Q8.

This question is about vanadium compounds and ions.

(a) Use data from Table 4 to identify the species that can be used to reduce VO_2^+ ions to VO^{2+} in aqueous solution and no further.

Explain your answer.

Electrode half-equation	***E*$^\ominus$ / V**
$VO_2^+(aq) + 2H^+(aq) + e^- \rightarrow VO^{2+}(aq) + H_2O(l)$	+1.00
$VO^{2+}(aq) + 2H^+(aq) + e^- \rightarrow V^{3+}(aq) + H_2O(l)$	+0.34
$Cl_2(aq) + 2e^- \rightarrow 2Cl^-(aq)$	+1.36
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	+0.77
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	–0.76

Reagent ____

Justification ____

____

____

(2)

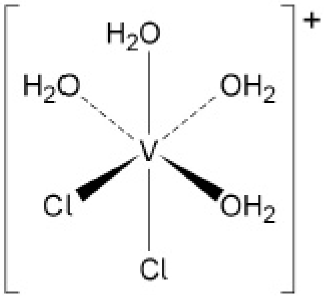
(b) Give the oxidation state of vanadium in $[VO(H_2O)_5]^{2+}$

____

(1)

(c) The $[V(H_2O)_4Cl_2]^+$ ion exists as two isomers. One isomer is shown.

Draw the structure of the other isomer and state the type of isomerism.



Type of isomerism ____

(2)

(d) Heating NH_4VO_3 produces vanadium(V) oxide, water and one other product.

Give an equation for the reaction.

____

(1)

(e) Vanadium(V) oxide is the catalyst used in the manufacture of sulfur trioxide.

Give **two** equations to show how the catalyst is used and regenerated.

____

____

(1)
(Total 7 marks)

Q9.

An oxide of vanadium catalyses the following reaction:

$$SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$$

What is the formula of the vanadium-containing intermediate formed in this reaction?

A V_2O ○

B VO ○

C V_2O_3 ○

D V_2O_4 ○

(Total 1 mark)

Q10.

In the Contact Process sulfur dioxide reacts with oxygen to form sulfur trioxide as shown in the equation.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

The table shows some thermodynamic data.

	$\Delta H_f^{\ominus}$/kJ mol^{-1}	$S^{\ominus}$/J K^{-1} mol^{-1}
$SO_2(g)$	–297	248
$O_2(g)$	0	205
$SO_3(g)$	–395	256

(a) Use data from the table to calculate the standard enthalpy change for this reaction.

(2)

(b) Use data from the table to calculate the standard entropy change for this reaction.

(2)

(c) State what the sign of the entropy change in your answer to part **(b)** indicates about the product of this reaction relative to the reactants.

(1)

(d) Use your answers to parts **(a)** and **(b)** to calculate a value for the free–energy change for this reaction at 50°C.

(If you were unable to calculate ΔH in part **(a)** assume a value of –250 kJ mol^{-1}.
If you were unable to calculate ΔS in part **(b)** assume a value of –250 J K^{-1} mol^{-1}.
These are not the correct values.)

(3)

(e) Use your answer to part **(d)** to explain whether the reaction is feasible at 50°C.

(1)

(f) Vanadium(V) oxide acts as a heterogeneous catalyst in the Contact Process.

(i) State what is meant by the term heterogeneous.

(1)

(ii) Write **two** equations that show how this catalyst is involved in the Contact Process.

(2)

(iii) Suggest why the vanadium(V) oxide is used in small pellet form rather than as large lumps.

(1)

(iv) State why the reactants should be purified before they come into contact with the vanadium(V) oxide.

____

____

(1)

(Total 14 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.

____

____

____

____

(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)

Q12.

The redox reaction, in aqueous solution, between acidified potassium manganate(VII) and sodium ethanedioate is autocatalysed.

(a) Write an equation for this redox reaction.

Identify the species that acts as the catalyst.

Explain how the properties of the species enable it to act as a catalyst in this reaction.

(6)

(b) Sketch a graph to show how the concentration of MnO_4^- ions varies with time in this reaction.
Explain the shape of the graph.

