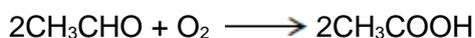


**Q15.**

This question explores some reactions and some uses of cobalt compounds.

- (a) Ethanal is oxidised to ethanoic acid by oxygen. The equation for this reaction is



This redox reaction is slow at room temperature but speeds up in the presence of cobalt compounds.

Explain why a cobalt compound is able to act as a catalyst for this process.

Illustrate your explanation with **two** equations to suggest how, in the presence of water and hydrogen ions, Co^{3+} and then Co^{2+} ions could be involved in catalysing this reaction.

(4)

- (b) In aqueous solution, the $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ion reacts with an excess of ethane-1,2-diamine to form the complex ion **Y**.

- (i) Write an equation for this reaction.

Explain, in terms of the chelate effect, why the complex ion **Y** is formed in preference to the $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ complex ion.

(3)

**Q16.**

Iron(II) ethanedioate is another insoluble solid used as a pigment in paints and glass. It occurs as a dihydrate ($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$). One procedure used for the preparation of iron(II) ethanedioate is outlined below.

Procedure

A 6.95 g sample of hydrated iron(II) sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) was added to 100 cm³ of water in a beaker and stirred until all of the solid dissolved. A 150 cm³ volume of 0.20 mol dm⁻³ sodium ethanedioate solution was added to the beaker. The mixture was stirred until precipitation was complete. After filtration, 3.31 g of the dihydrate ($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) were collected.

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

(1)

- (b) Calculate the amount, in moles, of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 6.95 g of hydrated iron(II) sulfate. Show your working.

(2)

- (c) Calculate the amount, in moles, of sodium ethanedioate in 150 cm³ of 0.20 mol dm⁻³ sodium ethanedioate solution.

(1)

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

(2)



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

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

(1)

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

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

(2)

(Total 9 marks)

Q17.

Transition metal compounds have a range of applications as catalysts.

- (a) State the general property of transition metals that allows the vanadium in vanadium(V) oxide to act as a catalyst in the Contact Process.

(1)

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

Equation 1

Equation 2

(2)



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

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

(1)

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

(1)

(d) The oxidation of $\text{C}_2\text{O}_4^{2-}$ ions by MnO_4^- ions in acidic solution is an example of a reaction that is autocatalysed.

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

(1)

(ii) Identify the autocatalyst in this reaction.

(1)

(iii) Write **two** equations to show how the autocatalyst is involved in this oxidation of $\text{C}_2\text{O}_4^{2-}$ ions.

Equation 1

Equation 2

(2)

(Total 9 marks)

**Q18.**

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

(2)

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

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

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

(6)



- (c) The complex ion formed in aqueous solution between cobalt(II) ions and chloride ions is a different colour from the $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ion.

Explain why these complex ions have different colours.

(3)

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

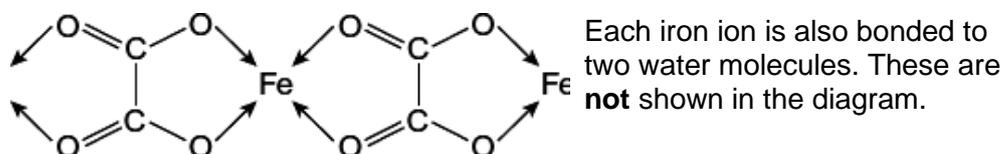
Calculate the minimum volume of $5.00 \text{ mol dm}^{-3} \text{ H}_2\text{O}_2$ solution required to oxidise the Co^{2+} ions in 9.87 g of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$

(5)

(Total 16 marks)

**Q19.**

Solid iron(II) ethanedioate dihydrate ($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) has a polymeric structure. Two repeating units in the polymer chain are shown.



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

(1)

- (b) In terms of electrons explain how the water molecules, **not** shown in the diagram, form bonds to the iron.

(2)

- (c) Predict the value of the bond angle between the two bonds to iron that are formed by these two water molecules.

