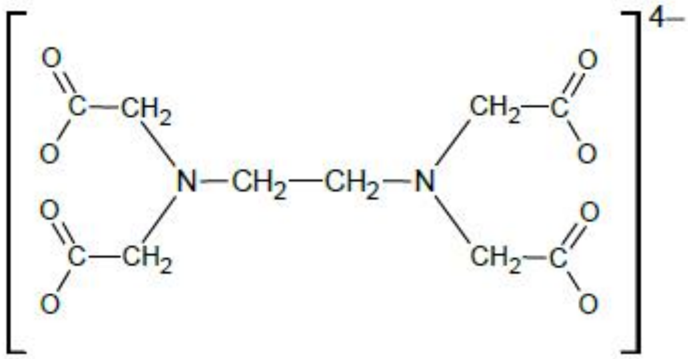
Q1. EDTA is a useful laboratory chemical and is found in a wide variety of commercial products including detergents. It is very soluble in water and is often used in its ionic form $EDTA^{4-}$ as shown in the diagram below.



(a) $EDTA^{4-}$ can act as a multidentate ligand.

Explain the meanings of the terms **multidentate** and **ligand** with reference to the reaction of $EDTA^{4-}$ with $[Cu(H_2O)_6{}^{2+}]$(aq) ions to form a complex ion.

Draw on the diagram above a separate circle around each atom that bonds to the Cu^{2+} ion in this complex ion.

Multidentate ____

____

Ligand ____

____

(3)

(b) Copper(II) compounds may be used as fungicides in vineyards. When used in this way, copper(II) ions can enter the water supply and cause problems because they are toxic in high concentrations.

The water supply near a vineyard can be tested for copper(II) ions by forming a blue aqueous complex with $EDTA^{4-}$ ions. The concentration of this complex can be determined using a colorimeter.

Outline the practical steps that you would follow, using colorimetry, to determine the concentration of this complex in a sample of water.

(3)

(c) The concentration of copper(II) ions, in the sample of water, determined by colorimetry was 7.56×10^{-5} mol dm^{-3}.

This result was checked by titrating a sample of the water with a solution containing $EDTA^{4-}$(aq) ions.

The $EDTA^{4-}$(aq) used in the titration had a concentration of 1.00×10^{-3} mol dm^{-3}.

Write an equation for the reaction between $[Cu(H_2O)_6]^{2+}$ and $EDTA^{4-}$ ions.

Calculate the volume of the $EDTA^{4-}$ solution needed to react with a 25.0 cm^3 sample of the water.

Justify whether this titration will give an accurate value for the concentration of copper(II) ions. If necessary, suggest a practical step that would improve the accuracy.

(5)

(Total 11 marks)

Q2. (a) A co-ordinate bond is formed when a transition metal ion reacts with a ligand.

Explain how this co-ordinate bond is formed.

(2)

(b) Describe what you would observe when dilute aqueous ammonia is added dropwise, to excess, to an aqueous solution containing copper(II) ions.
Write equations for the reactions that occur.

(4)

(c) When the complex ion $[Cu(NH_3)_4(H_2O)_2]^{2+}$ reacts with 1,2-diaminoethane, the ammonia molecules but not the water molecules are replaced.

Write an equation for this reaction.

(1)

(d) Suggest why the enthalpy change for the reaction in part **(c)** is approximately zero.

(2)

(e) Explain why the reaction in part **(c)** occurs despite having an enthalpy change that is approximately zero.

(2)

(Total 11 marks)

Q3. Solution **A** contains the compound $[Cu(H_2O)_6]Cl_2$

(a) State the type of bonding between the oxygen and hydrogen in this compound.

___

(1)

(b) State why the chloride ions in this compound are **not** considered to be ligands.

___

___

(1)

(c) An excess of ammonia was added to a sample of solution **A** to form solution **B**.

Write an ionic equation for the reaction that occurs when solution **A** is converted into solution **B** and state the colour of solution **B**.

Equation ___

___

Colour ___

(2)

(d) Aqueous sodium carbonate was added to another sample of solution **A** to form a blue-green solid **C**.

Identify the blue-green solid **C**.

___

(1)

(e) Reagent **D** was added to another sample of solution **A** to form a yellow-green solution.

Identify reagent **D** and write an ionic equation for the reaction that occurs when the yellow-green solution is formed from solution **A**.

