

AQA A2 CHEMISTRY

TOPIC 5.4

TRANSITION METALS

PART 2 – REDOX REACTIONS AND CATALYSIS

BOOKLET OF PAST EXAMINATION QUESTIONS

1. Chemical reactions can be affected by homogeneous or by heterogeneous catalysts.

- (a) Explain what is meant by the term *homogeneous* and suggest the most important feature in the mechanism of this type of catalysis when carried out by a transition-metal compound.

Homogeneous

.....

Most important mechanistic feature

.....

(2)

- (b) In aqueous solution, $\text{S}_2\text{O}_8^{2-}$ ions can be reduced to SO_4^{2-} ions by I^- ions.

- (i) Write an equation for this reaction.

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- (ii) Suggest why the reaction has a high activation energy, making it slow in the absence of a catalyst.

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- (iii) Iron salts can catalyse this reaction. Write two equations to show the role of the catalyst in this reaction.

Equation 1

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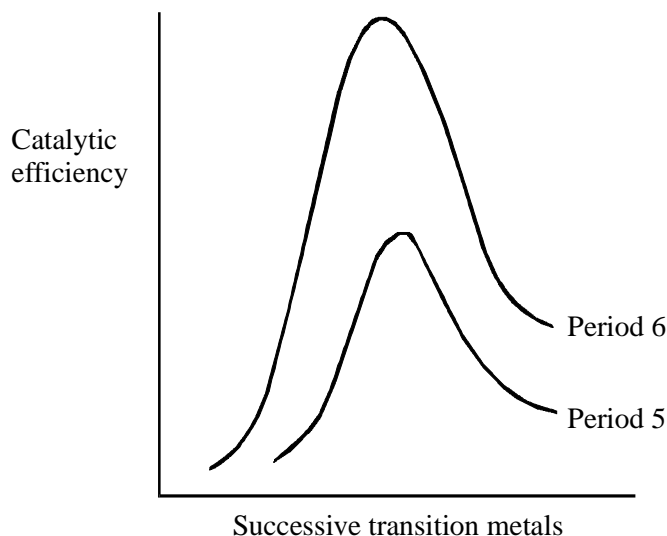
Equation 2

.....

.....

(4)

- (c) Below is a sketch showing typical catalytic efficiencies of transition metals from Period 5 (Rb to Xe) and Period 6 (Cs to Rn) when used in heterogeneous catalysis.



- (i) Identify two metals which lie at opposite ends of these curves and explain why they show rather low catalytic efficiency.

Identity of metal 1

Reason for low efficiency

Identity of metal 2

Reason for low efficiency

- (ii) Suggest why these curves pass through a maximum.

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.....

(5)

- (d) In catalytic converters which clean up petrol engine exhaust gases, a catalyst promotes the reduction of nitrogen oxides using another polluting gas as reductant. State a suitable catalyst for this task, identify the reductant, and write an equation for the reaction that results.

Catalyst

Identity of reductant

Equation

.....

(3)

(Total 14 marks)

2. (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.

.....

(2)

(Total 10 marks)

3. Transition elements and their compounds are often used as catalysts.

- (i) Explain why catalysts do not affect the position of an equilibrium.

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.....

- (ii) Write an equation for one large-scale industrial process in which a transition element is used as a catalyst. State the catalyst used.

Equation.....

Catalyst.....

(4)
(Total 4 marks)

4. A 0.263 g sample of impure iron, containing an unreactive impurity, was reacted with an excess of hydrochloric acid. All of the iron in the sample reacted, evolving hydrogen gas and forming a solution of iron(II) chloride. The volume of hydrogen evolved was 102 cm³, measured at 298 K and 110 kPa.

The percentage, by mass, of iron in the sample can be determined using either the volume of hydrogen produced or by titrating the solution of iron(II) chloride formed against a standard solution of potassium dichromate(VI).

- (a) (i) Write an equation for the reaction between iron and hydrochloric acid.

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- (ii) Calculate the number of moles of hydrogen produced in the reaction.

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- (iii) Use your answers to parts (a)(i) and (ii) to determine the number of moles of iron and the mass of iron in the original sample. (If you have been unable to complete part (a)(ii) you should assume the answer to be 4.25×10^{-3} mol. This is not the correct answer.)