(1)



- (b) Describe what you would observe when dilute aqueous sodium hydroxide is added, dropwise until in excess, to a dilute aqueous solution containing chromium(III) ions.

Write **two** equations to illustrate your observations.

In these equations you should give the full formula of each of the complexes, for example $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$.

(4)

- (c) When an aqueous solution containing $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ ions is warmed in the presence of Cl^- ions, $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$ ions are formed and the colour of the solution changes.

Name this type of reaction.

Suggest, in terms of electrons, why the colours of the complex ions are different.

(3)



Mark Scheme

Q15.

- (a) Cobalt has variable oxidation states
Allow exists as Co(II) and Co(III) 1
- (It can act as an intermediate that) lowers the activation energy
Allow (alternative route with) lower E_a 1
- $\text{CH}_3\text{CHO} + 2\text{Co}^{3+} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + 2\text{Co}^{2+} + 2\text{H}^+$
Allow multiples; allow molecular formulae
Allow equations with H_3O^+ 1
- $\frac{1}{2}\text{O}_2 + 2\text{Co}^{2+} + 2\text{H}^+ \rightarrow 2\text{Co}^{3+} + \text{H}_2\text{O}$ 1
- (b) (i) $[\text{Co}(\text{H}_2\text{O})_6]^{2+} + 3\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2 \rightarrow [\text{Co}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_3]^{2+} + 6\text{H}_2\text{O}$
Do not allow en in equation, allow $\text{C}_2\text{H}_8\text{N}_2$ 1
- The number of particles increases / changes from 4 to 7
Can score M2 and M3 even if equation incorrect or missing
provided number of particles increases 1
- So the entropy change is positive / disorder increases / entropy increases 1
- (ii) Minimum for **M1** is 3 bidentate ligands bonded to Co
Ignore all charges for M1 and M3 but penalise charges on any ligand in M2 1
- Ligands need not have any atoms shown but diagram must show 6 bonds from ligands to Co, 2 from each ligand
- Minimum for **M2** is one ligand identified as $\text{H}_2\text{N}-----\text{NH}_2$
Allow linkage as $-\text{C}-\text{C}-$ or just a line. 1
- Minimum for **M3** is one bidentate ligand showing two arrows from separate nitrogens to cobalt 1
- (c) Moles of cobalt = $(50 \times 0.203) / 1000 = \underline{0.01015}$ mol
Allow 0.0101 to 0.0102 1
- Moles of AgCl = $4.22/143.4 = 0.0294$
Allow 0.029



If not AgCl (eg AgCl₂ or AgNO₃), lose this mark and can only score **M1, M4 and M5**

1

Ratio = Cl⁻ to Co = 2.9 : 1

Do not allow 3 : 1 if this is the only answer but if 2.9:1 seen somewhere in answer credit this as **M3**

1

[Co(NH₃)₆]Cl₃ (square brackets not essential)

1

Difference due to incomplete oxidation in the preparation

Allow incomplete reaction.

Allow formation [Co(NH₃)₅Cl]Cl₂ etc.

Some chloride ions act as ligands / replace NH₃ in complex.

Do not allow 'impure sample' or reference to practical deficiencies

1

[15]**Q16.**

Allow multiples, including fractions.



Allow correct equation which includes water of crystallisation.

1



Allow if shown clearly in the calculation.

Allow 278

1

Moles = 6.95 / 277.9 = 2.5(0) × 10⁻²

Do not penalise precision but must be to a minimum of two significant figures.

Allow correct calculation using incorrect M_r.

Correct answer without working scores this mark only.

1

(c) 3(.00) × 10⁻²

1

(d) Theoretical mass = 2.50 × 10⁻² × 179.8 = 4.50g

as long as 2.50 × 10⁻² is the smaller of parts (b) and (c) (**M1**)

Allow consequential answer from parts (b) and (c).

Allow theoretical mass = (smaller of parts (b) and (c)) × 179.8

If larger of parts (b) and (c) used, lose **M1** but can score **M2**.

