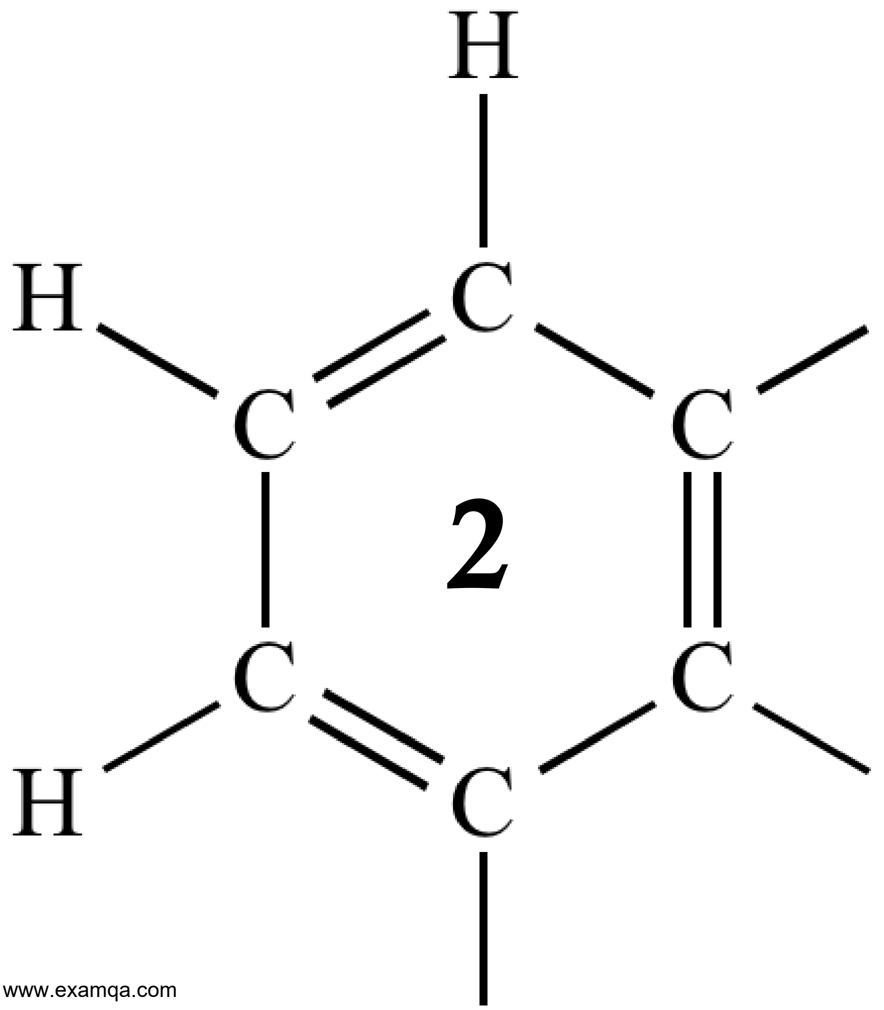
LONDON SCIENCE COLLEGE

AQA A2 CHEMISTRY

TRANSITION METALS



1 The characteristic properties of transition metals include coloured ions, complex formation and catalytic activity.

(a) Consider the chromium complexes **P** and **Q**.

$$[Cr(H_2O)_6]^{3+}(aq) \longrightarrow [Cr(H_2O)_5Cl]^{2+}(aq)$$

P		Q
$[Cr(H_2O)_6]^{3+}(aq)$	$\longrightarrow$	$[Cr(H_2O)_5Cl]^{2+}(aq)$
red-violet		green
P		**Q**

Explain, with reference to oxidation states and electron configurations, why the chromium ions in complexes **P** and **Q** contain the same number of d electrons.
You should **not** consider the electrons donated by the ligands.

Explain, in terms of electrons, why the complexes are **different** colours.
(You are **not** required to explain why the observed colours are red-violet and green.)

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(6)

(b) Write an equation to show how the $[Co(NH_3)_6]^{2+}(aq)$ ion reacts with 1,2-diaminoethane. Explain the thermodynamic reasons why this reaction occurs.

