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Transition metals 2

2002

XVIII

1583

CHEMISTRY

Question Paper

AQA
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Inorganic Chemistry

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1

- (a) Octahedral and tetrahedral complex ions are produced by the reaction of transition metal ions with ligands which form co-ordinate bonds with the transition metal ion. Define the term *ligand* and explain what is meant by the term *co-ordinate bond*.

(3)

- (b) (i) Some complex ions can undergo a ligand substitution reaction in which both the co-ordination number of the metal and the colour change in the reaction. Write an equation for one such reaction and state the colours of the complex ions involved.

- (ii) Bidentate ligands replace unidentate ligands in a metal complex by a ligand substitution reaction.

Write an equation for such a reaction and explain why this reaction occurs.

(8)

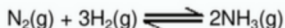
- (c) The frequency, ν , of light absorbed by a transition metal complex ion can be determined using the relationship $\Delta E = h\nu$. State what is meant by the symbols ΔE and h . Give **three** factors which result in a change in the frequency of light absorbed as a result of the reaction of a complex ion.

(5)

(Total 16 marks)

2

- (a) 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)



- (b) State what is observed when an excess of aqueous ammonia reacts with an aqueous iron(II) salt. Write an equation for this reaction.

(4)

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(Total 9 marks)

3

A 0.0720 g sample of reducing agent **R** was dissolved in water and acidified with an excess of dilute H_2SO_4 . The resulting solution was found to react with exactly 18.0 cm^3 of a $0.0200 \text{ mol dm}^{-3}$ solution of KMnO_4 .

In this reaction, 5 mol of **R** react with 3 mol of KMnO_4 . The M_r of **R** is

- A 120
- B 167
- C 240
- D 333

(Total 1 mark)



4

Summarised directions for recording responses to multiple completion questions			
A (i), (ii) and (iii) only	B (i) and (iii) only	C (ii) and (iv) only	D (iv) alone

Which of the following statements about a catalyst is / are true?

- (i) It speeds up the forward reaction and slows down the reverse action.
- (iii) It increases the proportion of molecules with higher energies.
- (iii) A homogeneous catalyst usually acts in the solid state.
- (iv) It does not alter the value of the equilibrium constant.

(Total 1 mark)

5

The vanadium does **not** have an oxidation state of +3 in

- A $[\text{V}(\text{H}_2\text{O})_6]^{3+}$
- B $[\text{V}(\text{C}_2\text{O}_4)_3]^{3-}$
- C $[\text{V}(\text{OH})_3(\text{H}_2\text{O})_3]$
- D $[\text{VCl}_4]^{3-}$

(Total 1 mark)

6

(a) State what is meant by each of the following terms.

- (i) *Ligand*
-
- (ii) *Complex ion*
-
- (iii) *Co-ordination number*
-

(3)

(b) Using complex ions formed by Co^{2+} with ligands selected from H_2O , NH_3 , Cl^- , $\text{C}_2\text{O}_4^{2-}$ and EDTA^{4-} , give an equation for each of the following.

- (i) A ligand substitution reaction which occurs with no change in either the co-ordination number or in the charge on the complex ion.

.....



EXAM PAPERS PRACTICE

- (ii) A ligand substitution reaction which occurs with both a change in the co-ordination number and in the charge on the complex ion.

.....

- (iii) A ligand substitution reaction which occurs with no change in the co-ordination number but a change in the charge on the complex ion.

.....

- (iv) A ligand substitution reaction in which there is a large change in entropy.

.....

(8)

- (c) An aqueous solution of iron(II) sulphate is a pale-green colour. When aqueous sodium hydroxide is added to this solution a green precipitate is formed. On standing in air, the green precipitate slowly turns brown.

- (i) Give the formula of the complex ion responsible for the pale-green colour.

.....

- (ii) Give the formula of the green precipitate.

.....

- (iii) Suggest an explanation for the change in the colour of the precipitate.

.....

.....

(4)

(Total 15 marks)

7

- (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)



8

Summarised directions for recording responses to multiple completion questions			
A	B	C	D
(i), (ii) and (iii) only	(i) and (iii) only	(ii) and (iv) only	(iv) alone

In which of the following conversions is the copper reduced?