Allow answers based on moles of reactant and product.

1

Yield = 3.31 × 100 / 4.50 = 73.6% (**M2**)

Award this mark only if answer given to 3 significant figures.



Correct answer without working scores this mark only, provided answer given to 3 significant figures.

- (e) Some left in solution / some lost during filtration

Do not allow 'incomplete reaction'.

Do not allow 'reaction is reversible'.

1

1

- (f) MnO_4^- will oxidise the iron(II) ion and the ethanedioate ion

1

MnO_4^- does not oxidise the Cu^{2+} ion / larger volume needed for iron(II) ethanedioate

1

[9]**Q17.**

- (a) Variable / many oxidation states

1

- (b) $\text{V}_2\text{O}_5 + \text{SO}_2 \rightarrow \text{V}_2\text{O}_4 + \text{SO}_3$

Equations can be in either order

Allow multiples

1



1

- (c) (i) In a different phase / state from reactants

1

- (ii) Impurities poison / deactivate the catalyst / block the active sites

Allow (adsorbs onto catalyst AND reduces surface area)

1

- (d) (i) The catalyst is a reaction product

1

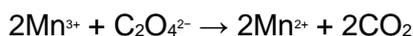
- (ii) Mn^{2+} / Mn^{3+} ion(s)

1

- (iii) $4\text{Mn}^{2+} + \text{MnO}_4^- + 8\text{H}^+ \rightarrow 5\text{Mn}^{3+} + 4\text{H}_2\text{O}$

Equations can be in either order

1



1

[9]**Q18.**

- (a) A ligand is an electron pair / lone pair donor

Allow uses lone / electron pair to form a co-ordinate bond

1



A bidentate ligand donates two electron pairs (to a transition metal ion) from different atoms / two atoms (on the same molecule / ion)

QoL

1

(b) CoCl_4^{2-} diagram

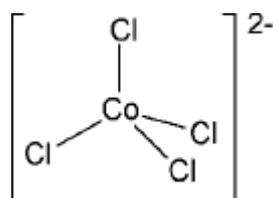
1

Tetrahedral shape

1

$109^\circ 28'$

1



Four chlorines attached to Co with net 2- charge correct

Charge can be placed anywhere, eg on separate formula

Penalise excess charges

Allow 109° to 109.5°

$[\text{Co}(\text{NH}_3)_6]^{2+}$ diagram

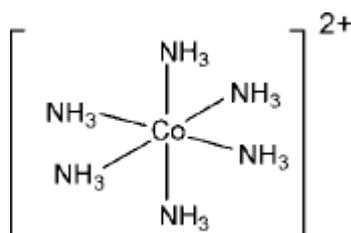
1

Octahedral shape

1

90°

1



Six ammonia / NH_3 molecules attached to Co with 2+ charge correct

Allow 180° if shown clearly on diagram

CE= 0 if wrong complex but mark on if only charge is incorrect

(c) In different complexes the d orbitals / d electrons (of the cobalt) will have different energies / d orbital splitting will be different

1

Light / energy is absorbed causing an electron to be excited

1

Different frequency / wavelength / colour of light will be absorbed / transmitted / reflected

1



- (d) 1 mol of H_2O_2 oxidises 2 mol of Co^{2+}
 Or $\text{H}_2\text{O}_2 + 2\text{Co}^{2+} \rightarrow 2\text{OH}^- + 2\text{Co}^{3+}$ 1

$M_r \text{CoSO}_4 \cdot 7\text{H}_2\text{O} = 281$
 If M_r wrong, max 3 for M1, M4, M5 1

