

1. This question is about Group 7 of the Periodic Table - the halogens. The standard electrode potentials for these elements are given below.

Electrode reaction	$E^\ominus / \text{V}$
$\frac{1}{2} \text{F}_2 + \text{e}^- \rightleftharpoons \text{F}^-$	+2.87
$\frac{1}{2} \text{Cl}_2 + \text{e}^- \rightleftharpoons \text{Cl}^-$	+1.36
$\frac{1}{2} \text{Br}_2 + \text{e}^- \rightleftharpoons \text{Br}^-$	+1.07
$\frac{1}{2} \text{I}_2 + \text{e}^- \rightleftharpoons \text{I}^-$	+0.54

- (a) (i) Define the term *standard electrode potential*.

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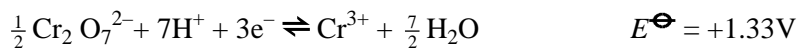
(2)

- (ii) State which element or ion in the table above is the strongest oxidising agent.

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(1)

- (b) The standard electrode potentials for chromium(III) changing to chromium(II) and for chromium(VI) changing to chromium(III) are given below.



- (i) On the basis of the data provided, list those halogens which will oxidise chromium(II) to chromium(III).

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(1)

- (ii) On the basis of the data provided, list those halogens which will oxidise chromium(II) to chromium(III) but not to chromium(VI).

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(1)

- (iii) Chromium(II) in aqueous solution is sky blue while aqueous chromium(III) solution is dark green. Describe how you would show that your prediction in part (ii) actually worked in practice.

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(2)

2. (a) The electronic configuration of a cobalt atom can be written as  $[\text{Ar}]3d^74s^2$ .  
Give the electronic configuration of the  $\text{Co}^{3+}$  ion.

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(1)

- (b) (i) By reference to the standard electrode potentials given below, suggest a reducing agent which might reduce aqueous  $\text{Co}^{3+}$  ions to cobalt metal. Give your reasoning.

	$E^\ominus / \text{V}$
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Zn}(\text{s})$	-0.76
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Fe}(\text{s})$	-0.44
$\text{Co}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Co}(\text{s})$	-0.28
$\text{Sn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Sn}(\text{s})$	-0.14
$\text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2\text{O}_2(\text{aq})$	+0.68
$\text{Co}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Co}^{2+}(\text{aq})$	+1.82

Suitable reducing agent .....

Reasoning .....

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- (ii) Suggest **two** factors that might prevent a reducing agent from being as effective as the electrode potentials might seem to suggest.

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(2)

- (c) (i) Write the formula of the hexaaquacobalt(II) ion.

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(1)

- (ii) Give an equation, involving the hexaaquacobalt(II) ion, to illustrate the process of ligand exchange.

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(2)

(Total 9 marks)

3. The concentration of iron(II) ions in a solution can be found by titration with standard potassium manganate(VII) solution. In the reaction iron(II) ions are oxidised to iron(III) ions.

If a solution contains both iron(II) and iron(III) ions, the concentration of each ion can be found by:

- titrating samples of the original solution with standard potassium manganate(VII) solution
- reacting samples of the original solution with zinc and dilute sulphuric acid and then titrating with the same potassium manganate(VII) solution.

The following standard electrode potentials are required:

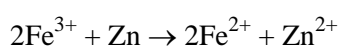
	$E^\ominus/V$
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	- 0.76
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	- 0.44
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+ 0.77
$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	+ 1.51

- (a) (i) Use suitable  $E^\ominus$  values to show that both iron(II) and iron(III) ions in solution should react with zinc to give iron metal.

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(3)

- (ii) In practice the reaction produces only iron(II) ions and no iron metal.



Suggest a reason for this.

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(1)

- (b) (i) Derive the ionic equation for the reaction between iron(II) ions and manganate(VII),  $\text{MnO}_4^-$ , ions.

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- (ii) State what you would see as iron(II) ions in solution are titrated with potassium manganate(VII). How would you detect the endpoint of the titration?

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- (c) A solution containing both iron(II) and iron(III) ions was titrated with  $0.0200 \text{ mol dm}^{-3}$  potassium manganate(VII) solution,  $18.20 \text{ cm}^3$  being required.

