1

(b) $\Delta S^\ominus = \Sigma S^\ominus \text{ products} - \Sigma S^\ominus \text{ reactants}$

1

$$= (2 \times 256) - 205 - (2 \times 248)$$

$$= -189 \text{ JK}^{-1} \text{ mol}^{-1}$$

Allow -0.189 kJ K⁻¹ mol⁻¹

Units must be given and must match value

1

(c) Causes an increase in order / a decrease in disorder

Allow products more ordered / products less disordered

If answer to (b) is +ve, allow products are less ordered / causes an increase in disorder / causes a decrease in order

1

(d) $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$

Do not insist on standard state symbol

1

$$= -196 - 323 (-189/1000)$$

If conversion of T or ΔS incorrect, then can only score M1

1

$$= -134.9 \text{ kJ mol}^{-1}$$

Must have correct units

Allow answers in J mol⁻¹

-135 kJ mol⁻¹

If both alternative values used then -169(.3) kJ mol⁻¹

Allow alternative ΔH and/or alternative ΔS in calculation

1

(e) Feasible because ΔG is negative

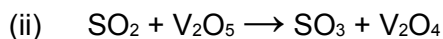
Allow mark if a correct deduction from answer to (d)

Both a reference to feasibility and to ΔG needed

1

(f) (i) (The catalyst is in) a different state or phase (from the reactants)

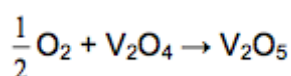
1



Allow 2VO₂ instead of V₂O₄

Allow multiples

1



Must have equations in this order

1

(iii) Surface area is increased

1

(iv) So that the catalyst is not poisoned

Allow correct reference to the blocking active sites

1

[14]

Q5.

(a) A reaction that produces its own catalyst/ one of the products is the catalyst

1

Mn^{2+}

Allow Mn^{3+}

1

(b) H_2SO_4

1

(c) There is no/very little catalyst at the start OR the reaction only speeds up when the catalyst is produced

1

Two negative ions (MnO_4^- and $\text{C}_2\text{O}_4^{2-}$) repel

Reference to molecules loses M2

1

The activation energy for the reaction is high / heat is required to overcome the activation energy

1

(d) M1 $5 \text{C}_2\text{O}_4^{2-}(\text{aq}) + 2 \text{MnO}_4^-(\text{aq}) + 16 \text{H}^+(\text{aq}) \rightarrow 10 \text{CO}_2(\text{g}) + 2 \text{Mn}^{2+}(\text{aq}) + 8 \text{H}_2\text{O}(\text{l})$

Ignore state symbols

1

M2 $n(\text{MnO}_4^-) = \frac{26.40 \times 0.02}{1000}$ OR $n(\text{MnO}_4^-) = 5.28 \times 10^{-4}$

1

M3 $n(\text{C}_2\text{O}_4^{2-}) = \frac{5}{2} \times 5.28 \times 10^{-4} = 1.32 \times 10^{-3}$

M3 is for $M2 \times 5/2$

If wrong ratio used then can only score M2, M4, M5 and M6

1

M4 $n(\text{C}_2\text{O}_4^{2-} \text{ in flask originally}) = 1.32 \times 10^{-3} \times 10 = 1.32 \times 10^{-2}$

M4 is for $M3 \times 10$

1

M5 $n(\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}) = \frac{1.32 \times 10^{-2}}{3} = 4.40 \times 10^{-3}$

(Mr $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O} = 491.1$)

M5 is for $M4 \div 3$

1

M6 Mass of $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ reacted = $4.40 \times 10^{-3} \times 491.1 = 2.16 \text{ g}$
M6 is for $M5 \times 491(.1)$

1

M7 % purity = $\frac{2.16}{2.29} \times 100 = 94.3 \text{ or } 94.4\%$

Answer must be to 3 s.f.

Correct answer scores 6 marks; mark equation separately

Alternative method using ratio by moles:

M5 $n(\text{C}_2\text{O}_4^{2-}) = 4.66 \times 10^{-3} \times 3 = 0.0140 \text{ moles in } 250\text{cm}^3$

M6 $n(\text{complex}) = 2.29/491.1 = 4.66 \times 10^{-3} \text{ moles in } 250\text{cm}^3$

M7 % = $0.0132/0.0140 \times 100 = 94.3 \text{ or } 94.4\%$

1

- (e) Make some known concentrations (of the coloured solution and read the absorbance of each one using a colorimeter)

Ignore addition of suitable ligand

1

Plot a graph of absorbance vs concentration

Not just "plot a calibration curve" / reference to Beer-Lambert graph is insufficient

Do not allow transmittance in M2

1

Read/compare unknown concentration from calibration curve/graph (and hence the concentration from the graph)

M3 can only be scored if graph/curve mentioned

1

[16]

Q6.

- (a) $2\text{MnO}_4^- + 16\text{H}^+ + 5\text{C}_2\text{O}_4^{2-} \rightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 10\text{CO}_2$

1

Mn^{2+} OR Mn^{3+}

If catalyst incorrect can only score M1 and M3

1

(Possible because) Mn can exist in variable oxidation states

1

E_a lowered because oppositely charged ions attract

These marks can be gained in any order

1

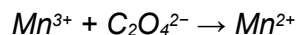
Mn^{3+} (reduced) to Mn^{2+} by $\text{C}_2\text{O}_4^{2-}$ / equation

M5 may appear before M2

1

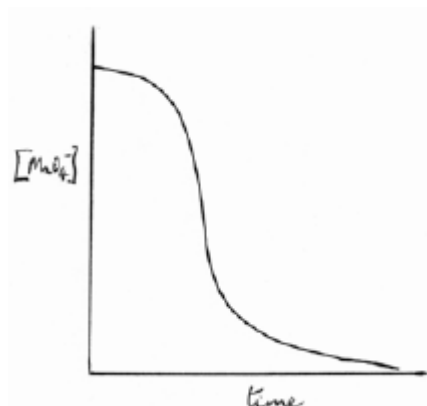
Mn^{2+} (oxidised (back)) to Mn^{3+} by MnO_4^- / equation

M5 and M6 can be scored in unbalanced equations or in words showing:



1

(b) **Graph marks**



S-shaped curve must not rise significantly and must not fall rapidly initially.