- (i) $[\text{Cu}(\text{H}_2\text{O})_6]^{2+} \rightarrow [\text{CuCl}_4]^{2-}$
- (ii) $[\text{Cu}(\text{H}_2\text{O})_6]^{2+} \rightarrow \text{Cu}(\text{H}_2\text{O})_4(\text{OH})_2$
- (iii) $\text{Cu} \rightarrow \text{CuCl}_2$
- (iv) $[\text{Cu}(\text{H}_2\text{O})_6]^{2+} \rightarrow \text{CuCl}$

(Total 1 mark)

9

Which one of the following electronic configurations is that of a transition element?

- A $[\text{Ar}] 4s^2 3d^{10}$
- B $[\text{Ar}] 4s^2 3d^9$
- C $[\text{A}] 4s^2 3d^0$
- D $[\text{Ar}] 4s^2 3d^{10} 4p^1$

(Total 1 mark)

10

When vanadium reacts with chlorine at 400°C , a brown compound is obtained. When an aqueous solution containing 0.193 g of this compound was treated with aqueous silver nitrate all the chlorine in the compound was precipitated as silver chloride. The mass of silver chloride (AgCl) produced was 0.574 g. Which one of the following could be the formula of the brown compound?

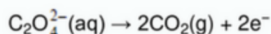
- A VCl
- B VCl_2
- C VCl_3
- D VCl_4

(Total 1 mark)



11

The oxidation of ethanedioate (*oxalate*) ions by manganate(VII) ions can be represented by the half equations:



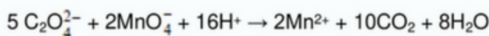
What volume (in cm^3) of 0.02 M KMnO_4 is required to oxidise completely a solution containing 0.02 mol of ethanedioate ions?

- A 25
- B 40
- C 250
- D 400

(Total 1 mark)

12

Aqueous $\text{C}_2\text{O}_4^{2-}$ ions react with MnO_4^- ions in acidic solution according to the equation



Under the same conditions Fe^{2+} ions also react with MnO_4^- ions. How many moles of MnO_4^- ions are required to react exactly with one mole of $\text{Fe}(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$?

- A 0.4
- B 0.6
- C 2.5
- D 7.5

(Total 1 mark)

13

Which of the species given below can behave as ligands?



- A all three
- B only NH_3
- C NH_3 and NH_4^+
- D NH_2^- and NH_3

(Total 1 mark)



- 14** In which one of the following reactions does the metal species undergo reduction?
- A** $\text{MnO}_2 + 4\text{HCl} \rightarrow \text{MnCl}_2 + 2\text{H}_2\text{O} + \text{Cl}_2$
- B** $[\text{Cu}(\text{H}_2\text{O})_6]^{2+} + 4\text{Cl}^- \rightarrow [\text{CuCl}_4]^{2-} + 6\text{H}_2\text{O}$
- C** $\text{CrO}_7^{3-} + 2\text{OH}^- \rightarrow 2\text{CrO}_4^{3-} + \text{H}_2\text{O}$
- D** $\text{TiO}_2 + 2\text{C} + 2\text{Cl}_2 \rightarrow \text{TiCl}_4 + 2\text{CO}$

(Total 1 mark)

- 15** Which one of the following statements is true?
- A** A blue solution containing the ion $[\text{CoCl}_4]^{2-}$ turns pink when added to an excess of water.
- B** A purple solution is formed when chlorine is bubbled into aqueous sodium bromide.
- C** A yellow precipitate is formed when aqueous silver nitrate is added to aqueous sodium chloride.
- D** A green solution containing the ion $[\text{CuCl}_4]^{2-}$ turns blue when added to an excess of concentrated hydrochloric acid.

(Total 1 mark)

- 16** The percentage of iron in a sample of impure iron(II) sulphate crystals can be determined by titrating solutions, made from separate weighed samples acidified with dilute sulphuric acid, against a standard solution of potassium manganate(VII).

Which one of the following would lead to an inaccurate result?

- A** transferring the weighed sample of iron(II) sulphate into a wet conical flask
- B** failing to measure accurately the volume of water used to dissolve each weighed sample of iron(II) sulphate
- C** transferring the standard solution of potassium manganate(VII) from its original container to the burette using a wet beaker
- D** failing to measure accurately the volume of dilute sulphuric acid added to the mixture before titration

(Total 1 mark)



- 17** The percentage of iron in a sample of impure iron(II) sulphate crystals can be determined by titrating solutions, made from separate weighed samples acidified with dilute sulphuric acid, against a standard solution of potassium manganate(VII).