Identity of reagent **D** ___

Equation ___

(2)

(f) Explain why colorimetry cannot be used to determine the concentration of solutions containing $[CuCl_2]^-$

In your answer refer to the electron configuration of the metal ion.

___

___

(2)

Q4. This question is about cobalt chemistry.

(a) Give the electron configuration of the Co atom and of the Co^{2+} ion.

State three characteristic features of the chemistry of cobalt and its compounds.

(5)

(b) Ethane-1,2-diamine can act as a bidentate ligand. When $[Co(H_2O)_6]^{2+}(aq)$ ions are treated with an excess of ethane-1,2-diamine, the water ligands are replaced.

Explain what is meant by the term bidentate ligand.

Explain, with the aid of an equation, the thermodynamic reasons why this reaction occurs.

Draw a diagram to show the structure of the complex ion formed.

(7)

(Total 12 marks)

Q5. A student weighed out a 2.29 g sample of impure $K_3[Fe(C_2O_4)_3].3H_2O$ and dissolved it in water. This solution was added to a 250 cm^3 volumetric flask and made up to 250 cm^3 with distilled water.
A 25.0 cm^3 portion was pipetted into a conical flask and an excess of acid was added.
The mixture was heated to 60°C and titrated with 0.0200 mol dm^{-3} $KMnO_4$ solution.
26.40 cm^3 of $KMnO_4$ solution were needed for a complete reaction.

In this titration only the $C_2O_4^{2-}$ ions react with the $KMnO_4$ solution.

(a) The reaction between $C_2O_4^{2-}$ ions and MnO4– ions is autocatalysed.

Explain what is meant by the term autocatalysed and identify the catalyst in the reaction.

____

____

____

____

(2)

(b) Select from the list the most suitable substance used to acidify the solution in the conical flask.
Put a tick (✓) in the correct box.

$H_2C_2O_4$ ☐

H_2SO_4 ☐

HCl ☐

HNO_3 ☐

(1)

(c) The reaction between $C_2O_4^{2-}$ ions and MnO_4^- ions is very slow at first.
Explain why the reaction is initially slow.

____

____

____

____

____

____

____

(3)

(d) Write an equation for the reaction between $C_2O_4^{2-}$ ions and MnO_4^- ions in acidic solution.
Calculate the percentage purity of the original sample of $K_3[Fe(C_2O_4)_3].3H_2O$.
Give your answer to 3 significant figures.

(7)

(e) A solution of $KMnO_4$ has an unknown concentration.

Describe briefly how colorimetry can be used to determine the concentration of this solution.

(3)
(Total 16 marks)

Mark schemes

Q1.

(a) Multidentate − EDTA can form many / six dative bonds with central cation. **1**

Ligand − lone pair (on N or O of EDTA) can form dative bond with copper(II) ions. **1**

6 circles drawn on $EDTA^{4-}$ structure − 2 × N and 4 × −O **1**

(b) Calibrate a colorimeter / produce a calibration curve. **1**

By testing the colorimeter with solutions of copper-EDTA complex of known concentration. **1**

Add excess EDTA salt to the sample. **1**

(c) $[Cu(H_2O)_6]^{2+} + EDTA^{4-} \longrightarrow [Cu(EDTA)]^{2-} + 6H_2O$ **1**

Amount of copper(II) = $(25.0 \times 7.56 \times 10^{-5})$ /1000 = 1.89×10^{-6} mol **1**

Volume of $EDTA^{4-}$ = $(1.89 \times 10^{-6} / 0.001) \times 1000 = 1.89$ cm^3 **1**

This is too small to be accurate. **1**

Dilute the $EDTA^{4-}$ solution / use larger volume of river water. **1**

[11]

Q2.