Another portion of the same volume of the same solution was reacted with zinc, and then titrated with the same potassium manganate(VII) solution;  $25.30 \text{ cm}^3$  was required.  
What mass of zinc had reacted?

(5)

- (d) (i) Explain, including an equation, why aqueous solutions of hexaaqua ions such as  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  are acidic.

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(3)

- (ii) Suggest with reasons which of  $0.1 \text{ mol dm}^{-3}$  aqueous solutions of  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  would be the more acidic.

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(Total 20 marks)

4. (a) (i) Define the term **standard electrode potential**, making clear the meaning of *standard* in this context.

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(2)

- (ii) Explain the need for a standard reference electrode in electrochemical measurements.

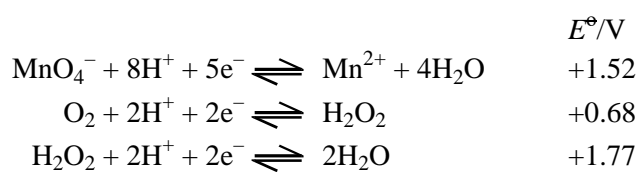
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(1)

- (b) The following data will be required in this part of the question.



- (i) Derive the equation for the reaction between hydrogen peroxide and manganate(VII) ions in acidic solution and use  $E^\ominus$  values to show that the reaction is feasible.

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(3)

- (ii) If a sample of hydrogen peroxide was titrated with potassium manganate(VII) solution, what would you see during the reaction, and then at the endpoint?

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(3)



- (iii) Derive the equation for the disproportionation of hydrogen peroxide and explain, in terms of oxidation states, why it is a disproportionation reaction.

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(3)  
 (Total 12 marks)

5. (a) (i) Give the electronic configuration of:

Fe [Ar].....

Fe<sup>2+</sup> [Ar].....

(2)

- (ii) Draw the structure of the hexaaquairon(II) ion,  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ , so as to clearly show its shape.

(1)

- (iii) Give the equation for the complete reaction of sodium hydroxide solution with a solution of hexaaquairon(II) ions.

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(1)

- (iv) State what you would **see** if the product mixture in (iii) is left to stand in air.

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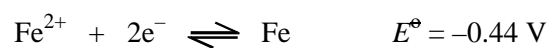
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- (v) Give the equation for a reaction in which iron metal is used as a catalyst.

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(1)

- (b) Consider the half reaction



- (i) Define the term **standard electrode potential** with reference to this electrode.

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(3)

- (ii) Explain, with the aid of an equation, why the value of  $E^\ominus$  suggests that iron will react with an aqueous solution of an acid to give  $\text{Fe}^{2+}$  ions and hydrogen gas.

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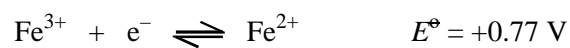
- (iii) State why  $E^\ominus$  values cannot predict that a reaction will occur, only that it is possible.

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(1)

- (c) Use the following standard electrode potentials to explain why iron(III) iodide does **not** exist in aqueous solution.



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(2)

(Total 15 marks)

6. (a) Define the term **standard electrode potential**.

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- (b) When a metal is placed in a solution of its ions, the electrical potential set up between the metal and the solution cannot be measured without using a reference electrode. Explain why this is so.

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(1)

- (c) The following data will be required in this part of the question.

	$E^\ominus/V$
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	-0.76
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	-0.44
$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$	-0.14
$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$	+0.40

- (i) Write an overall equation for the first stage in the rusting of iron.

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(2)

- (ii) Calculate  $E^\ominus$  for the reaction in (i) and show that it is feasible.

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(2)

- (iii) Use the  $E^\ominus$  values above to explain why zinc is used in preference to tin for preventing corrosion of steel car bodies.

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(3)

(Total 10 marks)

7. (a) The elements from scandium to zinc belong to the  $d$ -block. Some, but not all, of these elements are transition elements.

- (i) What is meant by the term **transition element**?

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(1)

- (ii) Which of the elements, from scandium to zinc inclusive, are in the  $d$ -block but are **not** transition elements?