(4)

(Total 10 marks)

Q13.

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.

(1)

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

(1)

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

(1)

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

(1)
(Total 4 marks)

Q14.

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

$$2CH_3CHO + O_2 \longrightarrow 2CH_3COOH$$

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 $[Co(H_2O)_6]^{2+}$ 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 $[Co(H_2O)_6]^{2+}$ complex ion.

(3)

(ii) Draw a diagram that shows the shape of the complex ion **Y** and shows the type of bond between the ethane-1,2-diamine molecules and the cobalt.

(3)

(c) Compound **Z** is a complex that contains only cobalt, nitrogen, hydrogen and chlorine.

A solid sample of **Z** was prepared by reaction of 50 cm^3 of 0.203 mol dm^{-3} aqueous cobalt(II) chloride with ammonia and an oxidising agent followed by hydrochloric acid.

When this sample of **Z** was reacted with an excess of silver nitrate, 4.22 g of silver chloride were obtained.

Use this information to calculate the mole ratio of chloride ions to cobalt ions in **Z**.

Give the formula of the complex cobalt compound **Z** that you would expect to be formed in the preparation described above.

Suggest **one** reason why the mole ratio of chloride ions to cobalt ions that you have calculated is different from the expected value.

(5)

(Total 15 marks)

Mark Scheme

Q8.

(a) Fe^{2+}

Accept any Fe(II) compound – correct formula or name

1

$E^{\ominus}$ VO_2^+(/ VO^{2+}) > $E^{\ominus}$ Fe^{3+}(/Fe^{2+}) > $E^{\ominus}$ VO^{2+}(/V^{3+})

If calculations of EMF are provided producing EMFs = 0.23(V) and -0.43(V), with a comment, allow M2

allow $\underline{E^{\ominus}\ Fe^{3+}}$ (/Fe^{2+}) value of +0.77 is between the $E^{\ominus}$ values for the electrode half-equations containing the V species or wtte

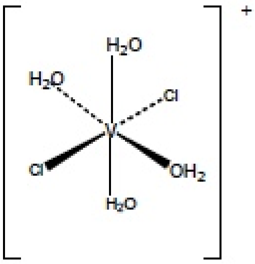
1

(b) (+) 4

IV or four

1

(c)



Ignore absence of charge

Wedges, dotted lines and [ ] not required

Do not penalise bond from H to V (in water ligands)

1

Cis/trans

allow E/Z, geometric and stereo(isomerism)

1

(d) 2 $NH_4VO_3 \rightarrow V_2O_5 + H_2O + 2NH_3$

Accept multiples

Ignore state symbols

1

(e) $V_2O_5 + SO_2 \rightarrow V_2O_4 + SO_3$

$V_2O_4 + \frac{1}{2}\ O2 \rightarrow V_2O_5$

Both equations needed for 1 mark in this order

Allow multiples

1

[7]

Q9.

D

[1]

Q10.

(a) $\Delta H^\ominus = \Sigma\Delta H_f^\ominus$ products - $\Sigma\Delta H_f^\ominus$ reactants
1

or $(2 \times -395) - (2 \times -297)$

$= -196$ (kJ mol^{-1})

Penalise incorrect units, ignore missing units
1

(b) $\Delta S^\ominus = \Sigma S^\ominus$ products - $\Sigma S^\ominus$ reactants
1

$= (2 \times 256) - 205 - (2 \times 248)$

$= -189$ <u>JK^{-1} mol^{-1}</u>

Allow -0.189 kJ K^{-1} mol^{-1}

Units must be given and must match value
1

(c) Causes an increase in order / a decrease in disorder

Allow products more ordered / products less disordered

If answer to (b) is +ve, allow products are less ordered / causes an increase in disorder / causes a decrease in order
1

(d) $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$

Do not insist on standard state symbol
1

$= -196 - 323\ (-189/1000)$

If conversion of T or ΔS incorrect, then can only score M1
1

$= -134.9$ kJ mol^{-1}

Must have correct units

Allow answers in J mol^{-1}

–135 kJ mol^{-1}

If both alternative values used then -169(.3) kJ mol^{-1}

Allow alternative ΔH and/or alternative ΔS in calculation
1

(e) Feasible because ΔG is negative

Allow mark if a correct deduction from answer to (d)

