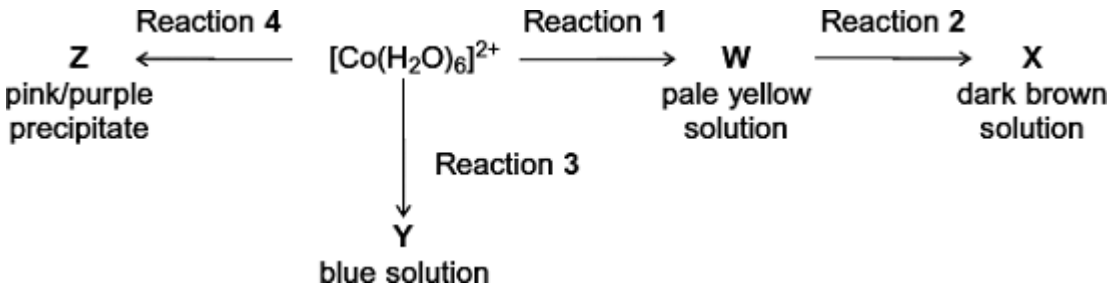
Q1. This question is about cobalt chemistry.

(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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(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)
(Total 16 marks)

Q2. 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 $S_2O_8^{2-}$ ions. Write equations for the reactions that occur.

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(Extra space) .....

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(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.

(i) Explain, with the aid of an equation, why iron(III) ions are more acidic than iron(II) ions in aqueous solution.

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(3)

(ii) In a titration, 0.321 g of a moss killer reacted with 23.60 cm^3 of acidified 0.0218 mol dm^{-3} $K_2Cr_2O_7$ solution.

Calculate the percentage by mass of iron in the moss killer. Assume that all of the iron in the moss killer is in the form of iron(II).

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(c) Some sodium carbonate solution was added to a solution containing iron(III) ions. Describe what you would observe and write an equation for the reaction that occurs.

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(Total 16 marks)

Q3. Transition metal ions can act as homogeneous catalysts in redox reactions. For example, iron(II) ions catalyse the reaction between peroxodisulfate ($S_2O_8^{2-}$) ions and iodide ions.

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

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(1)

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

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(1)

(c) Write an equation for the overall reaction that occurs, in aqueous solution, between $S_2O_8^{2-}$ ions and I^- ions.

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(1)

(d) Give **one** reason why, in the absence of a catalyst, the activation energy for the reaction between $S_2O_8^{2-}$ ions and I^- ions is high.

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(1)

(e) Write two equations to show how Fe^{2+} ions can catalyse the reaction between $S_2O_8^{2-}$ ions and I^- ions. Suggest **one** reason why the activation energy for each of these reactions is low.

Equation 1 .....

Equation 2 .....

Reason .....

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(3)

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

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(1)

(Total 8 marks)

Q4. 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.

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(1)

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

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(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.

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(1)

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

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(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.

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(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 B_{12}

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

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(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.

$$PR(aq) + [Fe(H_2O)_6]^{2+}(aq) \rightarrow [FePR(H_2O)_2]^{2+}(aq) + 4H_2O(l)$$

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

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(iii) In vitamin B_{12} 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 B_{12}
Suggest why vitamin B_{12} is **not** toxic.

Co-ordination number .....

Reason why vitamin B_{12} is **not** toxic

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(2)
(Total 16 marks)