Q9.

Iron forms many complexes that contain iron in oxidation states +2 and +3.

(a) Hexaaquairon(III) ions react with an excess of hydrochloric acid in a ligand substitution reaction.

Write an equation for this reaction.

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(1)

(b) Explain why the initial and final iron(III) complexes in the equation above have different shapes.

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(2)

(c) Hexaaquairon(II) ions react with an excess of $H_2NCH_2CH_2NH_2$ in a ligand substitution reaction.

Draw the structure of the iron(II) complex formed showing its charge.

(2)

(d) Hexaaquairon(II) ions react with an excess of $H_2NCH_2CH_2NH_2$ in a ligand substitution reaction.

Which of the following shows the correct change in entropy for a reaction of hexaaquairon(II) ions with $H_2NCH_2CH_2NH_2$?

Tick (✓) **one** box.

change in entropy is negative ☐

change in entropy is close to zero ☐

change in entropy is positive ☐

(1)

(e) The percentage of iron(II) sulfate in iron tablets can be determined by titration with potassium manganate(VII) in acidic solution.

Deduce an ionic equation for the reaction of iron(II) ions with manganate(VII) ions.

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(1)

(f) A student dissolved 1980 mg of iron tablets in an excess of dilute sulfuric acid. The solution was titrated with 0.0200 mol dm^{-3} potassium manganate(VII) solution. A 32.50 cm^3 volume of potassium manganate(VII) solution was required to reach the end point in the titration.

Calculate the percentage of iron in the sample of iron tablets.
Give your answer to the appropriate number of significant figures.

Percentage ____________________ %

(4)

(g) State the colour change at the end point in this titration.

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(1)

(Total 12 marks)

Q10.

The table below shows some successive ionisation energy data for atoms of three different elements **X**, **Y** and **Z**.

Elements **X**, **Y** and **Z** are Ca, Sc and V but not in that order.

	First	**Second**	**Third**	**Fourth**	**Fifth**	**Sixth**
X	648	1370	2870	4600	6280	12 400
Y	590	1150	4940	6480	8120	10 496
Z	632	1240	2390	7110	8870	10 720

(a) Which element is calcium?

X ☐

Y ☐

Z ☐

(1)

(b) Which element is vanadium?

X ☐

Y ☐

Z ☐

(1)

(c) Justify your choice of vanadium in part (b)

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(1)

(d) An acidified solution of NH_4VO_3 reacts with zinc.

Explain how observations from this reaction show that vanadium exists in at least two different oxidation states.

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(2)

(e) The vanadium in 50.0 cm^3 of a 0.800 mol dm^{-3} solution of NH_4VO_3 reacts with 506 cm^3 of sulfur(IV) oxide gas measured at 20.0 °C and 98.0 kPa.

Use this information to calculate the oxidation state of the vanadium in the solution after the reduction reaction with sulfur(IV) oxide.
Explain your working.
The gas constant R = 8.31 J K^{-1} mol^{-1}.

Oxidation state = ________________

(6)

(Total 11 marks)

Q11.

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.

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(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.

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(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)

Q12.

A green solution, **X**, is thought to contain $[Fe(H_2O)_6]^{2+}$ ions.

(a) The presence of these ions can be confirmed by reacting separate samples of solution **X** with aqueous ammonia and with aqueous sodium carbonate.

Write equations for each of these reactions and describe what you would observe.

(4)

(b) A 50.0 cm^3 sample of solution **X** was added to 50 cm^3 of dilute sulfuric acid and made up to 250 cm^3 of solution in a volumetric flask.

A 25.0 cm^3 sample of this solution from the volumetric flask was titrated with a 0.0205 mol dm^{-3} solution of $KMnO_4$
At the end point of the reaction, the volume of $KMnO_4$ solution added was 18.70 cm^3.

(i) State the colour change that occurs at the end point of this titration and give a reason for the colour change.

(2)

(ii) Write an equation for the reaction between iron(II) ions and manganate(VII) ions.

Use this equation and the information given to calculate the concentration of iron(II) ions in the original solution **X**.

(5)

(Total 11 marks)

Q13.