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(1)

- (b) (i) Complete the electronic configurations of the  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  ions below.

$\text{Fe}^{2+}$  [Ar] .....

$\text{Mn}^{2+}$  [Ar] .....

(1)

- (ii) Suggest why  $\text{Fe}^{2+}$  ions are readily oxidised to  $\text{Fe}^{3+}$  ions, but  $\text{Mn}^{2+}$  ions are **not** readily oxidised to  $\text{Mn}^{3+}$  ions.

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(2)

- (c) Draw a diagram to show the three-dimensional structure of the  $[\text{Fe}(\text{CN})_6]^{4-}$  complex ion.

(2)

- (d) A solution of potassium manganate(VII),  $\text{KMnO}_4$ , can be standardised by titration with arsenic(III) oxide,  $\text{As}_2\text{O}_3$ . In this reaction, 5 mol of arsenic(III) oxide are oxidised to arsenic(V) oxide,  $\text{As}_2\text{O}_5$ , by 4 mol of manganate(VII) ions,  $\text{MnO}_4^-$ .

Calculate the final oxidation number of the manganese.

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(4)

(e) Ammonium vanadate(V),  $\text{NH}_4\text{VO}_3$ , reacts with dilute sulphuric acid to form a solution containing yellow  $\text{VO}_2^+$  ions.

(i) Write an **ionic** equation for the reaction of the anion in  $\text{NH}_4\text{VO}_3$  with dilute sulphuric acid.

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(1)

(ii) Is the reaction in (i) a redox reaction? Justify your answer.

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(1)

(iii) Addition of zinc to the solution containing  $\text{VO}_2^+$  ions causes the colour to change from yellow to green then to blue, followed by green again and finally violet. State the formulae of the ions responsible for each of these colours.

The first green colour .....

The second green colour .....

The violet colour .....

(3)

(Total 16 marks)

8. Domestic bleaches contain sodium chlorate(I), NaOCl.

- (a) Write the **ionic** equation to show the disproportionation of the chlorate(I) ion. Use oxidation numbers to explain the meaning of the term disproportionation in this reaction.

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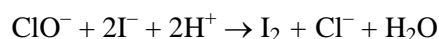
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(3)

- (b) Domestic bleaches are dilute solutions of sodium chlorate(I). The amount of ClO<sup>-</sup> ions in a sample can be found by reacting it with excess acidified potassium iodide solution.



The iodine produced is then titrated with standard sodium thiosulphate solution.

- 10.0 cm<sup>3</sup> of a domestic bleach was pipetted into a 250 cm<sup>3</sup> volumetric flask and made up to the mark with distilled water.
- A 25.0 cm<sup>3</sup> portion of the solution was added to excess acidified potassium iodide solution in a conical flask.
- This mixture was titrated with 0.100 mol dm<sup>-3</sup> sodium thiosulphate solution, using starch indicator added near the end point.
- The mean titre was 12.50 cm<sup>3</sup>.

- (i) Give the colour change you would see at the end point.

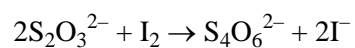
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(1)



- (ii) The equation for the reaction between iodine and thiosulphate ions is



Calculate the amount (moles) of chlorate(I) ions in 1.00 dm<sup>3</sup> of the **original** bleach.

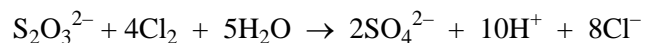
(5)

- (iii) Use the equation below to calculate the mass of chlorine available from 1.00 dm<sup>3</sup> of the **original** bleach. Give your answer to 3 significant figures.



(1)

- (c) Sodium thiosulphate can be used to remove the excess chlorine from bleached fabrics.



By considering the change in oxidation number of sulphur, explain whether chlorine or iodine is the stronger oxidising agent when reacted with thiosulphate ions.

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(2)

- (d) Starch-iodide paper can be used to test for chlorine. It contains starch and potassium iodide.

Explain the reactions taking place when a piece of damp starch-iodide paper is put in a gas jar of chlorine. State what you would see.