Moles of iron

Mass of iron

- (iv) Calculate the percentage of iron in the original sample.

.....
.....

(7)

- (b) (i) Write half-equations for the oxidation of Fe^{2+} and for the reduction of $\text{Cr}_2\text{O}_7^{2-}$ in acidic solution, and use these to construct an overall equation for the reaction between these two ions.

Half-equation for the oxidation of Fe^{2+}

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Half-equation for the reduction of $\text{Cr}_2\text{O}_7^{2-}$

.....

Overall equation

.....

- (ii) The number of moles of iron in the sample was determined in part (a)(iii). Use this answer to calculate the volume of a $0.0200 \text{ mol dm}^{-3}$ solution of potassium dichromate(VI) which would react exactly with the solution of iron(II) chloride formed in the reaction.

(If you have been unable to complete part (a)(iii) you should assume the answer to be $3.63 \times 10^{-3} \text{ mol}$. This is not the correct answer.)

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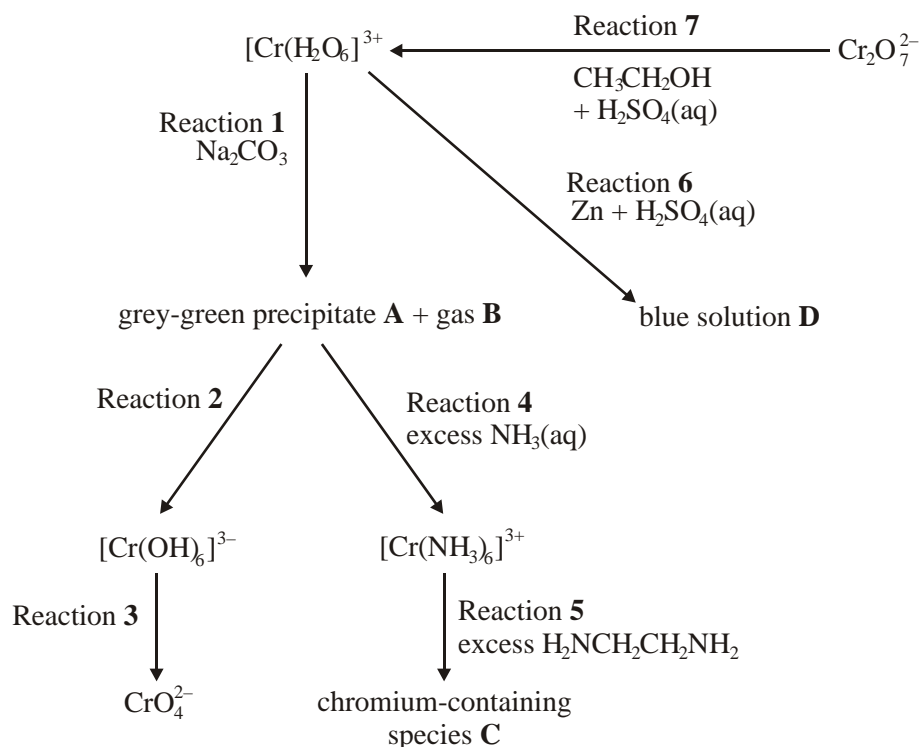
- (iii) Explain why an incorrect value for the number of moles of iron(II) chloride formed would have been obtained if the original solution had been titrated with potassium manganate(VII).

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(7)
(Total 14 marks)

5. The following scheme shows some reactions of chromium compounds in aqueous solution.



- (a) (i) Identify a reagent for Reaction 2.

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- (ii) Deduce the oxidation state of chromium in CrO_4^{2-}

.....

- (iii) Identify a reagent needed for Reaction 3. Write a half-equation for the conversion of $[\text{Cr}(\text{OH})_6]^{3-}$ into CrO_4^{2-}

Reagent

Half-equation

(4)

- (b) Identify the chromium-containing species present in the blue solution **D** formed in Reaction 6 and state the role of zinc in its formation.

Chromium-containing species

Role of zinc.....

(2)

- (c) Two organic compounds are formed in Reaction 7. One of these compounds has a low boiling point and can be distilled readily from the reaction mixture. The other compound has a higher boiling point and is the main organic product formed when the reaction mixture is refluxed.