Which one of the following would lead to the greatest error in the calculation of the percentage of iron(II) in the sample?

- A an error of 0.005 g made when weighing out a sample of mass 0.987 g
- B an end-point error of 0.1 cm³ in 25.0 cm³
- C an error of 5 cm³ when measuring out 25.0 cm³ of dilute sulphuric acid
- D using the average of the titration values 25.4, 25.7 and 25.9 when the correct value is 25.5 cm³

(Total 1 mark)

- 18** The percentage of iron in a sample of impure iron(II) sulphate crystals can be determined by titrating solutions, made from separate weighed samples acidified with dilute sulphuric acid, against a standard solution of potassium manganate(VII).

Which one of the following statements explains why dilute hydrochloric acid is unsuitable for use in this titration?

- A HCl will oxidise Fe²⁺ to Fe³⁺
- B Cl⁻ will reduce Fe³⁺ to Fe²⁺
- C Cl⁻ will reduce MnO₄⁻
- D HCl is a strong acid

(Total 1 mark)

- 19** Which one of the following can act as an oxidising agent but not as a reducing agent?

- A CH₃CHO
- B Fe²⁺
- C I⁻
- D MnO₄⁻

(Total 1 mark)



20

Which one of the following statements about the reaction below is **false**?



- A $[\text{Cu}(\text{EDTA})]^{2-}$ is a more stable complex than $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$
- B Both $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Cu}(\text{EDTA})]^{2-}$ are octahedral complexes.
- C There is an increase in entropy when the reaction occurs.
- D There is a redox reaction.

(Total 1 mark)

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

- (a) State what is meant by the term *co-ordinate bond*.

.....
.....

(2)

- (b) Define the terms *Brønsted–Lowry acid* and *Lewis acid*.

Brønsted–Lowry acid

Lewis acid

(2)

- (c) State what is meant by the term *bidentate ligand*.

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(2)

- (d) State how the co-ordination number of cobalt(II) ions in aqueous solution changes when an excess of chloride ions is added. Give a reason for the change.

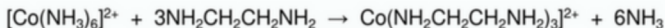
Change in co-ordination number

Reason for change

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(2)

- (e) Suggest why the enthalpy change for the following reaction is close to zero.



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(2)

- (f) Deduce the formula of the compound formed when ethane-1,2-diamine is treated with an excess of hydrochloric acid.

.....

(1)

(Total 11 marks)



- 23** (a) The reaction between aqueous persulphate ions, $S_2O_8^{2-}(aq)$, and iodide ions, $I^-(aq)$, is catalysed by $Fe^{2+}(aq)$ ions. Suggest why this reaction has a high activation energy. Write equations to explain the catalytic action of $Fe^{2+}(aq)$ ions. Suggest why $V^{3+}(aq)$ ions will also act as a catalyst for this reaction but $Mg^{2+}(aq)$ ions will not. (6)
- (b) Outline a mechanism for the reaction between benzene and ethanoyl chloride and explain why $AlCl_3$ acts as a Lewis acid catalyst for this reaction. Predict, with an explanation in each case, the suitability of $FeCl_3$ and of NH_4Cl to act as a catalyst for this reaction. (9)
- (Total 15 marks)

- 24** (a) State the origin of the colour of transition-metal complexes. (2)
-
-
- (b) Give **three** changes to a transition-metal complex which result in a change in colour. (3)
- Change 1
- Change 2
- Change 3
-



- (c) You are provided with a 1.00 mol dm^{-3} solution of iron(III) ions and a visible-light spectrophotometer (colorimeter). Outline a plan for experiments using this solution and this apparatus which would enable you to determine the concentration of iron(III) ions in a solution of unknown concentration.

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(5)
(Total 10 marks)

25

Transition metals form complex ions. Using actual examples of complex ions formed by transition metal ions, give the formula of

- a linear complex ion,
- a tetrahedral complex ion and
- an octahedral complex ion formed by using a bidentate ligand.

(Total 4 marks)

26

Use your knowledge of the chemistry of transition metals to predict which of the following will convert $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ into MnO_4^{2-}

- A an acid and a reducing agent
- B an acid and an oxidising agent
- C an alkali and a reducing agent
- D an alkali and an oxidising agent

(Total 1 mark)



27

(a) The ion $\text{C}_2\text{O}_4^{2-}$ can act as a bidentate ligand.