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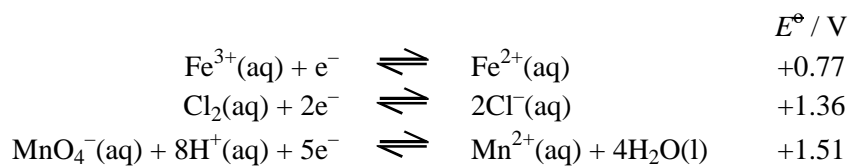
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(Total 14 marks)

9. This question concerns redox chemistry.

Consider the following data



- (a) (i) Use the data to explain why dilute hydrochloric acid is **not** used to acidify solutions of potassium manganate(VII).

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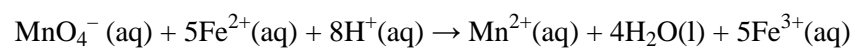
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- (ii) Explain why titrations involving potassium manganate(VII) solution do **not** require the addition of an indicator.

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(1)

- (b) (i) The ionic equation for the oxidation of iron(II) ions by manganate(VII) ions in acidic solution is



Explain, in terms of the half equations listed above, why the ratio of manganate(VII) ions to iron(ii) ions is 1 : 5 in this reaction.

(1)

- (ii) Patients suffering from iron deficiency are often prescribed tablets containing hydrated iron(II) sulphate,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ .

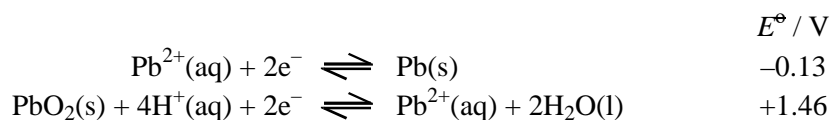
Some tablets, of total mass 6.00 g, were dissolved in distilled water and made up to  $200 \text{ cm}^3$  in a volumetric flask.  $25.0 \text{ cm}^3$  portions of this solution were titrated against a  $0.0200 \text{ mol dm}^{-3}$  solution of acidified potassium manganate(VII). The mean titre was  $20.10 \text{ cm}^3$ .

Calculate the percentage of hydrated iron(II) sulphate in the tablets.

[Molar mass  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O} = 278 \text{ g mol}^{-1}$ ]

(5)

- (c) An important application of redox reactions is in car batteries. The electrolyte is aqueous sulphuric acid and the standard electrode potentials involved are shown below.



- (i) Calculate the standard e.m.f. of the cell.

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(1)

- (ii) A single cell in a car battery has an e.m.f. of 2.00 V. Suggest why this value is different from the answer calculated in (i).

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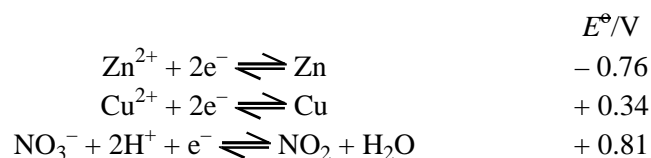
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(Total 11 marks)

10. Brass is a widely-used alloy that contains copper and zinc. There are many varieties of brass with different compositions.

In the volumetric analysis of the composition of brass, the first step is to react a weighed sample of the alloy with nitric acid. This gives a greenish-blue solution.

- (a) The following standard electrode potentials are needed for this question:



- (i) Use the **half equations given above** and the values of  $E^\ominus$  to calculate the standard electrode potential for the reaction between zinc and nitric acid and derive the equation.

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(2)

- (ii) Suggest why zinc does **not** produce hydrogen with nitric acid.

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(2)

- (iii) If the greenish-blue solution is diluted with water it turns light blue and contains hydrated copper(II) ions.

Name the light blue complex ion and draw its structure so as to show its shape.

Name .....

Structure:

(2)

- (iv) If concentrated hydrochloric acid is added to a portion of the light blue solution it turns green.

State the type of reaction that occurs and give an equation for the reaction.