Starts on concentration axis **and** is levelling out (can level out on time axis or above but parallel to time axis)

Cannot score graph marks (M1 and M2) if no axes and / or no labels

1

1

Explanation marks

Slope / rate increases as catalyst (concentration) forms

1

Slope / rate decreases as (concentration) of MnO_4^- ions / reactant(s) decreases (OR reactants are being used up)

Explanation marks can be awarded independent of graph.

1

[10]

Q7.

- (a) Negative ions repel one another

1

- (b) Positive ions attract negative ions in catalysed process

Allow activation energy decreases.

Allow alternative route with lower E_a

Ignore references to heterogenous catalysis.

1

- (c) $\text{S}_2\text{O}_8^{2-} + 2\text{e}^- \longrightarrow 2\text{SO}_4^{2-}$

Allow multiples including fractions.

Ignore state symbols.

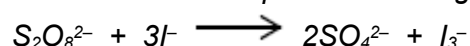
1

- (d) $\text{S}_2\text{O}_8^{2-} + 2\text{I}^- \longrightarrow 2\text{SO}_4^{2-} + \text{I}_2$

Allow multiples including fractions.

Ignore state symbols.

Allow the correct equation involving I_3^-

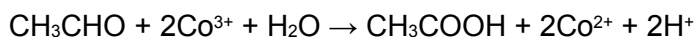
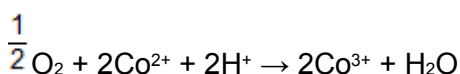


Q8.

- (a) Cobalt has variable oxidation states

Allow exists as Co(II) and Co(III)

(It can act as an intermediate that) lowers the activation energy

Allow (alternative route with) lower E_a *Allow multiples; allow molecular formulae**Allow equations with H_3O^+* 

- (b) (i)
- $[\text{Co}(\text{H}_2\text{O})_6]^{2+} + 3\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2 \rightarrow [\text{Co}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_3]^{2+} + 6\text{H}_2\text{O}$

Do not allow en in equation, allow $\text{C}_2\text{H}_8\text{N}_2$

The number of particles increases / changes from 4 to 7

Can score M2 and M3 even if equation incorrect or missing provided number of particles increases

So the entropy change is positive / disorder increases / entropy increases

- (ii) Minimum for
- M1**
- is 3 bidentate ligands bonded to Co

Ignore all charges for M1 and M3 but penalise charges on any ligand in M2

Ligands need not have any atoms shown but diagram must show 6 bonds from ligands to Co, 2 from each ligand

Minimum for **M2** is one ligand identified as $\text{H}_2\text{N}-\text{NH}_2$ *Allow linkage as $-\text{C}-\text{C}-$ or just a line.*Minimum for **M3** is one bidentate ligand showing two arrows from separate nitrogens to cobalt

- (c) Moles of cobalt =
- $(50 \times 0.203) / 1000 = 0.01015$
- mol

*Allow 0.0101 to 0.0102*Moles of AgCl = $4.22 / 143.4 = 0.0294$ *Allow 0.029*

*If not AgCl (eg AgCl₂ or AgNO₃), lose this mark and can only score **M1**, **M4** and **M5***

1

Ratio = Cl⁻ to Co = 2.9 : 1

*Do not allow 3 : 1 if this is the only answer but if 2.9:1 seen somewhere in answer credit this as **M3***

1

[Co(NH₃)₆]Cl₃ (square brackets not essential)

1

Difference due to incomplete oxidation in the preparation

Allow incomplete reaction.

Allow formation [Co(NH₃)₅Cl]Cl₂ etc.

Some chloride ions act as ligands / replace NH₃ in complex.

Do not allow 'impure sample' or reference to practical deficiencies

1

[15]

Q9.

- (a) Stoppered flask or similar with side arm

Allow gas outlet through stopper.

1

Calibrated container for collection eg gas syringe

Allow collection over water, but must use calibrated vessel for collection.

Lose 1 mark if apparatus is not gas tight.

1

- (b) Plot a graph of 'volume (of gas)' against 'time'

1

Determine the slope (gradient) at the beginning

1

- (c) Repeat with same volume **or** concentration of hydrogen peroxide and at the same temperature

Ignore references to results.

Do not allow 'keep everything the same' or words to that effect. Must mention volume or concentration and temperature.

1

Add cobalt(II) chloride to one experiment

1

[6]

Q10.

- (a) Variable / many oxidation states

1

- (b) $V_2O_5 + SO_2 \rightarrow V_2O_4 + SO_3$
Equations can be in either order
Allow multiples 1
- $V_2O_4 + \frac{1}{2}O_2 \rightarrow V_2O_5$ 1
- (c) (i) In a different phase / state from reactants 1
- (ii) Impurities poison / deactivate the catalyst / block the active sites
Allow (adsorbs onto catalyst AND reduces surface area) 1
- (d) (i) The catalyst is a reaction product 1
- (ii) Mn^{2+} / Mn^{3+} ion(s) 1
- (iii) $4Mn^{2+} + MnO_4^- + 8H^+ \rightarrow 5Mn^{3+} + 4H_2O$
Equations can be in either order 1
- $2Mn^{3+} + C_2O_4^{2-} \rightarrow 2Mn^{2+} + 2CO_2$ 1
- [9]

Q11.