Moles $\text{Co}^{2+} = 9.87 / 281 = 0.03512$ 1

Moles $\text{H}_2\text{O}_2 = 0.03512 / 2 = 0.01756$
 M4 is method mark for (M3) / 2 (also scores M1) 1

$$\begin{aligned} \text{Volume } \text{H}_2\text{O}_2 &= (\text{moles} \times 1000) / \text{concentration} \\ &= 0.01756 \times 1000 / 5.00 \end{aligned}$$

$$= 3.51 \text{ cm}^3 / (3.51 \times 10^{-3} \text{ dm}^3)$$

Units essential for answer

M5 is method mark for (M4) $\times 1000 / 5$

Allow 3.4 to 3.6 cm^3

If no 2:1 ratio or ratio incorrect Max 3 for M2, M3 & M5

Note: Answer of 7 cm^3 scores 3 for M2, M3, M5 (and any other wrong ratio max 3)

Answer of 16.8 cm^3 scores 3 for M1, M4, M5 (and any other wrong M_r max 3)

Answer of 33.5 cm^3 scores 1 for M5 only (so wrong M_r AND wrong ratio max 1)

1

[16]

Q19.

- (a) Co-ordinate / dative / dative covalent / dative co-ordinate
 Do not allow covalent alone 1

- (b) (lone) pair of electrons on oxygen/O
 If co-ordination to O^{2-} , CE=0 1

forms co-ordinate bond with Fe / donates electron pair to Fe
 'Pair of electrons on O donated to Fe' scores M1 and M2 1

- (c) 180° / 180 / 90
 Allow any angle between 85 and 95
 Do not allow 120 or any other incorrect angle
 Ignore units eg °C 1

- (d) (i) 3 : 5 / 5 FeC_2O_4 reacts with 3 MnO_4^-



Can be equation showing correct ratio

1

- (ii) **M1** Moles of MnO_4^- per titration = $22.35 \times 0.0193/1000 = \underline{4.31 \times 10^{-4}}$
Method marks for each of the next steps (no arithmetic error allowed for M2):

Allow $\underline{4.3 \times 10^{-4}}$ (2 sig figs)

Allow other ratios as follows:

eg from given ratio of 7/3

1

M2 moles of FeC_2O_4 = ratio from (d)(i) used correctly $\times 4.31 \times 10^{-4}$

$$\mathbf{M2} = 7/3 \times 4.31 \times 10^{-4} = 1.006 \times 10^{-3}$$

1

M3 moles of FeC_2O_4 in 250 cm^3 = M2 ans $\times 10$

$$\mathbf{M3} = 1.006 \times 10^{-3} \times 10 = 1.006 \times 10^{-2}$$

1

M4 Mass of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ = M3 ans $\times 179.8$

$$\mathbf{M4} = 1.006 \times 10^{-2} \times 179.8 = 1.81 \text{ g}$$

1

M5 % of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ = (M4 ans/1.381) $\times 100$

$$\mathbf{M5} = 1.81 \times 100/1.381 = 131 \% \text{ (130 to 132)}$$

1

(OR for M4 max moles of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ = $1.381/179.8$ (= 7.68×10^{-3})

for M5 % of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ = (M3 ans/above M4ans) $\times 100$)

eg using correct ratio 5/3:

Moles of FeC_2O_4 = $5/3 \times 4.31 \times 10^{-4} = 7.19 \times 10^{-4}$

Moles of FeC_2O_4 in 250 cm^3 = $7.19 \times 10^{-4} \times 10 = 7.19 \times 10^{-3}$

Mass of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ = $7.19 \times 10^{-3} \times 179.8 = 1.29 \text{ g}$

% of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ = $1.29 \times 100/1.381 = 93.4$ (allow 92.4 to 94.4)

Note correct answer (92.4 to 94.4) scores 5 marks

Allow consequentially on candidate's ratio

$$\text{eg } \mathbf{M2} = 5/2 \times 4.31 \times 10^{-4} = 1.078 \times 10^{-3}$$

$$\mathbf{M3} = 1.0078 \times 10^{-3} \times 10 = 1.078 \times 10^{-2}$$

$$\mathbf{M4} = 1.078 \times 10^{-2} \times 179.8 = 1.94 \text{ g}$$

$$\mathbf{M5} = 1.94 \times 100/1.381 = 140 \% \text{ (139 to 141)}$$

Other ratios give the following final % values

1:1 gives 56.1% (55.6 to 56.6)

5:1 gives 281% (278 to 284)

5:4 gives 70.2% (69.2 to 71.2)

[10]

Q20.