(i) Identify the organic product which has a low boiling point.

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(ii) Identify the main organic product formed when the mixture is refluxed.

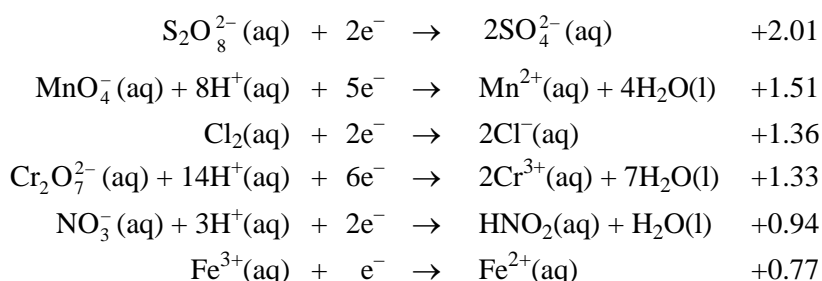
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(2)

(Total 8 marks)

6. Use the data below, where appropriate, to answer the following questions.

Standard electrode potentials E°/V



- (a) State the colours of the following species in aqueous solution.

(i) $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$

(ii) $\text{Cr}^{3+}(\text{aq})$

(iii) $\text{MnO}_4^-(\text{aq})$

(3)

- (b) The concentration of iron(II) ions in aqueous solution can be determined by titrating the solution, after acidification, with a standard solution of potassium manganate(VII).

(i) Explain, by reference to the data given in the table above, why hydrochloric acid should not be used to acidify the solution containing iron(II) ions.

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(ii) Explain, by reference to the data given in the table above, why nitric acid should not be used to acidify the solution containing iron(II) ions.

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(4)

(Total 7 marks)

7. (a) Give two examples of transition metals which, for different reasons, do not behave as good heterogeneous catalysts. In each case explain the poor catalytic activity.

Metal 1.....

Explanation.....

.....

Metal 2.....

Explanation.....

.....

(6)

- (b) (i) Explain why the rate of a reaction increases when a catalyst is used.

.....

.....

.....

- (ii) Give one example of a reaction in which a homogeneous catalyst is used. Identify the catalyst.

Reaction.....

Catalyst.....

(4)

(Total 10 marks)

8. (a) Define the term *oxidising agent* in terms of electrons.

.....

(1)

- (b) Give an example of a vanadium compound which acts as a catalyst, and give an equation for the process which it catalysed.

Catalyst

Equation for process catalysed.....

(2)

- (c) Describe briefly how you would show that manganese(II) ions catalyse the reaction between manganate(VII) ions and ethanedioate ions, $\text{C}_2\text{O}_4^{2-}$, in dilute sulphuric acid.

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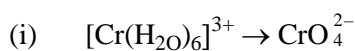
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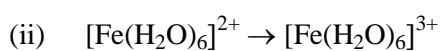
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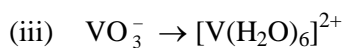
- (d) Give the reagents required to carry out each of the following conversions.



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(6)

(Total 12 marks)

9. (a) (i) State, in general terms, how a catalyst works.

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.....

- (ii) State a property of transition metal ions which enables them to act as homogeneous catalysts.

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- (iii) Give one example of a reaction in which a transition metal species is used as a homogeneous catalyst. Identify the catalyst used.

Reaction

Catalyst used

(5)

(b) Heterogeneous catalysts are used extensively in industrial processes.

(i) What is meant by the term *heterogeneous*?

.....

(ii) State three essential steps in the mechanism of heterogeneous catalysis.

Step 1

Step 2

Step 3

(4)

(c) (i) Identify the catalyst used in the Haber Process.

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(ii) Identify a substance which acts as a poison for this catalyst and explain how poisoning occurs.

Catalyst poison

Explanation

(3)

(Total 12 marks)

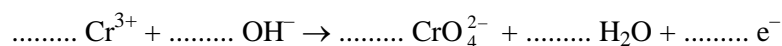
10. (a) Chromium(III) ions can be oxidised to CrO_4^{2-} ions by hydrogen peroxide in alkaline solution.

(i) State the oxidation state of chromium in CrO_4^{2-} .

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(1)

(ii) Balance the following ionic half-equation.