- (a) For reactions 1 to 3 must show complex ions as reactants and products
Take care to look for possible identification on flow chart

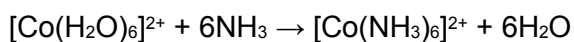
Reaction 1

ammonia solution

1

W is $[Co(NH_3)_6]^{2+}$

1



Correct equation scores all 3 marks

1

Reaction 2

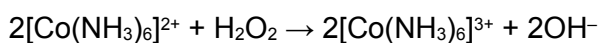
Allow oxygen, Do not allow air

H_2O_2

1

X is $[Co(NH_3)_6]^{3+}$

1



Allow $2[Co(NH_3)_6]^{2+} + \frac{1}{2}O_2 + H_2O \rightarrow 2[Co(NH_3)_6]^{3+} + 2OH^-$

Correct equations score all 3 marks

1

Reaction 3

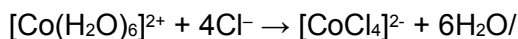
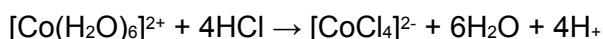
HCl

Do not allow Cl⁻ but mark on

1

Y is [CoCl₄]²⁻

1

*Correct equation scores previous mark**This equation scores all three marks*

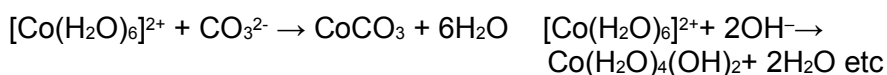
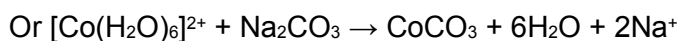
1

Reaction 4Na₂CO₃ Or NaOH/NH₃*Do not allow CaCO₃ as a reagent but mark on*

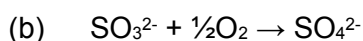
1

Z is CoCO₃ Co(OH)₂/Co(H₂O)₄(OH)₂

1

*Allow waters to stay co-ordinated to Co. This mark also previous mark**Allow Co²⁺ + CO₃²⁻ → CoCO₃*

1

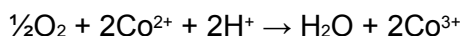
*Allow multiples*

1

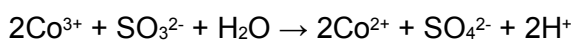
The activation energy is lower (for the catalysed route)

Or Co³⁺ attracts SO₃²⁻/Co²⁺ attracts SO₃²⁻/oppositely charged ions attract

1

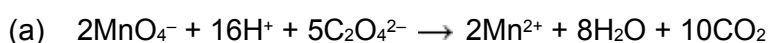


1

*Allow these equations in either order*

1

[16]

Q12.*For all species correct / moles and species correct but*

- charge incorrect* 1
- For balanced equation including all charges (also scores first mark)* 1
- (b) Manganate(VII) ions are coloured (purple) 1
- All other reactants and products are **not** coloured (or too faintly coloured to detect)
Allow (all) other species are colourless
Allow Mn²⁺ are colourless / becomes colourless / pale pink 1
- (c) The catalyst for the reaction is a reaction product 1
- Reaction starts off slowly / gradient shallow 1
- Then gets faster/rate increases / gradient increases
Allow concentration of MnO₄⁻ decreases faster / falls rapidly 1
- (d) Mn²⁺ ions
Allow Mn³⁺ ions 1
- (e) $\text{MnO}_4^- + 8\text{H}^+ + 4\text{Mn}^{2+} \rightarrow 5\text{Mn}^{3+} + 4\text{H}_2\text{O}$
Allow multiples 1
- $2\text{Mn}^{3+} + \text{C}_2\text{O}_4^{2-} \rightarrow 2\text{Mn}^{2+} + 2\text{CO}_2$ 1

[10]

Q13.

- (a) $2\text{Fe}^{2+} + \text{S}_2\text{O}_8^{2-} \rightarrow 2\text{Fe}^{3+} + 2\text{SO}_4^{2-}$ 1
- $2\text{Fe}^{3+} + 2\text{I}^- \rightarrow 2\text{Fe}^{2+} + \text{I}_2$ 1
- two negative ions repel / lead to reaction that is slow / lead to reaction that has high E_a 1
- iron able to act because changes its oxidation state
allow iron has variable oxidation state 1
- With iron ions have alternative route / route with lower activation energy 1
- (b) (i) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+} \rightarrow [\text{Fe}(\text{H}_2\text{O})_5\text{OH}]^{2+} + \text{H}^+$
can have H₂O on LHS and H₃O⁺ on R

do not penalise further hydrolysis equations
allow high charge density

1

Fe^{3+} ion has higher charge (to size ratio) (than Fe^{2+})

1

increases polarisation of co-ordinated water / attracts O
releasing an H^+ ion / weakens O–H bond

1

- (ii) $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{Fe}^{2+} \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} + 6\text{Fe}^{3+}$
or 6 mol Fe(II) react with 1 mol dichromate
If factor of 6 not used max = 3 for M2, M4 and M5
e.g. 1:1 gives ans= 8.93 to 8.98% (scores 3)

1

moles dichromate = $23.6 \times 0.218/1000 = 5.14 \times 10^{-4}$

1

moles iron = $5.14 \times 10^{-4} \times 6 = 0.00309$
M3 also scores M1

1

mass iron = $0.00309 \times 55.8 = 0.172$
Mark is for moles of iron $\times 55.8$ conseq
Allow use of 56 for iron

1

% by mass of iron = $0.172 \times 100/0.321 = 53.7\%$
Answer must be to at least 3 sig figures allow 53.6 to 53.9
Mark is for mass of iron $\times 100/0.321$ conseq

1

- (c) brown precipitate / solid
Allow red-brown / orange solid
Not red or yellow solid

1

bubbles (of gas) / effervescence/ fizz
Allow gas evolved / given off
Do not allow just gas or CO_2 or CO_2 gas

1

$2[\text{Fe}(\text{H}_2\text{O})_6]^{3+} + 3\text{CO}_3^{2-} \rightarrow 2\text{Fe}(\text{H}_2\text{O})_3(\text{OH})_3 + 3\text{CO}_2 + 3\text{H}_2\text{O}$
Allow
 $2[\text{Fe}(\text{H}_2\text{O})_6]^{3+} + 3\text{CO}_3^{2-} \rightarrow 2\text{Fe}(\text{OH})_3 + 3\text{CO}_2 + 9\text{H}_2\text{O}$
Use of Na_2CO_3
e.g. $\dots + 3\text{Na}_2\text{CO}_3 \rightarrow \dots + \dots + \dots + 6\text{Na}^+$

1

[16]

Q14.