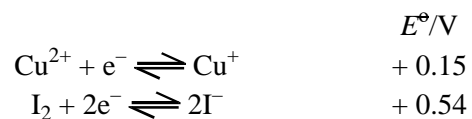
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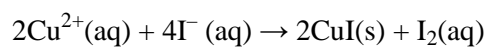
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- (b) The light blue solution from (a)(iii) is then neutralised, and reacted with an excess of potassium iodide solution.

The following standard electrode potentials are needed:



- (i) Use these  $E^\ominus$  values to explain why you would **not** expect the following reaction to occur.



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(1)

- (ii) Explain why, in practice, the reaction in (i) does occur and iodine is liberated.

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- (iii) When the precipitate formed in the reaction in (i) is filtered off and then dissolved in concentrated aqueous ammonia, a colourless solution is produced.

Suggest the formula of the cation in this solution.

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- (iv) If the colourless solution from (iii) is left to stand in air for some time, it turns blue.

State why this is so, naming the reactant responsible for the change.

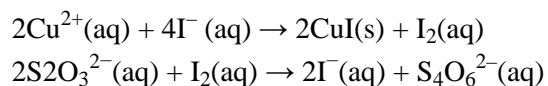
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- (c) In a determination of the composition of a sample of brass, 1.50 g of the alloy was treated to give 250 cm<sup>3</sup> of a neutral solution of copper(II) nitrate and zinc nitrate.

Excess potassium iodide solution was added to 25.0 cm<sup>3</sup> portions of this solution, and the liberated iodine titrated with 0.100 mol dm<sup>-3</sup> sodium thiosulphate solution. The mean titre was 16.55 cm<sup>3</sup>.



- (i) State which indicator you would use for the titration and the colour change seen at the end point.

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- (ii) Explain why the indicator is **not** added until the reaction is nearly complete.

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- (iii) Calculate the percentage of copper by mass in this brass.

(5)  
 (Total 22 marks)

11. (a) Define the term **standard electrode potential**, making clear the meaning of *standard*.

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(2)

- (b) Explain why a reference electrode is needed whenever a standard electrode potential is measured.

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(1)

- (c) Hydrogen peroxide decomposes in a disproportionation reaction.

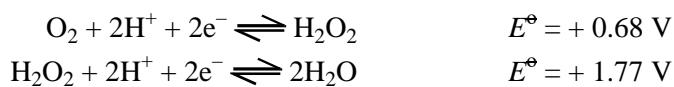
- (i) Explain the meaning of **disproportionation**.

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(2)

- (ii) Use the following information to derive the equation for the disproportionation of hydrogen peroxide.

Calculate  $E^\circ_{\text{cell}}$  and explain whether the reaction is thermodynamically feasible.



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- (iii) Explain why your answer to (ii) does not necessarily show that hydrogen peroxide will disproportionate under standard conditions.

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(Total 9 marks)

12. (a) The conversion of butan-2-ol to 2-bromobutane can be performed as outlined below:

- Butan-2-ol is heated with a mixture of 50 % aqueous sulphuric acid and sodium bromide for 45 minutes.
- The crude 2-bromobutane is distilled off.
- The crude 2-bromobutane is shaken with pure water, which removes the sulphuric acid and some of the butan-2-ol that contaminates the product.
- The organic layer is separated and then shaken with concentrated hydrochloric acid to remove residual butan-2-ol.
- The organic layer is then shaken with dilute sodium carbonate solution.
- Anhydrous calcium chloride is added to the organic layer and allowed to stand for some hours.
- The organic layer is then redistilled in a dry apparatus.

(i) Explain, in terms of kinetic factors, why the mixture is heated for a significant amount of time.

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(ii) Why is sulphuric acid necessary in the reaction mixture?

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(iii) Suggest why butan-2-ol, which is only partially miscible with water, is much more soluble in concentrated hydrochloric acid.

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(2)

(iv) Why is the organic layer shaken with dilute sodium carbonate solution?

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(1)

(v) What is the purpose of the anhydrous calcium chloride?

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(1)

(vi) How would you heat the mixture safely? Explain your choice of method.