(1)

(b) (i) Write an equation for the reaction that occurs when an aqueous solution containing CrO_4^{2-} ions is acidified.

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(1)

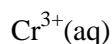
(ii) State the colour change observed as the reaction in (d)(i) takes place.

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(2)

(Total 5 marks)

11. Describe by stating essential reagents and conditions how, starting from potassium dichromate(VI), you would obtain a solution containing each of the following ions as the only chromium species. Give an equation for the reaction in each case.



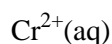
Reagent(s)

Conditions

Equation

.....

.....



Reagent(s)

Conditions

Equation

.....

.....

(9)

(Total 9 marks)

12. (a) Explain why the strengths of adsorption of reactants and products onto the surface of a catalyst are important factors in determining catalytic activity.

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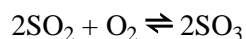
(2)

- (b) Give a reason, other than strength of adsorption, why the adsorption of reactants onto a catalyst surface does not always result in a reaction.

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(1)

- (c) Although the equilibrium constant, K_p , for the reaction



is $4 \times 10^{22} \text{ kPa}^{-1}$ at 298 K, sulphur dioxide does not react readily with oxygen at this temperature.

- (i) Explain why this reaction does not occur readily.

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- (ii) The reaction between sulphur dioxide and oxygen is catalysed by nitrogen dioxide, NO_2 . The mechanism involves the formation of nitrogen monoxide, NO . Suggest two equations to show how NO_2 could be involved as a catalyst in this reaction.

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(3)

(Total 6 marks)

13. Wilkinson's catalyst is a complex compound containing the transition metal rhodium, bonded to one chloride and three triphenylphosphine ligands. It can be represented by the formula $[\text{RhCl}(\text{PPh}_3)_3]$ where the phenyl group, C_6H_5 , is written as Ph. In solution, this compound is a homogeneous catalyst for the hydrogenation of alkenes.

- (a) (i) State three characteristic features of a catalyst.

Feature 1

Feature 2

Feature 3

- (ii) Explain what is meant by the term *homogeneous* in the paragraph above.

.....

- (iii) Deduce the oxidation state and the co-ordination number of rhodium in Wilkinson's catalyst.

Oxidation state

Co-ordination number

- (iv) What feature of the triphenylphosphine molecule enables it to act as a ligand?

.....

(7)

- (b) In the mechanism of the reaction of cyclohexene with hydrogen, catalysed by Wilkinson's catalyst, the intermediate $[\text{RhCl}(\text{H})_2(\text{PPh}_3)_3]$ is formed.

- (i) Write an overall equation for the reaction of cyclohexene with hydrogen.

.....

- (ii) By stating a reagent and an observation, give a chemical test which would show that this hydrogenation reaction has gone to completion.

Reagent(s)

Observation(s)

- (iii) What feature of rhodium chemistry allows this catalyst to function?

.....

(4)

(Total 11 marks)

14. (a) State the difference between homogeneous and heterogeneous catalysis.

.....

.....

.....

(2)

- (b) Explain the term *activation energy*.

.....

.....

.....

(2)

- (c) In the examples below, decide whether the catalyst is homogeneous or heterogeneous, and explain how it provides an alternative route of lower activation energy in each case.

- (i) The Contact Process

Homogeneous or heterogeneous.....

Explanation of catalysis.....

.....

- (ii) Enzyme catalysed reactions

Homogeneous or heterogeneous.....

Explanation of catalysis.....

.....

(6)

- (d) Suggest **two** different measures that can be taken to maximise the efficiency and minimise the costs associated with a very expensive heterogeneous catalyst.

Measure 1.....

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Measure 2.....

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(2)

(Total 12 marks)

15. In a practical assessment, a candidate was required to analyse a sample of ammonium iron(II) sulphate-6-water, $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, by titrating weighed samples against 0.0200 M KMnO_4

- (a) The candidate was told to dissolve the weighed sample in water and to add one further reagent before titrating against 0.0200M KMnO_4 . Identify a suitable reagent and state the colour change at the end-point of the titration.

Reagent.....

End-point.....

(2)

- (b) Write the half-equations for the two reactions occurring in the redox reaction of iron(II) with manganate(VII) ions and deduce an overall equation for this reaction.