- (a) Incomplete (or partially filled) d orbitals/sub-shells
Do not allow d shell 1
- (b) Variable oxidation states 1
- (c) (i) $[\text{H}_3\text{N}-\text{Ag}-\text{NH}_3]^+$
Allow $[\text{Cl}-\text{Ag}-\text{Cl}]^-$ or similar Cu(I) ion
Allow compounds in (i), (ii) and (iii) (eg Cl-Be-Cl)
Allow no charge shown, penalise wrong charge(s) 1
- (ii) Cis platin drawn out as square planar
Allow NiX_4^{2-} etc 1
- (iii) $[\text{CuCl}_4]^{2-}$ drawn out as tetrahedral ion
Or $[\text{CoCl}_4]^{2-}$ drawn out 1
- (d) (i) $\text{SO}_2 + 1/2\text{O}_2 \rightarrow \text{SO}_3$
Allow multiples
Allow $\text{SO}_2 + 1/2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$
ignore state symbols 1
- (ii) In a different phase/state (from the reactants) 1
- (iii) $\text{V}_2\text{O}_5 + \text{SO}_2 \rightarrow \text{V}_2\text{O}_4 + \text{SO}_3$
can be in either order 1
- $\text{V}_2\text{O}_4 + 1/2\text{O}_2 \rightarrow \text{V}_2\text{O}_5$
allow multiples 1
- (iv) Surface area is increased 1
- By use of powder or granules or finely divided
Allow suspending/spreading out onto a mesh or support 1
- (e) (i) Forms two or more co-ordinate bonds
Allow more than one co-ordinate bond or donates more than 1 electron pair.
Do not allow "has more than one electron pair"
Allow uses more than one atom to bond (to TM) 1
- (ii) Number of product particles > Number of reactant particles
Allow molecules/entities instead of particles

Penalise incorrect numbers (should be 2→5)

1

Disorder increases or entropy increases
(or entropy change is positive)

Allow ΔG must be negative because $\Delta H = 0$ and ΔS is +ve

1

(iii) 6

1

Cyanide strongly bound to Co (by co-ordinate/covalent bond)

1

[16]

Q15.

(a) Same phase/state

1

(b) Because only exist in one oxidation state

Allow do not have variable oxidation states

1

(c) $2\text{I}^- + \text{S}_2\text{O}_8^{2-} \rightarrow \text{I}_2 + 2\text{SO}_4^{2-}$

Ignore state symbols

Allow multiples

1

(d) Both (ions) have a negative charge

Or both have the same charge

Or (ions) repel each other

Do not allow both molecules have the same charge
(contradiction)

1

(e) $2\text{Fe}^{2+} + \text{S}_2\text{O}_8^{2-} \rightarrow 2\text{Fe}^{3+} + 2\text{SO}_4^{2-}$

1

$2\text{Fe}^{3+} + 2\text{I}^- \rightarrow 2\text{Fe}^{2+} + \text{I}_2$

1

Equations can be in any order

Positive and negative (ions)/oppositely charged (ions)

Mark independently

1

(f) Equations 1 and 2 can occur in any order

Allow idea of Fe^{3+} converted to Fe^{2+} then Fe^{2+} converted
back to Fe^{3+}

1

[8]

Q16.

(a) FeCl_3 accepts electron pairs from water

1

Hence acts as a Lewis acid	1
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ donates protons	1
Hence acts as a Bronsted-Lowry acid	1
(b) The Fe^{2+} ion has a smaller charge to size ratio	1
Hence less polarising than Fe^{3+} or less weakening effect on O-H bonds	1
(c) (i) $\text{V}_2\text{O}_5 + \text{SO}_2 \rightarrow \text{V}_2\text{O}_4 + \text{SO}_3$	1
$\text{V}_2\text{O}_4 + \text{O}_2 \rightarrow \text{V}_2\text{O}_5$	1
(ii) Both ions are negative or ions repel	1
$2\text{Fe}^{2+} + \text{S}_2\text{O}_8^{2-} \rightarrow 2\text{Fe}^{3+} + 2\text{SO}_4^{2-}$	Species
	Balanced
$2\text{Fe}^{3+} + 2\text{I}^- \rightarrow 2\text{Fe}^{2+} + \text{I}_2$	Species
	Balanced

[13]

Q17.

(a) Alternative route	
<i>Allow mechanism outlined</i>	
<i>allow forms intermediate species</i>	1
Lower activation energy	1
(b) Variable oxidation state	
<i>allow changes oxidation states</i>	1
(c) (i) $\text{SO}_2 + \text{V}_2\text{O}_5 \rightarrow \text{SO}_3 + \text{V}_2\text{O}_4$	
<i>allow 2VO_2 instead of V_2O_4</i>	1
$\text{O}_2 + 2\text{V}_2\text{O}_4 \rightarrow 2\text{V}_2\text{O}_5$	1
(ii) Poison attaches to surface	

Allow blocks active site/surface
Decreases surface area

1

(iii) Purify reactants

Allow remove impurities

1

[7]

Q18.

C

[1]

Q19.

(a) effect on reaction rate: catalyst provides an alternative reaction route.;

1

with a lower E_a ;

1

more molecules able to react or rate increased;

1

equilibrium: forward and backward rates changes by the same amount;

1

hence concentration of reactants and products constant or yield unchanged;

1

(b) heterogeneous: catalyst in a different phase or state to that of the reactants;

1

active site: place where reactants adsorbed or attached or bond etc.;

1

reaction occurs or an explanation of what happens;
(allow absorbed)

1

reasons: large surface area;
reduce cost or amount of catalyst;

2

catalyst poison: lead adsorbed;
lead not desorbed or site blocked;
(lead adsorbed irreversibly scores both of these marks)

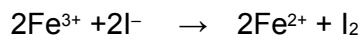
2

(c) reaction slow as: both ions negatively charged or ions repel;

1

$2\text{Fe}^{2+} + \text{S}_2\text{O}_8^{2-} \rightarrow 2\text{Fe}^{3+} + 2\text{SO}_4^{2-}$ Species;
Balanced;

2



Species ;
Balanced;

2

[17]

Q20.