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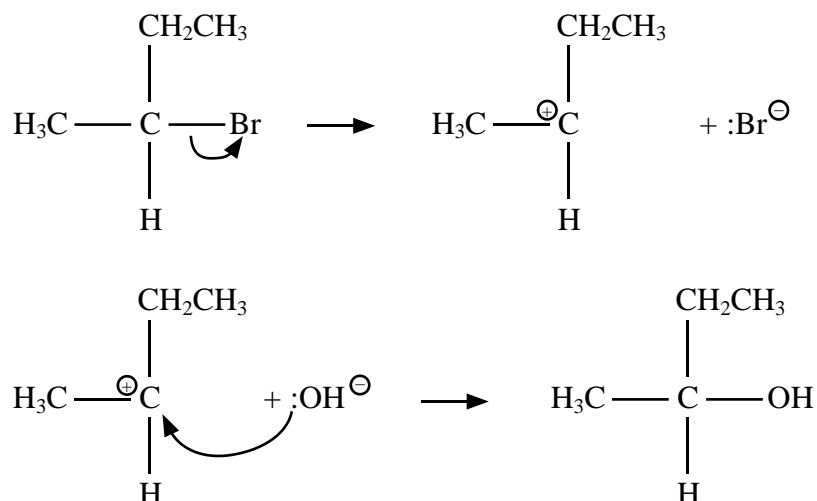
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- (b) Both 2-bromobutane and butan-2-ol are chiral molecules.

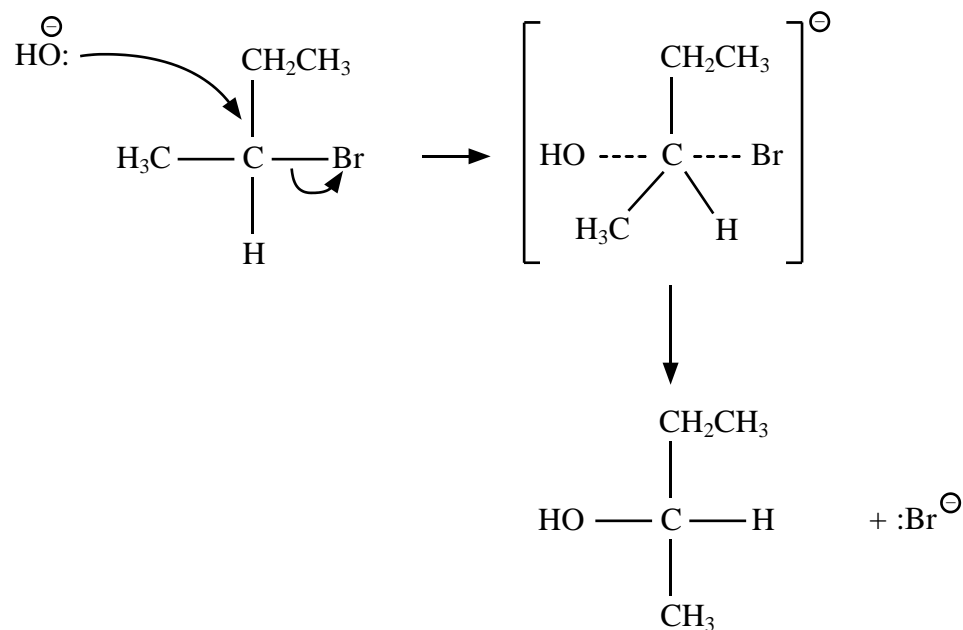
If one optical isomer of 2-bromobutane is used to make butan-2-ol by reaction with aqueous hydroxide ions, the product mixture is **not** optically active.

The mechanism for the reaction is either  $S_N1$  or  $S_N2$ ; these are given below

$S_N1$



$S_N2$



Explain which one of these mechanisms is consistent with the lack of optical activity in the product mixture.

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(3)

(c) The oxidation of butan-2-ol with hot potassium dichromate(VI) in acidic solution produces butanone,  $\text{CH}_3\text{COCH}_2\text{CH}_3$ .

(i) What would you **see** as the reaction proceeds?

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(1)

(ii) The dichromate(VI) ion is reduced under these conditions to chromium(III) ions.

The half-equation for the oxidation of butan-2-ol to butanone is



Write the ionic half-equation for the reduction of dichromate(VI) ions, and hence derive the overall equation for the oxidation of butan-2-ol.