Half-equation for iron (II).....

Half-equation for manganate(VII).....

Overall equation.....

(3)

- (c) Calculate the mass of pure $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ which reacts exactly with 25.0 cm^3 of 0.0200M KMnO_4

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(4)

(Total 9 marks)

16. A chemist was given three aqueous solutions of metal sulphates and asked to identify the cation present in each of the solutions. The table below shows the results of some tests that were carried out by the chemist.

Solution	Colour of Solution	Result of reacting the solution with aqueous sodium hydroxide	Result of reacting an acidified solution with a strong oxidising agent
A	Blue	Pale blue gelatinous precipitate	No change
B	Pale pink	Buff precipitate	Purple solution
C	Green	Green gelatinous precipitate	Orange solution

- (a) Give the formula of the hydrated coloured ion in:

- (i) solution A;

.....

(1)

- (ii) solution C.

.....

(1)

- (b) Give the formula of the coloured ion produced by oxidation of:

- (i) solution B;

.....

(1)

- (ii) solution C.

.....

(1)

- (c) A standard solution of the purple ion obtained from **B** can be used to determine the concentration of a solution of ethanedioate ions.

- (i) Outline the experimental procedure for carrying out this determination.

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(5)

- (ii) Write an ionic equation to represent the reaction occurring.

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(2)

- (d) (i) Complete the electronic configuration of an iron atom.

$1s^2$

(1)

- (ii) Suggest why iron has **two** common oxidation states in its aqueous chemistry.

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(2)

(Total 14 marks)

17. (a) State the difference between homogeneous and heterogeneous catalysis.

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.....

(1)

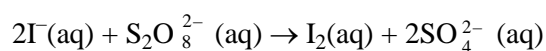
- (b) State **two** reasons why an inert medium is sometimes used as a support for a heterogeneous catalyst.

Reason 1.....

Reason 2.....

(2)

- (c) Soluble iron salts catalyse the following reaction.



Suggest a reason why the reaction is likely to be slow in the absence of a catalyst. Write **two** equations to illustrate the action of the catalyst and explain why both iron(II) salts and iron(III) salts can catalyse this reaction.

Reason.....

Equation 1.....

Equation 2.....

Explanation for catalysis by iron (II) or iron(III) salts.....

.....
.....

(4)

- (d) (i) State **three** important features in the mechanism of heterogeneous catalysis.

Feature 1.....

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Feature 2.....

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Feature 3.....

.....

- (ii) Write equations for **two** reactions which undergo heterogeneous catalysis by a transition metal or one of its compounds.

Equation 1.....

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Equation 2.....

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(5)

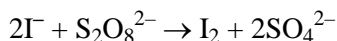
(Total 12 marks)

18. 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)

(Total 6 marks)

19. (a) Explain the following, writing equations where appropriate.
- (i) When aqueous potassium manganate(VII) solution is added dropwise to an acidified solution of ethanedioate ions, the potassium manganate(VII) solution is decolourised slowly at first but more rapidly as more potassium manganate(VII) solution is added. (In this reaction the ethanedioate ions, $\text{C}_2\text{O}_4^{2-}$ are oxidised to carbon dioxide.)
- (ii) The aqueous reaction between iodide ions and peroxodisulphate ions proceeds very slowly.



The addition of a little iron(II) sulphate increases the rate of reaction but the addition of magnesium sulphate has no effect on the rate.

(10)

- (b) A catalyst containing molybdenum(VI) was analysed for its molybdenum content by reducing a sample to the molybdenum(III) state and then titrating with acidified potassium manganate(VII) which oxidises molybdenum(III) back to molybdenum(VI).

A 0.330 g sample of the catalyst, after reduction, was found to require 27.5 cm^3 of 0.0200 M potassium manganate(VII) to convert the molybdenum(III) into molybdenum(VI).

Calculate the percentage by mass of molybdenum in the catalyst.

(5)

(Total 15 marks)

20. (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)

21. (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.

(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 potassium manganate(VII) solution were required to oxidise all vanadium(II) ions to vanadium(V) ions.

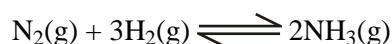
Using half-equations, construct an overall equation for the reduction of VO_2^+ to V^{2+} by zinc in acidic solution.