(a) Iron

1

Heterogeneous; catalyst in a different phase from that of the reactants

1

Poison; a sulphur compound (allow sulphur)

1

Poison strongly adsorbed onto active sites/ blocked

1

Poison not desorbed or reactants not adsorbed or catalyst surface area reduced

1

(b) Pale green solution

1

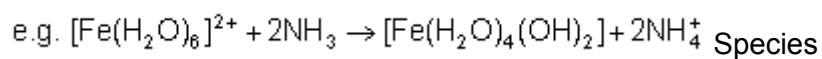
Green precipitate formed

1

Insoluble in excess ammonia

1

Equation:



1

Balance

1

NB Allow equations with H₂O and OH⁻ if reaction of H₂O with NH₃ also given

Max 4

[9]

Q21.

(a) A catalyst in the same phase/phase as the reactants

1

(b) (i) A reaction in which a product acts as a catalyst

1

(ii) Mn^{2+} or Mn^{3+}
"Self-catalysing" not allowed

1

(c) (i) $2\text{CO} + 2\text{NO} \rightarrow 2\text{CO}_2 + \text{N}_2$

or $4\text{CO} + 2\text{NO}_2 \rightarrow 4\text{CO}_2 + \text{N}_2$

C not allowed as a product

1

Reducing agent CO

1

(ii) Pt, Pd or Rh

1

Deposited on a ceramic honeycomb or matrix or mesh or sponge

1

To increase surface area of catalyst

1

(d) (i) Reactants cannot move on surface or products not desorbed or
Active sites blocked

1

(ii) Reactants not brought together or
No increase in reactant concentration on catalyst surface or
Reactants not held long enough for a reaction to occur or
Reactant bonds not weakened

1

[10]

Q22.

- (a) (i) Heterogeneous:- In a different phase to reactants (1)
Catalyst:- Increases reaction rate (1)
Alternative route or route described (1)
Lower E_a (1)
Unchanged at end of reaction (1) Max 4
- (ii) Feature:- QoL Variable oxidation states shown by vanadium (1)
Equations $V_2O_5 + SO_2 \rightarrow V_2O_4 + SO_3$ (1)
 $2V_2O_4 + O_2 \rightarrow 2V_2O_5$ (1)

7

(b) $VO_2^+ + 4H^+ + 3e^- \rightarrow V^{2+} (aq) + 2H_2O$ (1)

$Zn \rightarrow Zn^{2+} + 2e^-$ (given)

$2VO_2^+ + 8H^+ + 3Zn \rightarrow 3Zn^{2+} + 2V^{2+} (aq) + 4H_2O$ (1)

2

Mol $KMnO_4 = mv/1000 = 0.0200 \times 38.5/1000 = 7.70 \times 10^{-4}$ (1)

Mole ratio MnO_4^- to $V(II)$ = 3:5 deduced

or equation

$5V^{2+} + 3MnO_4^- + 4H^+ \rightarrow 2H_2O + 3Mn^{2+} + 5VO_2^+$ (2)

Mol $V(II) = 7.70 \times 10^{-4} \times 5/3$ (1) = 1.283×10^{-3}

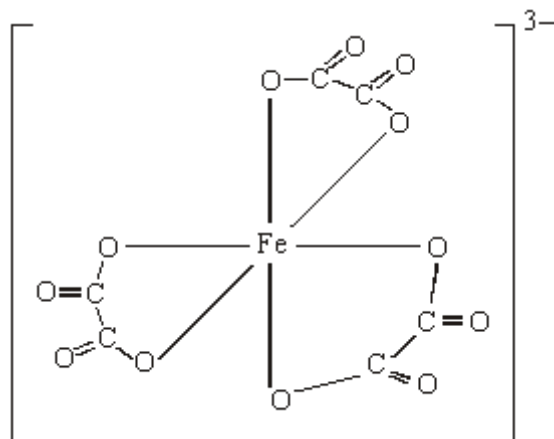
Mass V = $1.283 \times 10^{-3} \times 50.9$ (1) = 0.0653 g

% V in sample = $0.06532 \times 100/0.160 = 40.8$ (1)

Q23.

- (a) (i) Two **(1)** lone pair donor / electron pair donor **(1)** atoms
 Allow:– forms two co-ordinate bonds **(1)**
NOT atom with two lone pairs

(ii)



Correct ligand structure **(1)**
 ($\begin{array}{c} \text{O} \\ \parallel \\ \text{C} \end{array}$ not essential)

penalise any error

Six correct O–Fe bonds **(1)**

Correct charge **(1)**

N.B. Penalise the second mark if arrow from Fe shown

N.B. Ignore charges on atoms

5

- (b) (Substitution of a monodentate ligand by a bi or multidentate ligand **(1)** giving a more stable complex **(1)** or with an increase in entropy / disorder or forming a ring / cage complex / structure (crab like)

2

- (c) (i) $[\text{AgCl}_2]^-$ or AgCl_2^- **(1)**
 (ii) Chloride or Cl^- big or large or repel **(1)**
NOT Cl_2 or Cl^+ or Cl
Allow 'chlorine ion'

2

- (d) (i) (Both) ions are negative or ions repel or High E_a **(1)**
 (ii) *Meaning of the term autocatalytic:* A product of the reaction acts as a catalyst **(1)**
NOT a self catalysing reaction (0)
 Catalyst: Mn^{2+} or Mn^{3+} **(1)**
 (iii) Mn^{2+} converted into Mn^{n+} or Mn^{2+} oxidised **(1)**

Q24.

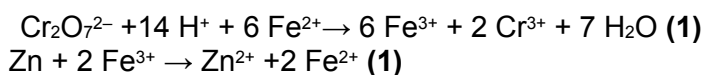
- (a) reactants brought together / increased concentration on surface or increased collision frequency (1)
 reactants must be correctly orientated (1)
 reaction on the surface (1)
 products desorbed (1)
 example of a catalysed reaction (not a named process) (1)
 a suitable catalyst for this reaction (1)

penalise incorrect second reactions and catalysts

If absorption too weak reactants not brought together (1)
 e.g. silver (1)
 If adsorption too strong products not desorbed (1)
 e.g. tungsten (1)

max 8

- (b) Equations:



Method

Titrate measured volume solution against K₂Cr₂O₇ (1)

Reduce same volume solution with zinc (1)

Filter off excess zinc (1)

Titrate total Feⁿ⁺ using K₂Cr₂O₇ (1)

Percentage Fe³⁺ = 100 × (titre2 - titre1) / titre 2
 or equivalent (1)

7

Q25.