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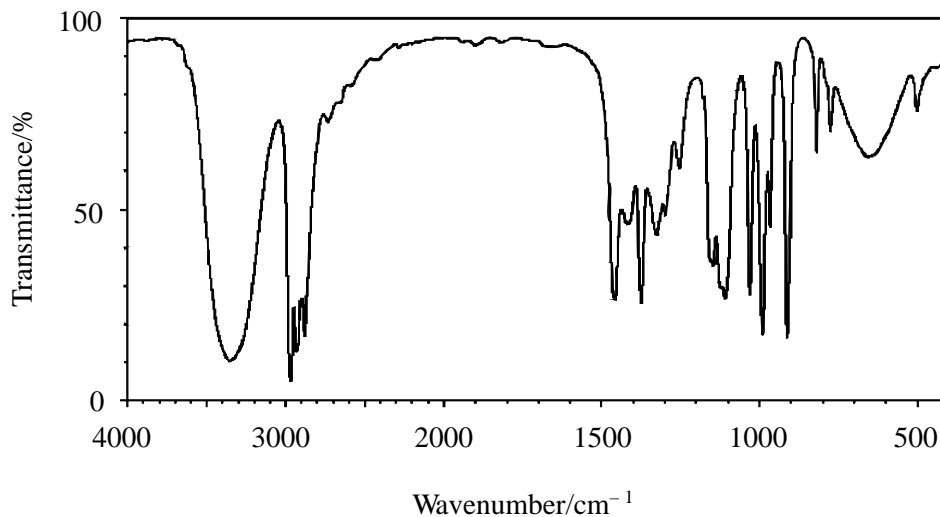
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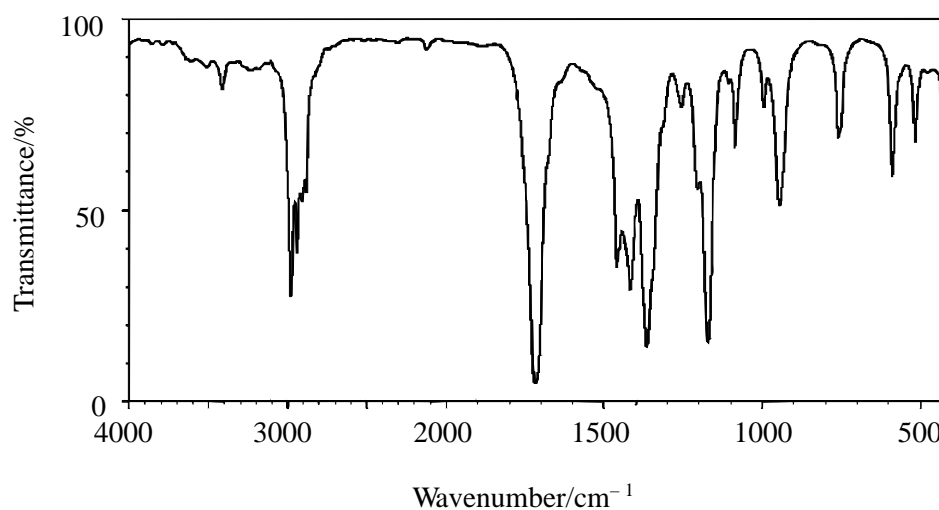
(2)

- (iii) The IR spectra of butan-2-ol and of the organic product from its oxidation with dichromate(VI) ions are given below.

Spectrum of butan-2-ol



Spectrum of the organic product from the oxidation of butan-2-ol



Bond	Wavenumber/cm <sup>-1</sup>	Bond	Wavenumber/cm <sup>-1</sup>
C—H (alkanes)	2850–3000	C—O (alcohols, esters)	1000–1300
C—H (alkenes)	3000–3100	O—H (hydrogen-bonded alcohols)	3230–3550
C=O (aldehydes, ketones, carboxylic acids)	1680–1750	O—H (hydrogen-bonded carboxylic acids)	2500–3300



What evidence is there from the spectra that the reaction in part (ii) has occurred?

