

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

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(2)

(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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(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)

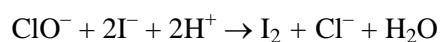
2. Domestic bleaches contain sodium chlorate(I), NaOCl.

(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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(3)

- (b) Domestic bleaches are dilute solutions of sodium chlorate(I). The amount of ClO^- 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.

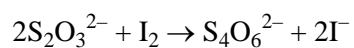
- 10.0 cm^3 of a domestic bleach was pipetted into a 250 cm^3 volumetric flask and made up to the mark with distilled water.
- A 25.0 cm^3 portion of the solution was added to excess acidified potassium iodide solution in a conical flask.
- This mixture was titrated with $0.100 \text{ mol dm}^{-3}$ sodium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

- (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 dm³ of the **original** bleach.

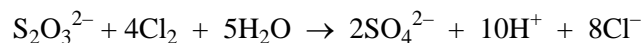
(5)

- (iii) Use the equation below to calculate the mass of chlorine available from 1.00 dm³ 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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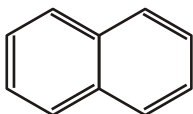
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(2)
(Total 14 marks)

3. This question is about the arene, naphthalene. The structure of naphthalene can be shown as

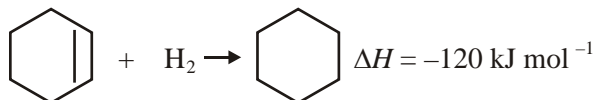


(a) What is the molecular formula of naphthalene?

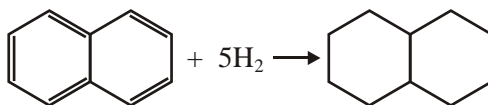
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(1)

(b) The enthalpy change, ΔH , for the addition of hydrogen to cyclohexene to form cyclohexane is -120 kJ mol^{-1} .



(i) Calculate the enthalpy change of the hydrogenation reaction shown below.



$\Delta H = \dots\dots\dots \text{ kJ mol}^{-1}$

(1)

(ii) Experimental work shows that ΔH for the hydrogenation of naphthalene is actually -333 kJ mol^{-1} . What does this suggest about the stability and structure of naphthalene?

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(2)

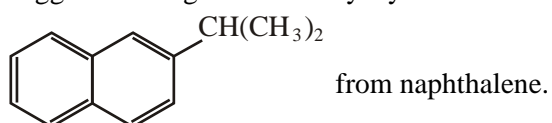
- (iii) Would you expect naphthalene to decolorise bromine solution? Justify your answer.

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(1)

- (c) The Friedel-Crafts reaction enables an alkyl group to be attached to an arene ring.

- (i) Suggest the reagent and catalyst you would need to make



Reagent

Catalyst

(2)

- (ii) Name the type of reaction and its mechanism.

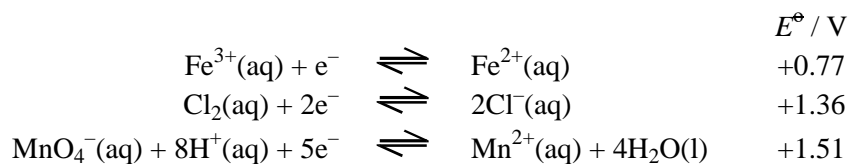
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(2)

(Total 9 marks)

4. 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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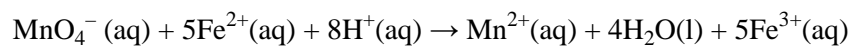
(2)

- (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, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.

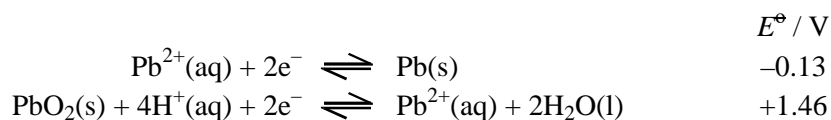
Some tablets, of total mass 6.00 g, were dissolved in distilled water and made up to 200 cm^3 in a volumetric flask. 25.0 cm^3 portions of this solution were titrated against a $0.0200 \text{ mol dm}^{-3}$ solution of acidified potassium manganate(VII). The mean titre was 20.10 cm^3 .

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)

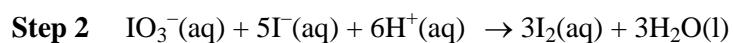
- (ii) A single cell in a car battery has an e.m.f. of 2.00 V. Suggest why this value is different from the answer calculated in (i).

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(1)
(Total 11 marks)

5. The element iodine can be produced from the mineral Chile saltpetre, which contains sodium iodate, NaIO₃. The iodate ions are converted to iodine in a two-step process.

Ionic equations for the reactions are shown below.



- (a) (i) Describe a test you could carry out to confirm the presence of iodide **ions** in a solution. Indicate the result of the test.