- (a) High E_a: S₂O₈²⁻ repels I⁻ **or** both ions negative (1)
 $2\text{Fe}^{2+} + \text{S}_2\text{O}_8^{2-} \rightarrow 2\text{Fe}^{3+} + 2\text{SO}_4^{2-} \quad (1)$
 $2\text{Fe}^{3+} + 2\text{I}^- \rightarrow 2\text{Fe}^{2+} + \text{I}_2 \quad (1)$

N.B. Ignore additional incorrect equations

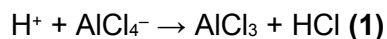
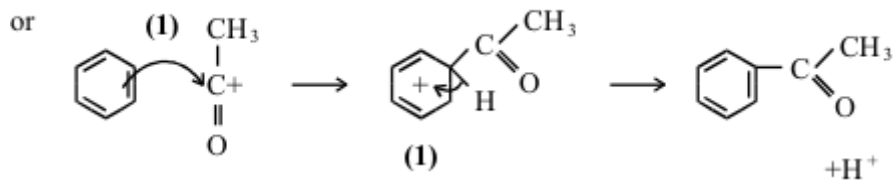
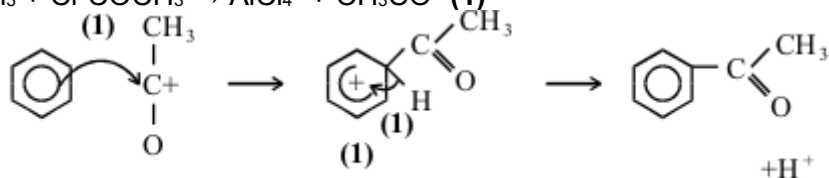
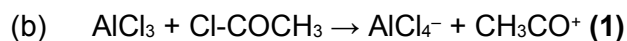
Vanadium is a transition element **or** Magnesium is not a transition element (1)

Vanadium has variable oxidation states (1)

Magnesium only forms Mg²⁺, **or** has only one oxidation state (1)

N.B. Score two marks for "Only vanadium has variable oxidation states"

6



Lewis acid: AlCl_3 accepts electron pair

N.B. penalise incorrect acyl chloride by one

N.B. penalise chloroethane by two marks i.e. first equation mark, attack on benzene mark

NH_4Cl : Not a catalyst (1)

FeCl_3 : A catalyst (1)

has a low energy vacant shell

or has spaces or vacancies in d shell

or has a partially filled d shell

or able to accept an electron pair

or can form FeCl_4^- (1)

9

[15]

Q26.

D

[1]

Examiner reports

Q1.

- (a) Nearly all students (91.1%) gained both marks here.
- (b) Although 73.9% of students scored two marks, common errors here included a failure to convert temperature into kelvin or using inconsistent energy units.
- (c) Students found the explanation in this part more challenging and many could not state that the Gibbs free-energy would become more negative. Many students, however, scored the second mark for a correct reference to a change in entropy.
- (d) Many students discussed the general principles of homogeneous catalysis or the lowering of activation energy rather than the reaction on the platinum surface. The mark most commonly missed was the idea that the product desorbed from or left the surface of the catalyst. Surprisingly, over 10% of students made no attempt at this question.
- (e) 74.4% of students answered this correctly, although a few students thought the oxidation state of N in ammonia was +3.
- (f) Many students gave hydrogen as the other product or failed to balance an equation in which water was the other product.

Q2.

- (a) Only 11.3% of students scored both marks here; sometimes Fe^{2+} was chosen but students could not explain their choice. The most common incorrect answer was Zn^{2+} .
- (b) Just over three-quarters of students could give the oxidation state.
- (c) The structure was often given, incorrectly, as a mirror image and the type of isomerism as optical; only 37.2% of students scored both marks.
- (d) This was poorly answered, with only just over a third of students giving the correct equation.
- (e) Over half of the students (55.6%) gave the correct equations; incorrect equations included charged vanadium species. Surprisingly, 12% of students were unable to make any attempt at this question.

Q4.

Most students scored highly in part (a). Incorrect units for entropy change were often seen in part (b). Students generally understood the concept of disorder and scored the mark in part (c). The majority of students could use their own values to calculate the free-energy change in part (d); common errors included incorrect units, failure to convert temperature into Kelvins and using a mixture of joules and kilojoules in their calculation. The relationship between ΔG and feasibility was well known in part (e). The meaning of heterogeneous was well known in part (f)(i) and the equations in part (f)(ii) were generally well known. Students answered part (f)(iii) well although in part (f)(iv) a few referred to impurities being produced without any reference to poisoning of the catalyst.

Q5.

In part (a) most students could identify the autocatalyst in the reaction however some students thought that an autocatalyst was a reagent and identified the catalyst as MnO_4^- . Many students correctly identified the acid in part (b). Most students knew that two negative ions would repel in part (c) but did not link this to high activation energy. Some students did not state that the reaction was initially slow or would only speed up when the catalyst was produced. The equation in part (d) was generally well done. Some students had the correct ratio of reagents but missed charges on the ions or did not produce the correct amount of CO_2 . Many students scored the first few marks but then failed to divide by 3 or multiplied by the wrong M_r . In part (e) many students described a colorimeter and the absorbance of visible light but did not answer the question as set and hence could not score the marks. Most students who used a series of concentrations knew that a calibration curve was used but often did not give correct labels for the axes. Those that did use a calibration curve mostly scored the last mark. A few very good students drew a diagram of the graph, with labelled axes, and showed how this would be used to find the concentration.

Q6.