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(5)

(c) The toxic complex cisplatin is an effective anti-cancer drug because it reacts with the DNA in cancer cells, preventing cell division.

(i) Draw the **displayed** structure of cisplatin.
On your structure, show the value of one of the bond angles at platinum.
State the charge, if any, on the complex.

(3)

(ii) When cisplatin is ingested, an initial reaction involves one of the chloride ligands being replaced by water.

Write an equation for this reaction.

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(1)

(iii) Suggest how the risk associated with the use of this drug can be minimised.

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(1)

(d) Explain, with the aid of equations, how and why vanadium(V) oxide is used in the Contact Process.

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(4)
(Total 20 marks)

2 A student carried out an experiment to find the mass of $FeSO_4.7H_2O$ in an impure sample, **X**.
The student recorded the mass of **X**. This sample was dissolved in water and made up to 250 cm^3 of solution.
The student found that, after an excess of acid had been added, 25.0 cm^3 of this solution reacted with 21.3 cm^3 of a 0.0150 mol dm^{-3} solution of $K_2Cr_2O_7$

(a) Use this information to calculate a value for the mass of $FeSO_4.7H_2O$ in the sample of **X**.

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(5)

(b) The student found that the calculated mass of $FeSO_4.7H_2O$ was greater than the actual mass of the sample that had been weighed out. The student realised that this could be due to the nature of the impurity.

Suggest **one** property of an impurity that would cause the calculated mass of $FeSO_4.7H_2O$ in **X** to be greater than the actual mass of **X**.
Explain your answer.

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(2)
(Total 7 marks)

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

$$I_2 + I^- \longrightarrow I_3^-$$

The reaction above between I^- ions and $S_2O_8^{2-}$ ions has a high activation energy and $S_2O_8^{2-}$ 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 $S_2O_8^{2-}$ ions is slow.

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(1)

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

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(1)

(c) Write a half-equation for the reduction of $S_2O_8^{2-}$ ions to SO_4^{2-} ions.

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(1)

(d) Construct an overall equation for the reaction between $S_2O_8^{2-}$ ions and I^- ions.

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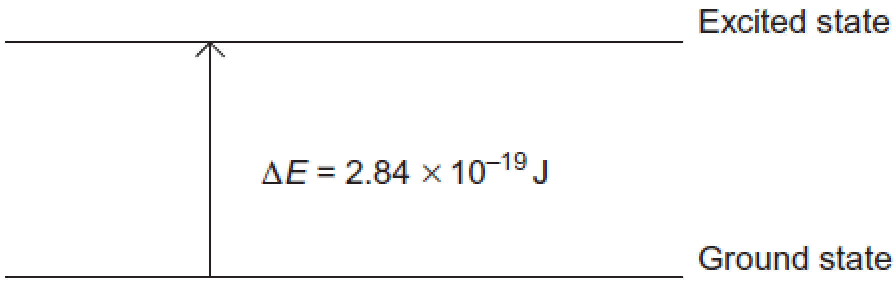
(1)
(Total 4 marks)

4 This diagram represents the energy change that occurs when a d electron in a transition metal ion is excited by visible light.



(a) Give the equation that relates the energy change ΔE to the Planck constant h and the frequency of the visible light v.

Use this equation and the information in the diagram to calculate a value for the frequency of the visible light, and state the units.
The Planck constant $h = 6.63 \times 10^{-34}$ J s.

Equation ....

Calculation ....

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(2)

(b) Explain why this electron transition causes a solution containing the transition metal ion to be coloured.

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(2)

(c) The energy change shown in the diagram represents the energy of red light and leads to a solution that appears blue.
Blue light has a higher frequency than red light.

Suggest whether the energy change *ΔE* will be bigger, smaller or the same for a transition metal ion that forms a red solution. Explain your answer.

Energy change ....

Explanation ....

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(2)

(d) State **three** different features of transition metal complexes that cause a change in the value of *ΔE*, the energy change between the ground state and the excited state of the d electrons.

Feature 1 ....

Feature 2 ....