Test

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Result

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(2)

- (ii) Identify the TWO elements in **Step 1** which show a change of oxidation number during the reaction.

Give their initial and final oxidation numbers.

First element Second element

Initial oxidation number Initial oxidation number

Final oxidation number Final oxidation number

(3)

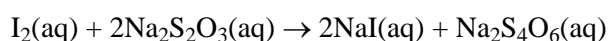
- (iii) The equation for **Step 1** shows that 1 mole of iodate ions, IO_3^- , reacts with 3 moles of hydrogensulphite ions, HSO_3^- . Show that your answers to (ii) agree with this ratio.

(1)

- (b) An experiment was carried out to determine the concentration of the iodine prepared in **Step 2**

A 10.0 cm^3 portion of the iodine solution was titrated with sodium thiosulphate solution of concentration $0.0100 \text{ mol dm}^{-3}$. The volume of sodium thiosulphate solution added at the end-point was 24.0 cm^3 .

The equation for the reaction is



- (i) What piece of apparatus would you use to measure out the 10.0 cm^3 portion?

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(1)

- (ii) Suggest a suitable indicator to show the end-point of this titration. State the colour change you would see.

Indicator

Fromto

(2)

(iii) Calculate the number of moles of sodium thiosulphate used in the titration.

(1)

(iv) Calculate the number of moles of iodine which reacted with the sodium thiosulphate solution.

(1)

(v) Calculate the concentration, in mol dm^{-3} , of the iodine solution.

(1)
(Total 12 marks)

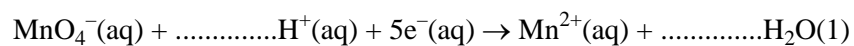
6. Air is drawn through 10.0 cm³ of an aqueous solution of vanadium(II) chloride of concentration 0.100 mol dm⁻³. The colour of the solution slowly changes as oxidation takes place.

The air-oxidised solution is titrated with a solution of acidified potassium manganate(VII) of concentration 0.0200 mol dm⁻³. The end point is found to be 20.0 cm³.

- (i) Draw a diagram of suitable apparatus for carrying out the air-oxidation of the vanadium(II) chloride solution.

(1)

- (ii) Complete the half equation for acidified manganate(VII) ions acting as an oxidising agent.



(1)

- (iii) Calculate the number of moles of manganate(VII) ions used in the titration, and hence the number of moles of electrons removed by the manganate(VII) ions.

Calculate the number of moles of vanadium(II) ions in the 10 cm³ of solution used. Find the oxidation number of vanadium in the air-oxidised solution given that vanadium(V) ions are formed in the titration.

(4)

- (iv) Suggest ONE reason why acidified potassium manganate(VII) is a useful oxidising agent in redox titrations.

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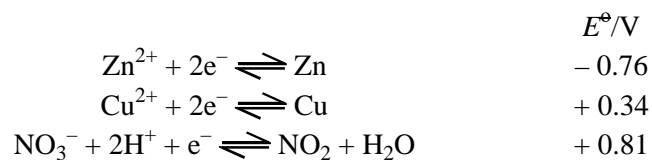
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(Total 7 marks)

7. 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.

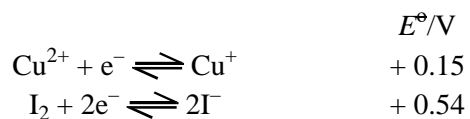
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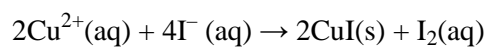
(2)

- (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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(2)

- (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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(1)

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

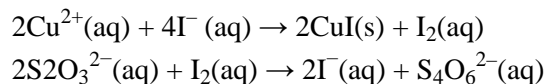
State why this is so, naming the reactant responsible for the change.

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(2)

- (c) In a determination of the composition of a sample of brass, 1.50 g of the alloy was treated to give 250 cm³ of a neutral solution of copper(II) nitrate and zinc nitrate.

Excess potassium iodide solution was added to 25.0 cm³ portions of this solution, and the liberated iodine titrated with 0.100 mol dm⁻³ sodium thiosulphate solution. The mean titre was 16.55 cm³.



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

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(2)

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

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(1)

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

(5)
(Total 22 marks)

8. (a) Give the electronic configuration of:

Cu : [Ar]

Cu⁺: [Ar]

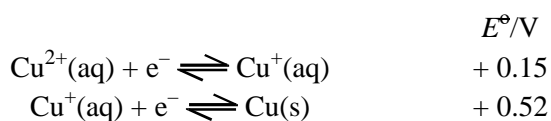
(1)

(b) (i) Explain why Cu⁺ ions are colourless.

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(2)

(ii) Copper(I) ions disproportionate in aqueous solution. Give the equation for the reaction and use the standard electrode potentials given below to explain why the reaction occurs.



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(2)

(iii) Explain why your answer to (ii) does **not** rule out the existence of Cu⁺(aq) under standard conditions.