(i) Explain the meaning of the term *bidentate ligand*.

.....
.....

(ii) Sketch the structure of the octahedral complex ion formed by Fe^{3+} ions which contains $\text{C}_2\text{O}_4^{2-}$ as the only ligand. Include the overall charge on the complex ion.

(5)

(b) Explain the meaning of the term *chelate effect*.

.....
.....

(2)

(c) The chloride ion can act as a monodentate ligand.

(i) Deduce the formula of the linear complex formed when an excess of concentrated hydrochloric acid is added to silver chloride.

.....

(ii) Explain why metal(II) ions do not usually form octahedral complexes when chloride ions are the only ligands.

.....

(2)

(d) The concentration of $\text{C}_2\text{O}_4^{2-}$ ions can be determined by titration in acidic solution using a standard solution of potassium manganate(VII). At room temperature, the reaction proceeds very slowly at first but becomes faster after some of the manganate(VII) ions have reacted.

(i) Suggest why this reaction is very slow at first.

.....



- (ii) This is an example of an autocatalytic reaction. State the meaning of the term *autocatalytic* and identify the catalyst.

Meaning of the term autocatalytic

Catalyst

- (iii) Suggest how this catalyst might be involved in the reaction.

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(5)
(Total 14 marks)

28

Which one of the following would **not** react with aqueous silver nitrate to produce a precipitate that is soluble in concentrated aqueous ammonia?

- A CaBr_2
B $[\text{COCl}_4]^{2-}$
C $(\text{CH}_3)_4\text{N}^+\text{I}^-$
D CH_3COCl

(Total 1 mark)

29

Which one of the following would **not** reduce an acidified aqueous solution of potassium dichromate(VI)?

- A CH_3COOH
B Zn
C CH_3CHO
D $\text{Fe}^{2+}(\text{aq})$

(Total 1 mark)



30 Which one of the following could **not** act as a ligand?

- A F^-
B CH_3CH_3
C NH_2NH_2
D CH_3OCH_3

(Total 1 mark)

31 In the table below, which one of the following complex ions has a correct shape, co-ordination number and oxidation state?

	Complex	Shape	Co-ordination number	Oxidation state of central cation
A	$[Ag(CN)_2]^-$	Linear	2	-1
B	$[CuCl_4]^{2-}$	Tetrahedral	4	-2
C	$[Cr(C_2O_4)_3]^{3-}$	Octahedral	3	+3
D	$[Cu(NH_3)_4(H_2O)_2]^{2+}$	Octahedral	6	+2

(Total 1 mark)

32 (a) Give **one** example of a bidentate ligand.

.....

(1)

(b) Give **one** example of a linear complex ion formed by a transition metal.

.....

(1)

(c) Write an equation for a substitution reaction in which the complete replacement of ligands in a complex ion occurs with a change in **both** the co-ordination number and the overall charge of the complex ion.

.....

(2)

(d) Write an equation for a substitution reaction in which the complete replacement of ligands in a complex ion occurs without a change in either the co-ordination number or the overall charge of the complex ion.

.....

(2)



30 Which one of the following could **not** act as a ligand?

- A F^-
B CH_3CH_3
C NH_2NH_2
D CH_3OCH_3

(Total 1 mark)

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D	$[Cu(NH_3)_4(H_2O)_2]^{2+}$	Octahedral	6	+2

(Total 1 mark)

32 (a) Give **one** example of a bidentate ligand.

.....

(1)

(b) Give **one** example of a linear complex ion formed by a transition metal.

.....

(1)

(c) Write an equation for a substitution reaction in which the complete replacement of ligands in a complex ion occurs with a change in **both** the co-ordination number and the overall charge of the complex ion.

.....

(2)

(d) Write an equation for a substitution reaction in which the complete replacement of ligands in a complex ion occurs without a change in either the co-ordination number or the overall charge of the complex ion.

.....

(2)



- (e) When a solution containing $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ions is treated with a solution containing EDTA^{4-} ions, a more stable complex is formed. Write an equation for this reaction and explain why the complex is more stable.

Equation

Explanation

.....

(3)
(Total 9 marks)

33

- (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)