- (a) Orange dichromate

Allow max 2 for three correct colours not identified to species but in correct order

1

Changes to purple / green / ruby / red-violet / violet Chromium(III)

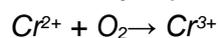


- (Note green complex can be $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$ etc)
Do not allow green with another colour 1
- That changes further to blue Chromium(II)
Allow max 1 for two correct colours not identified but in correct order 1
- $[\text{Cr}_2\text{O}_7]^{2-} + 14\text{H}^+ + 3\text{Zn} \rightarrow 2\text{Cr}^{3+} + 3\text{Zn}^{2+} + 7\text{H}_2\text{O}$
 $2\text{Cr}^{3+} + \text{Zn} \rightarrow 2\text{Cr}^{2+} + \text{Zn}^{2+}$ /
Ignore any further reduction of Cr^{2+} 1
- $[\text{Cr}_2\text{O}_7]^{2-} + 14\text{H}^+ + 4\text{Zn} \rightarrow 2\text{Cr}^{2+} + 4\text{Zn}^{2+} + 7\text{H}_2\text{O}$
Ignore additional steps e.g. formation of CrO_4^{2-} 1
- (b) Green precipitate 1
- (Dissolves to form a) green solution
Solution can be implied if 'dissolves' stated 1
- $[\text{Cr}(\text{H}_2\text{O})_6]^{3+} + 3\text{OH}^- \rightarrow \text{Cr}(\text{H}_2\text{O})_3(\text{OH})_3 + 3\text{H}_2\text{O}$
Penalise $\text{Cr}(\text{OH})_3$ once only 1
- $\text{Cr}(\text{H}_2\text{O})_3(\text{OH})_3 + 3\text{OH}^- \rightarrow [\text{Cr}(\text{OH})_6]^{3-} + 3\text{H}_2\text{O}$
Allow $[\text{Cr}(\text{H}_2\text{O})_6]^{3+} + 6\text{OH}^- \rightarrow [\text{Cr}(\text{OH})_6]^{3-} + 6\text{H}_2\text{O}$
Allow formation of $[\text{Cr}(\text{H}_2\text{O})_2(\text{OH})_4]^-$ and $[\text{Cr}(\text{H}_2\text{O})(\text{OH})_5]^{2-}$ in balanced equations
Ignore state symbols, mark independently 1
- (c) (ligand) substitution / replacement / exchange
Allow nucleophilic substitution 1
- The energy levels/gaps of the d electrons are different (for each complex)
Ignore any reference to emission of light 1
- So a different wavelength/frequency/colour/energy of light is absorbed (when d electrons are excited)
- OR light is absorbed and a different wavelength/frequency/colour/energy (of light) is transmitted/reflected 1
- (d) $E_{\text{O}_2} (/ \text{H}_2\text{O}) > E_{\text{Cr}^{3+}} (/ \text{Cr}^{2+}) / \text{e.m.f} = 1.67 \text{ V}$
Allow $E(\text{cell}) = 1.67$ 1



So Cr^{2+} ions are oxidised by oxygen/air

Allow any equation of the form:



1

With $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ get CrCO_3

If named must be chromium(II) carbonate

1

with $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ get $\text{Cr}(\text{H}_2\text{O})_3(\text{OH})_3$ / $\text{Cr}(\text{OH})_3$

Allow 0 to 3 waters in the complex

1

and CO_2

Can score M3, M4, M5 in equations even if unbalanced

1

$\text{Cr}(\text{III})$ differs from $\text{Cr}(\text{II})$ because it is acidic / forms H^+ ions

1

because Cr^{3+} ion polarises water

Ignore charge/size ratio and mass/charge

1

[19]