A student carried out an experiment to find the mass of $FeSO_4.7H_2O$ in an impure sample, **X**.
The student recorded the mass of **X**. This sample was dissolved in water and made up to 250 cm^3 of solution.
The student found that, after an excess of acid had been added, 25.0 cm^3 of this solution reacted with 21.3 cm^3 of a 0.0150 mol dm^{-3} solution of $K_2Cr_2O_7$

(a) Use this information to calculate a value for the mass of $FeSO_4.7H_2O$ in the sample of **X**.

(5)

(b) The student found that the calculated mass of $FeSO_4.7H_2O$ was greater than the actual mass of the sample that had been weighed out. The student realised that this could be due to the nature of the impurity.

Suggest **one** property of an impurity that would cause the calculated mass of $FeSO_4.7H_2O$ in **X** to be greater than the actual mass of **X**.
Explain your answer.

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(2)
(Total 7 marks)

Q14.

When iodine molecules are dissolved in aqueous solutions containing iodide ions, they react to form triiodide ions (I_3^-).

$$I_2 + I^- \longrightarrow I_3^-$$

The reaction above between I^- ions and $S_2O_8^{2-}$ ions has a high activation energy and $S_2O_8^{2-}$ ions are only reduced slowly to SO_4^{2-} ions.
The reaction is catalysed by Fe^{2+} ions.

(a) Explain why the reaction between I^- ions and $S_2O_8^{2-}$ ions is slow.

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(1)

(b) Other than having variable oxidation states, explain why Fe^{2+} ions are good catalysts for this reaction.

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(1)

(c) Write a half-equation for the reduction of $S_2O_8^{2-}$ ions to SO_4^{2-} ions.

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(1)

(d) Construct an overall equation for the reaction between $S_2O_8^{2-}$ ions and I^- ions.

(1)

(Total 4 marks)

Mark Scheme

Q9.

(a) $[Fe(H_2O)_6]^{3+} + 4Cl^- \longrightarrow FeCl_4^- + 6H_2O$

1

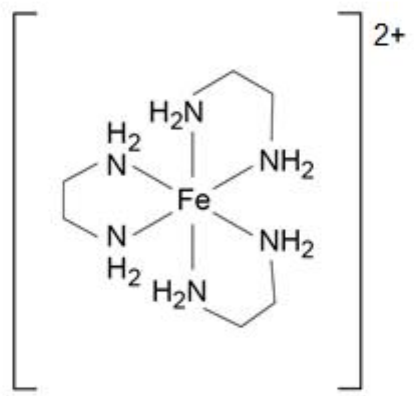
(b) Cl^- is a bigger ligand

1

So only $4Cl^-$ can fit around the metal

Allow fewer Cl^- can fit around the metal

1



(c)

M1 for structure of complex

M2 for correct charge

1
1

(d) Change in entropy is positive

1

(e) $5Fe^{2+} + MnO_4^- + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

1

(f) Amount of manganate (VII) = 6.50×10^{-4} mol

1

Amount of iron(II) = 3.25×10^{-3} mol

ie M1 × 5

1

Mass of iron = 0.181 g = 181 mg

Allow M2 × 55.8

1

Percentage Fe = 181/1980 × 100 = 9.14(%) 3 sf

1

(g) Colourless to pale pink

1

[12]

Q10.

(a) **Y** 1

(b) **X** 1

(c) Jump in trend of ionisation energies after removal of fifth electron

Fits with an element with 5 outer electrons ($4s^2 3d^3$) like V 1

(d) Explanation: Two different colours of solution are observed 1

Because each colour is due to vanadium in a different oxidation state 1

(e) **Stage 1:** mole calculations in either order

Moles of vanadium = 50.0 × 0.800 / 1000 = 4.00×10^{-2}

Extended response

Maximum of 5 marks for answers which do not show a sustained line of reasoning which is coherent, relevant, substantiated and logically structured. 1

Moles of SO_2 = pV / RT = (98 000 × 506 × 10^{-6}) / (8.31 × 293)

= 2.04×10^{-2} 1

Stage 2: moles of electrons added to NH_4VO_3

When SO_2 (sulfur(IV) oxide) acts as a reducing agent, it is oxidised to sulfate(VI) ions so this is a two electron change 1

Moles of electrons released when SO_2 is oxidised = $2.04 \times 10^{-2} \times 2$

= 4.08×10^{-2} 1

Stage 3: conclusion

But in NH_4VO_3 vanadium is in oxidation state 5 1

4.00×10^{-2} mol vanadium has gained 4.08×10^{-2} mol of electrons therefore 1 mol vanadium has gained 4.08×10^{-2} / 4.00 × 10 – 2 = 1 mol of electrons to the nearest integer, so new oxidation state is 5 – 1 = 4 1

[11]

Q11.