(a) An electron pair on the ligand **1**

Is donated from the ligand to the central metal ion **1**

(b) Blue precipitate **1**

Dissolves to give a dark blue solution **1**

$[Cu(H_2O)_6]^{2+} + 2NH_3 \longrightarrow Cu(H_2O)_4(OH)_2 + 2NH_4^+$ **1**

$Cu(H_2O)_4(OH)_2 + 4NH_3 \longrightarrow [Cu(NH_3)_4(H_2O)_2]^{2+} + 2OH^- + 2H_2O$ **1**

(c) $[Cu(NH_3)_4(H_2O)_2]^{2+} + 2H_2NCH_2CH_2NH_2 \longrightarrow [Cu(H_2NCH_2CH_2NH_2)_2(H_2O)_2]^{2+} + 4NH_3$

1

(d) Cu–N bonds formed have similar enthalpy / energy to Cu–N bonds broken

1

And the same number of bonds broken and made

1

(e) 3 particles form 5 particles / disorder increases because more particles are formed / entropy change is positive

1

Therefore, the free-energy change is negative

M2 can only be awarded if M1 is correct

1

[11]

Q3.

(a) Covalent

Do not allow dative covalent or coordinate (covalent)

1

(b) $Cl^{(-)}$ not donating lone pair (to $Cu^{(2+)}$)

$Cl^{(-)}$ does not form a coordinate/dative bond (to $Cu^{(2+)}$)

Allow without charges but penalise incorrect charges

Cl^{-}/it is bonded ionically (to Cu^{2+})

1

(c) $[Cu(H_2O)_6]^{2+} + 4NH_3 \longrightarrow [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$

1

Deep blue / Royal blue / Dark blue (solution)

1

Allow combination of:

$[Cu(H_2O)_6]^{2+} + 2NH_3 \longrightarrow [Cu(H_2O)_4(OH)_2] + 2NH_4^{+}$

$[Cu(H_2O)_4(OH)_2] + 4NH_3 \longrightarrow [Cu(NH_3)_4(H_2O)_2]^{2+} + 2H_2O + 2OH^{-}$

Do not penalise missing square brackets

Ignore initial colour of Cu^{2+} (aq)

(d) $CuCO_3$ or copper carbonate

Penalise incorrect oxidation state

Allow correct formula for basic copper carbonate

1

(e) HCl/ hydrochloric acid

Ignore concentration

Allow soluble chloride salt

Also allow any reagent which leads to a change in colour of solution due to a change in ligands (e.g. $NH_2CH_2CH_2NH_2$) or change in oxidation state (e.g. SO_2) and associated correct *equations.*

1

$[Cu(H_2O)_6]^{2+} + 4Cl^- \longrightarrow [CuCl_4]^{2-} + 6H_2O$

$[Cu(H_2O)_6]^{2+} + 4HCl \longrightarrow [CuCl_4]^{2-} + 6H_2O + 4H^+$

Mark independently

1

(f) (3)d^{10} or has full (3)d (sub) shell/orbital

Penalise incorrect principal quantum number

1

It is colourless/cannot absorb (frequencies of) visible light

Ignore clear

1

[9]

Q4.

(a) [Ar] $4s^2\ 3d^7$ or $1s^22s^22p^63s^23p^64s^23d^7$

Allow 4s and 3d in either order

1

[Ar] $3d^7$ or $1s^22s^22p^63s^23p^63d^7$

1

Any 3

Variable oxidation state

Act as catalysts

Form complexes

Form coloured ions/compounds

3

(b) Two atoms that each donate a lone pair (of electrons) / coordinate bonds from two atoms

1

Formula of ethane-1,2- diamine: $NH_2CH_2CH_2NH_2$

M2 gained from equation or structure

1

$[Co(H_2O)_6]^{2+} + 3NH_2CH_2CH_2NH_2 \longrightarrow [Co(NH_2CH_2CH_2NH_2)_3]^{2+} + 6H_2O$

Equation must be balanced inc charges

Allow en or $C_2H_8N_2$ in equation for ethane-1,2-diamine

1

There is an increase in the number of particles / the reaction goes from 4 moles to 7 moles

Allow increase number of molecules/moles. Allow numbers that match an incorrect equation