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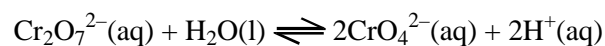
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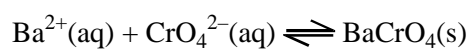
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(2)

- (d) When potassium dichromate(VI) is dissolved in water, the following equilibrium is set up



- (i) If a solution of barium ions is then added to **this solution**, solid barium chromate,  $\text{BaCrO}_4$ , is precipitated; it is sparingly soluble in water, so the equilibrium given below also exists in the solution



Explain what happens to the pH when the barium ions are added.

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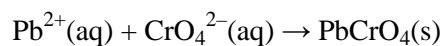
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(2)

- (ii) If a solution of lead(II) ions is added instead of barium ions, solid  $\text{PbCrO}_4$  is precipitated. This is almost completely insoluble in water so all chromate(VI) ions are removed from solution



State how the pH of this solution differs from your answer in part (i).

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(1)

(Total 20 marks)

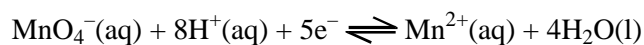
13. In a standard hydrogen electrode
- A the hydrogen gas is at one atmosphere pressure
  - B a solution of  $1 \text{ mol dm}^{-3}$  sulfuric acid is used
  - C a temperature of 273 K is maintained
  - D a piece of shiny platinum foil is used

(Total 1 mark)

14. For a redox reaction to be thermodynamically feasible,  $E_{\text{cell}}$  must be
- A positive
  - B negative
  - C greater than +0.3 V
  - D more negative than -0.3 V

(Total 1 mark)

15. The standard electrode potential for the electrode system based on the equation below is +1.51 V.



Which of the following statements about the electrode system is correct?

- A the electrode potential at pH 5 is +1.51 V.
- B  $\text{Mn}^{2+}(\text{aq})$  is acting as an oxidising agent.
- C changing the concentration of  $\text{Mn}^{2+}(\text{aq})$  would cause a change in the electrode potential.
- D the electrode used in this half-cell is made of manganese.

(Total 1 mark)

16. Which of the following is always proportional to  $E_{\text{cell}}$  for a chemical reaction?

- A  $\Delta H_{\text{r}}$
- B  $\Delta S_{\text{system}}$
- C  $\Delta S_{\text{surroundings}}$
- D  $\Delta S_{\text{total}}$

(Total 1 mark)

17. Methanol can be vigorously oxidised with an acidified solution containing dichromate(VI) ions,  $\text{Cr}_2\text{O}_7^{2-}$ , to form methanoic acid and chromic(III) ions.

- (a) What are the oxidation numbers of **carbon** in methanol and methanoic acid?

	Methanol	Methanoic acid
A	-1	+1
B	-2	+2
C	+1	-1
D	+2	-2

(1)

(b) How many moles of methanol react with one mole of dichromate(VI) ion,  $\text{Cr}_2\text{O}_7^{2-}$ ?

- A 1
- B  $\frac{3}{4}$
- C  $1\frac{1}{2}$
- D 3

(1)  
(Total 2 marks)

18. (a) (i) Give the electron configuration of:

Fe [Ar] .....

$\text{Fe}^{2+}$  [Ar] .....

(1)

(ii) Draw the structure of the hexaaquairon(II) ion,  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ , clearly showing its shape.

(1)

(iii) Give the equation for the complete reaction of hydroxide ions with a solution of hexaaquairon(II) ions.

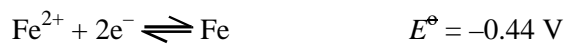
(1)

- (iv) State what you would **see** if the product mixture in (iii) is left to stand in air.

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(1)

- (b) Consider the equation for the half reaction



- (i) Define the term **standard electrode potential** with reference to this electrode.

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(3)

- (ii) Explain why the value of  $E^{\ominus}$  suggests that the iron will react with an aqueous solution of an acid to give  $\text{Fe}^{2+}$  ions and hydrogen gas.

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(2)

- (iii) State why  $E^\ominus$  values cannot predict that a reaction will occur, only that it is possible.

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(1)  
(Total 10 marks)