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(1)

- (c) (i) When a **small** amount of dilute ammonia solution is added to a solution of copper(II) sulphate, a turquoise blue precipitate, **F**, is formed.

F has the composition Cu 49.4%, S 12.5%, O 37.4%, H 0.78% by mass. Calculate its empirical formula.

(2)

- (ii) When **F** is dissolved in dilute hydrochloric acid, the resulting blue solution gives a white precipitate with barium chloride solution.

Suggest a formula for **F**, given that all the hydrogen is present in hydroxide ions.

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(2)

- (iii) When excess concentrated ammonia is added to **F**, a deep blue solution is formed. Give the formula of the ion responsible for this colour.

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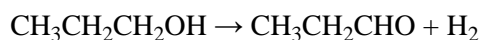
(1)

- (iv) What **type** of reaction is occurring in (iii)?

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(1)

- (d) Copper metal can be used as a catalyst. When propan-1-ol vapour is passed over heated copper, the following reaction occurs:



- (i) **Outline** how, by the use of 2,4-dinitrophenylhydrazine and suitable tables of data, you could show that the product is propanal.

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(4)

- (ii) When propan-1-ol is oxidised with a solution of potassium dichromate(VI) in dilute sulphuric acid care must be taken to avoid further oxidation of the aldehyde product. How is this achieved?

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(1)

- (iii) What is the further oxidation product of the aldehyde?

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(1)

- (iv) Suggest why the oxidation of the alcohol by passing it over heated copper does **not** lead to further oxidation of the aldehyde.

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(1)

- (v) There are a few places on the surface of the metal where catalysis can occur. These are called 'active sites'.

Suggest why this leads to the rate of reaction being independent of the gas pressure unless this pressure is extremely low.

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(1)

(Total 20 marks)

9. (a) (i) Complete the electronic configurations of:

Cr: [Ar].....

Cu: [Ar].....

(1)

- (ii) The electronic configurations of chromium and of copper are not readily predictable from a consideration of the elements on either side of them in the first transition series in the Periodic Table.

State how these electronic configurations differ from others in the first transition series and explain why this difference arises.

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(2)

(b) Chromium can form the ion $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ in aqueous solution.

(i) Draw the structure of this ion so as to clearly show its shape.

(1)

(ii) How are the bonds between the water ligands and the metal ion formed?

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(1)

(iii) Write an equation to show what happens initially when a solution containing hydroxide ions is added to a solution of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ ions.

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(2)

(iv) State what you would **see** as dilute sodium hydroxide is gradually added to a solution of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ until it is in excess.

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(2)

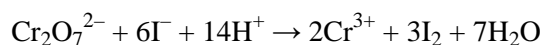
(v) What property of chromium(III) hydroxide is shown by the reaction in part (iv)?

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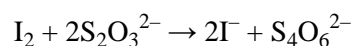
(1)

(c) (i) A 1.00 g sample of a metal alloy that contains chromium was converted into 250 cm³ of an acidified solution of potassium dichromate(VI).

25.0 cm³ of this solution was added to an excess of potassium iodide solution.



The iodine liberated was titrated with 0.100 mol dm⁻³ sodium thiosulphate solution.



The mean (average) titre was 37.2 cm³.

Calculate the amount (moles) of iodine liberated and hence the percentage, by mass, of chromium in the alloy.

(5)

(ii) In titrations involving iodine, starch is usually added near the end-point to make the colour change clearer, although in many cases it is not really necessary.

Suggest why starch **is** necessary in the titration in (i).

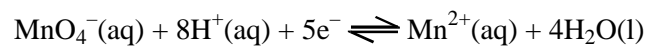
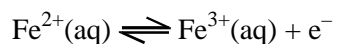
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(Total 16 marks)

10. A firm claims that their iron tablets contain 10 mg of Fe^{2+} per tablet. A chemist wishes to check this by titration using potassium manganate(VII) and dilute sulfuric acid.



- (a) Why is the acid necessary?

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(1)

- (b) How many moles of Fe^{2+} react with one mole of MnO_4^{-} ?

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(1)

- (c) Each tablet contains 10 mg of Fe^{2+} .

- (i) How many moles of Fe^{2+} are in one tablet?

(1)

(ii) Use your answer to (i) to calculate the volume of $0.010 \text{ mol dm}^{-3}$ potassium manganate(VII) solution that would be needed to react with one tablet.

(2)

(iii) Is this a suitable volume to verify the integrity of the firm's claim? How would you alter the experiment to obtain a more suitable volume?

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(1)

- (d) The recommended consumption of Fe^{2+} per day is 14 mg. The tolerable upper level of consumption of Fe^{2+} per day is 45 mg.

The “10 mg iron tablets” produced by a pharmaceutical company contain between 9 and 11 mg of Fe^{2+} .

Discuss whether or not this range of iron content is acceptable.

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(2)
(Total 8 marks)