This question proved to be difficult and discriminating. In part (a), only the best students could write a correct equation. The catalyst was usually identified correctly but the way in which the manganese(II) and manganese(III) ions were involved and regenerated in the reaction and the way in which contributed to the lowering of the activation energy were not understood by most students. In part (b) some excellent graphs were sketched although weaker students did not show the expected 'S' shaped curve. In the explanation of the shape of the curve, the increase in reaction rate caused by the increase in catalyst concentration was usually correct but fewer students explained correctly why the rate of reaction then decreased.

Q7.

Parts (a), (c) and (d) were generally very well answered. In part (b), the most common wrong answers referred to the catalyst providing a surface for the adsorption of reactants. Where students did talk about the opposite charges of the ions, they often did not specifically talk about attraction between these ions

Q8.

This stretch and challenge question proved testing for many students, particularly parts (a) and (c). The most frequent mark for part (a) was one out of four for stating that cobalt has variable oxidation states. Attempts at the two equations were poor. Equations should be balanced and should not be half-equations with electrons. Despite the parallel with similar catalysed systems in the specification, students did not appreciate that the Co^{3+} ions would be the oxidising agents, reacting with ethanal and that Co^{2+} ions would be oxidised by oxygen back to Co^{3+} . In part (b)(i), weaker students did not know that the chelate effect is explained by entropy changes and they often, incorrectly, attempted to explain the effect in terms of the stability of a complex ion with bidentate ligands. Part (b)(ii) was answered well by most students. Part (c) proved to be very discriminating with only the very best students scoring more than three out of five marks. The most difficult marks to achieve were the formula of **Z**, $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ and an explanation for the difference between the expected and the given ratio of cobalt ions to chloride ions in the complex. Many students lost marks because they did not use a correct formula for silver chloride—incorrectly using AgCl_2 or AgNO_3 . Another common error was to ignore the precision of the data given in the question and to give the calculated molar ratio to only 1 significant figure whereas 3 significant figures were required, consistent with the data given.

Q9.

The diagram in part (a) was well drawn by the majority of students. Most students were able to describe the graph needed in part (b) but many were unable to suggest an appropriate method for measuring the initial rate. In part (c), some students were allowed the first mark even though they did not describe the conditions to be kept constant.

Despite the long catalogue of points listed above, this was, overall, another very positive session in many schools and colleges. The teachers in these schools and colleges have successfully and securely delivered the practical assessment and have impressed with the accurate and consistent standard of their marking. In my last report as a Principal Moderator, I am grateful for the opportunity to salute these superb professionals and wish them well in the future.

Q10.

This question was answered well by most students. The most difficult part was part (d)(iii) where only the best students were able to write correct equations.

Q11.

Answers to part (a), a question that required recall of cobalt chemistry, produced a wide spread of marks. As always, a full identification of reagents was required and many students lost marks by failing to do so, specifying Cl^- (instead of HCl), carbonate (instead of sodium carbonate) and hydroxide (instead of NaOH). Missing or incorrect charges and inaccurate formulae were also common eg CoCl_4 and $\text{Co}(\text{OH})_2$. Reaction 1 was well known. Air was a common insufficient reagent for reaction 2. The equation mark for reaction 2 was often the missing mark from an otherwise perfect answer. Reaction 3 was the least well known of the four reactions. Many students did not recognise the blue solution to be $[\text{CoCl}_4]^{2-}$ and instead attempted to use an excess of NaOH to give a cobaltate(II) ion. In reaction 4, NaCO_3 and CO^{3-} were common wrong answers. In part (b), most students gained the first two marks. Although most students attempted the last two equations, very few were correct. Common wrong answers involved the wrong cobalt species being used. For example, students tried to oxidise sulfate(IV) ions with cobalt(II). They did not recognise that an oxidising agent must react with a reducing agent and they went on with an attempt to reduce cobalt(III) to cobalt(II) with oxygen.

Q12.

The equation required in part (a) is recognised to be discriminating and it proved to be so with only 34% of students giving a correct answer. Part (b) was a 'how science works' question and only 20% of students could explain that a spectrometer can be used because manganate(VII) ions are coloured but the products of the reaction are effectively colourless. Some students tried to use a mass spectrometer. Answers to parts (c) and (d) were pleasing. However, as expected, part (e) proved to be very discriminating and only the very best students could write balanced equations for the two reactions.

Q13.

Each part of this question discriminated very effectively between able and less able candidates. In part (a) a common omission was a failure to state that iron ions are able to catalyse redox reactions because they are able to change oxidation state. In this part, the most usual errors were to give an unbalanced equation for the reaction between iron (II) ions and persulfate ions and for the reaction between iron (III) ions and iodide ions. Candidates often used only one mole of iron ions, presumably because they omitted to check that charges, as well as numbers of moles, should balance. In part (b)(i), most candidates knew that the increased acidity of aqueous iron (III) ions could be attributed to

their increased charge to size ratio compared with iron (II) ions. However, the reason why this high charge to size ratio caused an increase in ionisation of the $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ was less well understood. Very few correct equations were seen. Many did not show the release of one proton into the aqueous solution. They showed incorrectly the formation of $\text{Fe}(\text{H}_2\text{O})_3(\text{OH})_3$ often by reaction with hydroxide or carbonate ions. There were many good answers to part (b)(ii) with about 40% of candidates scoring full marks. Answers to part (c) were not so impressive. Although a brown precipitate was usually described, evolution of a gas was often missing and the difficult equation was not balanced correctly.

Q14.

This question proved to be discriminating with a facility for most parts of only about 50%. In part (c), as expected, the hardest example to recall was that of a square planar complex but it was also surprising to find that a common error in part (c)(iii) was to show an octahedral complex. In part (d)(i), many candidates gave an incorrect equation using O instead of O_2 but other parts were answered quite well. It was disappointing to find that in part (e)(i) about one third of candidates could not give the correct meaning of the term multidentate. In part (e)(ii), it was pleasing to note that about half of candidates scored full marks. In part (e)(iii), only the best candidates were able to explain clearly that the cyanide ion is bound strongly to the cobalt so it is not toxic when complexed in vitamin B₁₂.