(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 $C_2O_4^{2-}$) repel

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 $= \frac{2.16}{2.29} \times 100 =$ 94.3 or 94.4%

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 × 10^{-3} × 3 = 0.0140 moles in 250cm^3

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

M7 % = 0.0132/0.0140 × 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]

Q12.

(a) $[Fe(H_2O)_6]^{2+} + 2NH_3 \rightarrow Fe(H_2O)_4(OH)_2 + 2NH_4^+$

Allow equation with OH^- provided equation showing formation of OH^- from NH_3 given

1

Green precipitate

1

$[Fe(H_2O)_6]^{2+} + CO_3^{2-} \rightarrow FeCO_3 + 6H_2O$

1

Green precipitate

effervescence incorrect so loses M4

1

(b) (i) Colourless / (pale) green changes to pink / purple (solution)

Do not allow pale pink to purple

1

Just after the end−point MnO_4^- is in excess / present

1

(ii) $MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$

1

Moles $KMnO_4$ = 18.7 × 0.0205 / 1000 = (3.8335 × 10^{-4})

Process mark

1

Moles Fe^{2+} = 5 × 3.8335 × 10^{-4} = 1.91675 × 10^{-3}

Mark for M2 × 5

1

Moles Fe^{2+} in 250 cm^3 = 10 × 1.91675 × 10^{-3} = 0.0191675 moles in 50 cm^3

Process mark for moles of iron in titration (M3) × 10

1

Original conc Fe^{2+} = 0.0191675 × 1000 / 50 = 0.383 mol dm^{-3}

Answer for moles of iron (M4) × 1000 / 50

Answer must be to at least 2 sig. figs. (0.38)

1

[11]

Q13.

(a) moles of $Cr_2O_7^{2-}$ per titration = 21.3 × 0.0150 / 1000 = 3.195 × 10^{-4}

1

($Cr_2O_7^{2-}$ + $14H^+$ + $6Fe^{2+}$ → $2Cr^{3+}$ + $7H_2O$ + $6Fe^{3+}$) $Cr_2O_7^{2-}$:Fe^{2+} = 1:6

If 1:6 ratio incorrect cannot score M2 or M3

1

moles of Fe^{2+} = 6 × 3.195 × 10^{-4} = 1.917 × 10^{-3}

Process mark for M1 × 6 (also score M2)

1

original moles in 250 cm^3 = 1.917 × 10^{-3} × 10 = 1.917 × 10^{-2}

Process mark for M3 × 10

1

mass of $FeSO_4.7H_2O$ = 1.917 × 10^{-2} × 277.9 = 5.33 (g)

Mark for answer to M4 × 277.9

(allow 5.30 to 5.40)

*Answer **must** be to at least 3 sig figs*

Note that an answer of 0.888 scores M1, M4 and M5 (ratio 1:1 used)

1

(b) (Impurity is a) reducing agent / reacts with dichromate / impurity is a version of $FeSO_4$ with fewer than 7 waters (not fully hydrated)

Allow a reducing agent or compound that that converts Fe^{3+} into Fe^{2+}

1

Such that for a given mass, the impurity would react with more dichromate than a similar mass of $FeSO_4.7H_2O$

OR for equal masses of the impurity and $FeSO_4.7H_2O$, the impurity would react with more dichromate.

Must compare mass of impurity with mass of $FeSO_4.7H_2O$

1

[7]

Q14.

(a) Negative ions repel one another

1

(b) Positive ions attract negative ions in catalysed process

Allow activation energy decreases.

Allow alternative route with lower E_a

Ignore references to heterogenous catalysis.

1

(c) $S_2O_8^{2-} + 2e^- \longrightarrow 2SO_4^{2-}$

Allow multiples including fractions.

Ignore state symbols.

1

(d) $S_2O_8^{2-} + 2I^- \longrightarrow 2SO_4^{2-} + I_2$

Allow multiples including fractions.

Ignore state symbols.

Allow the correct equation involving I_3^-

$S_2O_8^{2-} + 3I^- \longrightarrow 2SO_4^{2-} + I_3^-$

1

[4]