Both a reference to feasibility and to ΔG needed
1

(f) (i) (The catalyst is in) a different state or phase (from the reactants)
1

(ii) $SO_2 + V_2O_5 \longrightarrow SO_3 + V_2O_4$

Allow $2VO_2$ instead of V_2O_4

Allow multiples

1

$\frac{1}{2}O_2 + V_2O_4 \rightarrow V_2O_5$

Must have equations in this order

1

(iii) Surface area is increased

1

(iv) So that the catalyst is not poisoned

Allow correct reference to the blocking active sites

1

[14]

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 $C_2O_4^{2-}$) <u>repel</u>

Reference to molecules loses M2

1

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

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

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

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 = $\frac{2.16}{2.29}$ x100 = <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]

Q12.

(a) $2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 8H_2O + 10CO_2$

1

Mn^{2+} OR Mn^{3+}

If catalyst incorrect can only score M1 and M3

1

(Possible because) <u>Mn</u> can exist in variable oxidation states

1

E_a lowered because oppositely charged ions attract

These marks can be gained in any order

1

Mn^{3+} (reduced) to Mn^{2+} by $C_2O_4^{2-}$ / equation

M5 may appear before M2

1

Mn^{2+} (oxidised (back)) to Mn^{3+} by MnO_4^- / equation

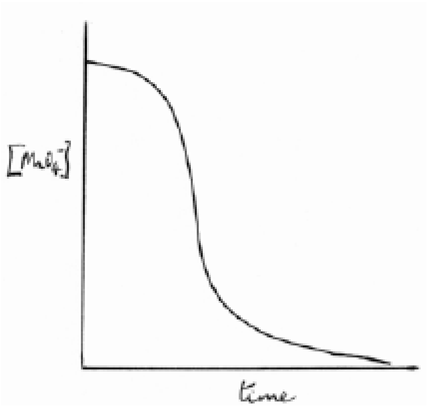
M5 and M6 can be scored in unbalanced equations or in words showing:

$Mn^{3+} + C_2O_4^{2-} \rightarrow Mn^{2+}$

$Mn^{2+} + MnO_4^- \rightarrow Mn^{3+}$

1

(b) **Graph marks**



S-shaped curve must not rise significantly and must not fall rapidly initially.

Starts on concentration axis **and** is levelling out (can level out on time axis or above but parallel to time axis)

Cannot score graph marks (M1 and M2) if no axes and / or no labels

1
1

Explanation marks
<u>Slope</u> / rate increases as catalyst (concentration) forms

1

Slope / rate decreases as (concentration) of MnO_4^- ions / reactant(s) decreases (OR reactants are being used up)

Explanation marks can be awarded independent of graph.

1

[10]

Q13.

(a) Negative ions <u>repel</u> one another

1

(b) Positive ions <u>attract</u> 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]

Q14.

(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

$CH_3CHO + 2Co^{3+} + H_2O \rightarrow CH_3COOH + 2Co^{2+} + 2H^+$

Allow multiples; allow molecular formulae

Allow equations with H_3O+

1

$\frac{1}{2}O_2 + 2Co^{2+} + 2H^+ \rightarrow 2Co^{3+} + H_2O$

1

(b) (i) $[Co(H_2O)_6]^{2+} + 3H_2NCH_2CH_2NH_2 \rightarrow [Co(H_2NCH_2CH_2NH_2)_3]^{2+} + 6H_2O$

Do not allow en in equation, allow $C_2H_8N_2$

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 $H_2N\text{-----}NH_2$

Allow linkage as −C−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 × 0.203) / 1000 = 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 $AgCl_2$ or $AgNO_3$), 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

$[Co(NH_3)_6]Cl_3$ (square brackets not essential)

1

Difference due to incomplete oxidation in the preparation

Allow incomplete reaction.

Allow formation $[Co(NH_3)_5Cl]Cl_2$ etc.

Some chloride ions act as ligands / replace NH_3 in complex.

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

1

[15]