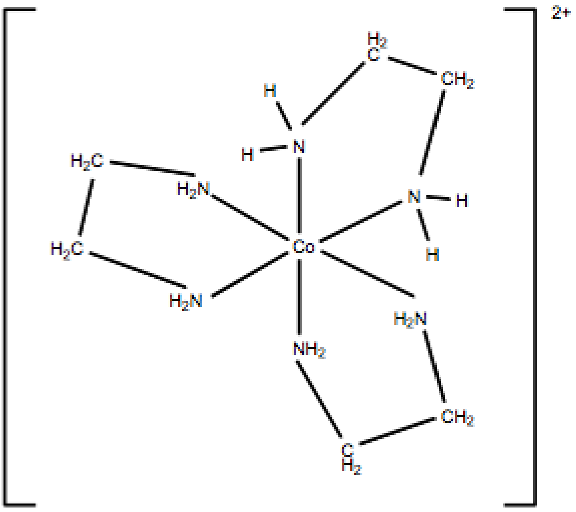
1

Disorder/entropy increases / ΔS is positive

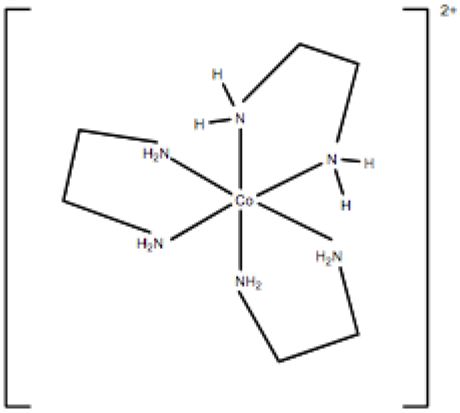
1

ΔG negative

1



Or



Mark for correct structure (ignore charges -even if wrong)

NH_2 can be shown in either way – see structure

1

[12]

Q5.

(a) A reaction that produces its own catalyst/ one of the products is the catalyst

1

Mn^{2+}

Allow Mn^{3+}

1

(b) H_2SO_4

1

(c) There is no/very little catalyst at the start OR the reaction only speeds up when the catalyst is produced

1

Two negative ions (MnO_4^- and $C_2O_4^{2-}$) <u>repel</u>

Reference to molecules loses M2

1

The activation energy for the reaction is high / heat is required to overcome the activation energy

1

(d) M1 $5\ C_2O_4^{2-}(aq) + 2\ MnO_4^{-}(aq) + 16\ H^{+}(aq) \longrightarrow$
$10\ CO_2(g) + 2\ Mn^{2+}(aq) + 8\ H_2O(l)$

Ignore state symbols

1

M2 $n(MnO_4^-) = \frac{26.40 \times 0.02}{1000}$ OR $n(MnO_4^-) = 5.28 \times 10^{-4}$

1

M3 $n(C_2O_4^{2-}) = \frac{5}{2} \times 5.28 \times 10^{-4} = 1.32 \times 10^{-3}$

M3 is for M2 × 5/2

If wrong ratio used then can only score M2, M4, M5 and M6

1

M4 $n(C_2O_4^{2-}$ in flask originally$) = 1.32 \times 10^{-3} \times 10 = 1.32 \times 10^{-2}$

M4 is for M3 × 10

1

M5 $n(K_3[Fe(C_2O_4)_3].3H_2O) = \frac{1.32 \times 10^{-2}}{3} = 4.40 \times 10^{-3}$

(M_r $K_3[Fe(C_2O_4)_3].3H_2O = 491.1$)

M5 is for M4 ÷ 3

1

M6 Mass of $K_3[Fe(C_2O_4)_3].3H_2O$ reacted $= 4.40 \times 10^{-3} \times 491.1 = 2.16$ g

M6 is for M5 × 491(.1)

1

M7 % purity $= \frac{2.16}{2.29} \times 100 =$ <u>94.3 or 94.4</u>%

Answer must be to 3 s.f.

Correct answer scores 6 marks; mark equation separately

Alternative method using ratio by moles:

M5 $n(C_2O_4^{2-}) = 4.66 \times 10^{-3} \times 3 = 0.0140$ moles in 250cm^3

M6 n(complex) $= 2.29/491.1 = 4.66 \times 10^{-3}$ moles in 250cm^3

M7 % $= 0.0132/0.0140 \times 100 =$ <u>94.3 or 94.4</u>%

1

(e) Make <u>some known</u> concentration<u>s</u> (of the coloured solution and read the absorbance of each one using a colorimeter)

Ignore addition of suitable ligand

1

Plot a graph of absorbance vs concentration

Not just "plot a calibration curve" / reference to Beer-Lambert graph is insufficient

Do not allow transmittance in M2

1

Read/compare unknown concentration from calibration curve/graph (and hence the concentration from the graph)

M3 can only be scored if graph/curve mentioned

1

[16]