Feature 3 ....

(3)
(Total 9 marks)

5 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

$$2CH_3CHO + O_2 \longrightarrow 2CH_3COOH$$

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.

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(4)

(b) In aqueous solution, the $[Co(H_2O)_6]^{2+}$ 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 $[Co(H_2O)_6]^{2+}$ complex ion.

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(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 cm^3 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.

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(5)
(Total 15 marks)

6 The pigment 'Cobalt Yellow' contains an octahedral complex of cobalt(III) and nitrate(III) ions (NO_2^-). Analysis shows that Cobalt Yellow contains 13.0% of cobalt, 18.6% of nitrogen and 25.9% of potassium by mass. The remainder is oxygen.

(a) Use these data to calculate the empirical formula of Cobalt Yellow. Show your working.

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(3)

(b) Deduce the structural formula of the cobalt-containing ion in Cobalt Yellow.

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(1)
(Total 4 marks)

7 Iron(II) ethanedioate is another insoluble solid used as a pigment in paints and glass. It occurs as a dihydrate ($FeC_2O_4.2H_2O$). One procedure used for the preparation of iron(II) ethanedioate is outlined below.

Procedure

A 6.95 g sample of hydrated iron(II) sulfate ($FeSO_4.7H_2O$) was added to 100 cm^3 of water in a beaker and stirred until all of the solid dissolved. A 150 cm^3 volume of 0.20 mol dm^{-3} sodium ethanedioate solution was added to the beaker. The mixture was stirred until precipitation was complete. After filtration, 3.31 g of the dihydrate ($FeC_2O_4.2H_2O$) were collected.

(a) Write an equation for the reaction between iron(II) sulfate and sodium ethanedioate.

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(1)

(b) Calculate the amount, in moles, of $FeSO_4.7H_2O$ in 6.95 g of hydrated iron(II) sulfate. Show your working.

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(2)

(c) Calculate the amount, in moles, of sodium ethanedioate in 150 cm^3 of 0.20 mol dm^{-3} sodium ethanedioate solution.

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(1)

(d) Calculate the percentage yield of iron(II) ethanedioate dihydrate (M_r = 179.8) formed in this reaction.
Give your answer to the appropriate precision. Show your working.

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(2)

(e) In this experiment, no side reactions take place, the reagents are pure and the reaction goes to completion.

Suggest **one** reason why the yield of iron(II) ethanedioate dihydrate in this experiment is less than 100%.

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(1)

(f) When dissolved in dilute sulfuric acid, the number of moles of ethanedioate ions in a pigment can be determined by titration with acidified potassium manganate(VII).

Explain why the titration of a sample of iron(II) ethanedioate would require a different amount of potassium manganate(VII) than a titration of an equimolar amount of copper(II) ethanedioate.

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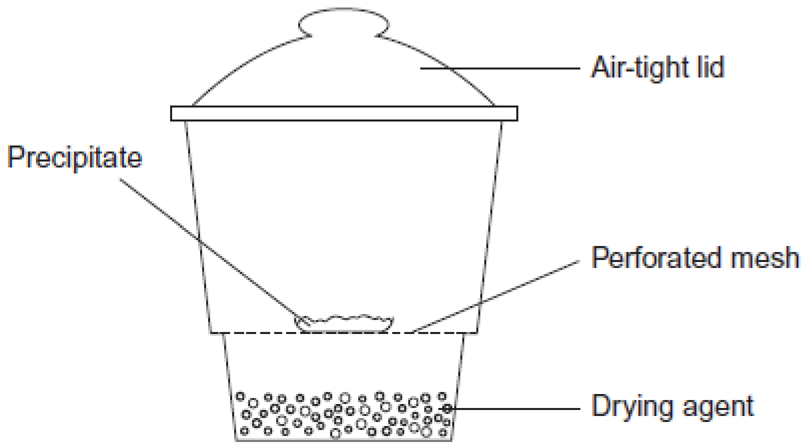
(2)
(Total 9 marks)

8 A desiccator can be used to dry precipitates as shown in the diagram.



(a) Explain briefly how the precipitate in the desiccator becomes dry.