Q15.

Part (a) was answered well but part (b) was more difficult and weak candidates confused ions with atoms. In part (c) it was disturbing to note the large number of candidates who gave a wrong formula for the sulfate ion produced, usually showing only a single negative charge. Part (d) was answered well. Part (e) proved to be challenging, especially the equations. Only the best candidates could write balanced equations, the most common error being to use only one mole of iron ions, despite requiring two moles of electrons for reaction of the $\text{S}_2\text{O}_8^{2-}$ ion and for the formation of I_2 . In part (f) most candidates attempted to answer in general terms by mentioning activation energy rather than giving an answer specific to iron(II) and iron(III) ions.

Q17.

This question produced a range of answers. Parts (a), (b) (c)(i) and (c)(ii) were answered well by most candidates. The answer to part (c)(iii) was less well known and only 54% of candidates could suggest how to minimise poisoning of the catalyst by removing impurities from the reactants.

Q19.

Parts (a) and (b) were both well answered and many candidates scored full, or nearly full, marks. Almost all candidates stated that the reaction between I^- and $\text{S}_2\text{O}_3^{2-}$ was slow as they were both negative and would repel each other, few gave correct equations showing the involvement of iron(II) and iron(III) ions in the reaction. Sadly some candidates, who gave correct species, lost a mark as they failed to balance the equations.

Q20.

In answer to part (a), most candidates identified iron as the heterogeneous catalyst in the Haber process and explained the term *heterogeneous* correctly. Although poisoning of the

iron catalyst by sulphur is clearly stated in the Specification, many other elements and compounds were stated incorrectly to poison this catalyst. The method by which the poison works was well known and well explained. Only the best candidates gave a correct equation for the reaction of an aqueous iron(II) salt with an excess of aqueous ammonia as required in part (b). Candidates who gave equations involving the reaction of either water or hydroxide ions were allowed to score full marks provided that they also gave an equation showing the equilibrium reaction of ammonia with water. Correct observations were given by most of the good candidates but others either failed to state any observations or gave incorrect answers.

Q21.

Parts (a) and (b) were generally well done but part (c) proved to be surprisingly difficult. Incorrect and unbalanced equations were common errors in section (i) and many candidates failed to identify the reducing agent in the reaction. Although most candidates gave a correct transition element used as a catalyst in section (ii) there were numerous other incorrect answers. The chemistry tested in part (d) was generally well known but candidates whose answers merely restated the question lost marks.

Q22.

Although some candidates confused the terms *homogenous* with *heterogeneous*, the terms *heterogeneous* and *catalyst* were generally well known and most candidates gave correct explanations of how, in general terms, a catalyst works. The role of vanadium(V) oxide in the Contact Process was also well known and many candidates scored full marks for their answers to part (a). Part (b) proved, as expected, to be more difficult. Many candidates were able to use half-equations to construct an overall equation for the reduction of VO_2^+ to V^{2+} by zinc in acidic solution. Almost all were also able to calculate correctly the number of moles of potassium manganate(VII) used to oxidise the vanadium(II) ions back to vanadium(V) ions. However, in order to calculate the number of moles of vanadium(II) in the solution, it was necessary to deduce the mole ratio MnO_4^- : V^{2+} . The best students made this deduction and went on to determine the percentage of vanadium in the sample. Candidates who failed to make this deduction were able to score an additional mark if they used the correct A_r of vanadium when calculating the mass of vanadium in the sample from their value for moles of V^{2+} in the solution.

Q23.

The term 'bidentate ligand' was well understood and most candidates were able to sketch the structure of the required complex in (a)(ii). The term 'chelate effect' was less well understood but many candidates were able to score both marks. In part (c) almost all explained correctly that chloride ions do not usually form octahedral complexes with metal(II) ions because of their relatively large size. Most were able to deduce correctly the formula of the linear complex formed when silver chloride dissolves in concentrated hydrochloric acid. Section 1 (i) and (ii) of part (d) were well answered but, having recognised Mn^{2+} as the catalyst for the reaction between the negative ions, MnO_4^- and $\text{C}_2\text{O}_4^{2-}$, the suggestions of how the catalyst might be involved in the reaction were sometimes given in general terms rather than by specific reference to the involvement of the Mn^{2+} ion.

Q24.

Most candidates gave good explanation of how a heterogeneous catalyst works and high marks were scored in part (a). By contrast, few gave a good outline plan for the experiment to determine the percentage of iron as iron(III) in a solution containing Fe^{3+} (aq) and Fe^{2+} (aq) ions. Most stated correctly that the concentration of Fe^{2+} (aq) in solution

can be determined by a titration using potassium dichromate(VI) but few clearly stated that the volumes of both solution would need to be measured. Although most used the fact that zinc can reduce $\text{Fe}^{3+}(\text{aq})$ to $\text{Fe}^{2+}(\text{aq})$, very few stated that, after the reduction, excess zinc would need to be removed by filtration. Marks were awarded for correct equations but many candidates did not give them.

Q25.

The reaction between persulphate ions and iodide ions was well known and almost all candidates stated correctly that the reaction has a high activation energy as these ions are both negative and repel each other. Good candidates gave correct equations explaining the catalytic action of iron(II) ions but a significant number of weaker candidates lost marks when they failed to balance these equations.

Many candidates completed their answer to part (a) by predicting correctly that the variable oxidation states of the transition element vanadium would enable $\text{V}^{3+}(\text{aq})$ to function as a catalyst for the reaction whilst $\text{Mg}^{2+}(\text{aq})$ would not. The role of AlCl_3 in the reaction between benzene and ethanoyl chloride was well known by many candidates. Some, however, lost marks when they failed to show the involvement of AlCl_3 in the formation of the acylium intermediate and the reformation of AlCl_3 at the end of the reaction. Marks were lost by candidates who drew inaccurate structures in the organic reaction mechanism. The link between the ability of AlCl_3 to behave as a Lewis acid and accept a lone electron pair was made by good students who then predicted correctly that FeCl_3 would function as a catalyst but NH_4Cl would not. Marks in this section were not awarded to candidates who made vague predictions.