Calculate the percentage by mass of vanadium in the sample of ammonium vanadate(V).

(8)

(Total 15 marks)

22. 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)

(Total 5 marks)

23. (a) Explain why the reaction between sodium ethanedioate, $\text{Na}_2\text{C}_2\text{O}_4$, and potassium manganate(VII) in acidified aqueous solution is initially slow but gradually increases in rate. Write equations to illustrate your answer.

(6)

- (b) State what is meant by the term *active site* as applied to a heterogeneous catalyst. Explain how the number of active sites can be increased for a given mass of catalyst. The efficiency of a heterogeneous catalyst often decreases during use. Explain, using a specific example, why this happens.

(4)

(Total 10 marks)

24. (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)

25. A 0.223 g sample of a mixture of ammonium dichromate(VI), $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$, and ammonium chloride was dissolved in dilute sulphuric acid. When this solution was titrated with 0.100 M iron(II) sulphate solution, 24.0 cm^3 were required to reduce all the dichromate(VI) ions.

Construct an ionic equation for the reaction between dichromate(VI) ions and iron(II) ions in acidic solution and use it to calculate the ratio of the number of moles of ammonium dichromate(VI) to ammonium chloride in the mixture.

(Total 10 marks)

26. (a) A proprietary moss killer is a mixture of sand and hydrated iron (II) sulphate. Outline the plan of an experiment to determine the percentage by mass of iron (II) in a sample of this moss killer using a standard solution of potassium dichromate(VI). You must show in your answer how you would calculate the result of the experiment.

(8)

- (b) Explain the following observations.

- (i) Sulphur dioxide reacts quickly with oxygen if vanadium(V) oxide is present.
- (ii) When a solution of potassium manganate(VII) is added dropwise to an acidified solution of sodium ethanedioate, the purple colour is decolourised only slowly at first but then more rapidly as more potassium manganate(VII) is added.

(7)

(Total 15 marks)

27. (a) Explain why some elements in the d block of the Periodic Table are poor heterogeneous catalysts. Illustrate your answer by reference to specific elements.

(4)

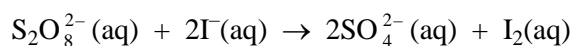
- (b) Explain why, in some commercial processes, gaseous reactants are blown through powder coated with solid catalyst.

(4)

- (c) Very small amounts of impurity in mixtures of reactants can drastically reduce catalytic activity. Give **one** example of this effect and explain why this happens.

(4)

- (d) Suggest why the following reaction



is slow unless a small amount of a soluble iron salt is added.

(3)

(Total 15 marks)

28. (a) Describe what you would see, and explain the changes which occur, when each of the following solutions is treated with an excess of zinc and hydrochloric acid in an apparatus which excludes air.

(i) potassium dichromate(VI)

(ii) ammonium vanadate(V)

(10)

- (b) (i) Explain fully the meaning of the term *homogeneous catalyst* and explain, with an example, how transition metal ions are able to act as homogeneous catalysts.
- (ii) Outline an experiment to determine whether manganese(II) ions will catalyse the reaction between persulphate ions and iodide ions in aqueous solution according to the equation

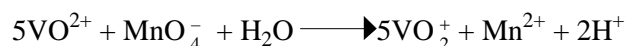


(12)

- (c) In a heterogeneous catalysis experiment, vanadium(V) oxide was heated in sulphur dioxide to produce vanadium(IV) oxide, but the reaction did not go to completion. In order to determine how much vanadium(IV) oxide was produced, the mixture of oxides was dissolved in dilute sulphuric acid to give a solution containing ions of both vanadium(IV) (as VO^{2+}) and vanadium(V) (as VO_2^+)



The mixture of ions was titrated against potassium manganate(VII) solution when the vanadium(IV) ions were oxidised to vanadium(V) ions according to the equation



The vanadium(V) ions do not react with manganate(VII) ions.

A 0.300g sample of the mixed oxides required 25.0 cm³ of 0.0200 M potassium manganate(VII) solution for complete reaction.

- (i) Write the equation for the reaction of vanadium(V) oxide with sulphur dioxide.
- (ii) Calculate the percentage of VO_2 in the mixture of oxides.

(8)

(Total 30 marks)