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(1)

(b) Anhydrous cobalt(II) chloride is blue. It is often added to the drying agent to indicate the amount of moisture in the drying agent.

State the colour change of this cobalt compound that you would observe as the drying process takes place.

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(1)
(Total 2 marks)

9 An equation for the decomposition of hydrogen peroxide is

$$2H_2O_2 \longrightarrow 2H_2O \quad + \quad O_2$$

(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.

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(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).

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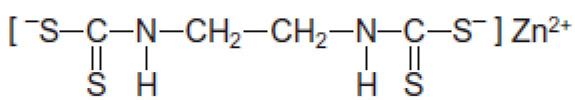
(2)
(Total 6 marks)

10 (a) Because of the toxic nature of the copper(II) ion, a wide range of alternative anti-fungal drugs has been developed for use in agriculture. One example is Zineb.



Zineb

(i) The negative ion in Zineb could act as a bidentate ligand.

On the structure above, draw a ring around each of **two** atoms that could provide the lone pairs of electrons when this ion acts as a bidentate ligand.

(1)

(ii) Calculate the M_r of Zineb. Give your answer to the appropriate precision.

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(1)

(iii) Name the functional group formed at each end of the negative ion when all the sulfur atoms in the structure of Zineb are replaced by oxygen atoms.

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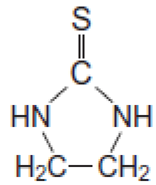
(1)

(b) Zineb has been investigated for harmful effects. Generally, Zineb has been found to be safe to use in agriculture. It is only slightly soluble in water and is sprayed onto plants. A breakdown product of Zineb is ethylene thiourea (ETU), which is very soluble in water. The structure of ETU is shown below.



Determine the percentage, by mass, of sulfur in ETU (M_r = 102.1).

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(1)

(c) Chromatography is a technique used to show the presence of a small amount of ETU in Zineb.

Outline how this technique is used to separate and identify ETU from a sample of Zineb powder.

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(4)

(Total 8 marks)

11 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.

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(1)

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

Equation 1

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Equation 2

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(2)

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

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

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(1)

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

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(1)

(d) The oxidation of $C_2O_4^{2-}$ 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*.

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(1)

(ii) Identify the autocatalyst in this reaction.

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(1)

(iii) Write **two** equations to show how the autocatalyst is involved in this oxidation of $C_2O_4^{2-}$ ions.

Equation 1

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Equation 2

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(2)
(Total 9 marks)

12 (a) Explain the meaning of the terms *ligand* and *bidentate* as applied to transition metal complexes.

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(2)

(b) Aqueous cobalt(II) ions react separately with an excess of chloride ions and with an excess of ammonia.

For each reaction, draw a diagram to illustrate the structure of, the shape of and the charge on the complex ion formed.

In each case, name the shape and indicate, on the diagram, a value for the ligand-metal-ligand bond angle.

(6)

(c) The complex ion formed in aqueous solution between cobalt(II) ions and chloride ions is a different colour from the $[Co(H_2O)_6]^{2+}$ ion.

Explain why these complex ions have different colours.

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(3)

(d) In aqueous ammonia, cobalt(II) ions are oxidised to cobalt(III) ions by hydrogen peroxide. The H_2O_2 is reduced to hydroxide ions.

Calculate the minimum volume of 5.00 mol dm^{-3} H_2O_2 solution required to oxidise the Co^{2+} ions in 9.87 g of $CoSO_4.7H_2O$

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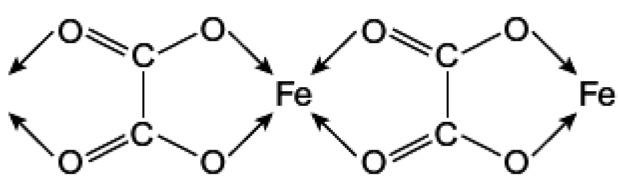
(5)
(Total 16 marks)

13 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.

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

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(1)

(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)

(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)

(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).

(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)

(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)
(Total 10 marks)