M1.(a) $\quad\left[\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}+2 \mathrm{NH}_{3} \rightarrow \mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{4}(\mathrm{OH})_{2}+2 \mathrm{NH}_{4}^{+}$
Allow equation with $\mathrm{OH}^{-}$provided equation showing formation of $\mathrm{OH}^{-}$from $\mathrm{NH}_{3}$ given

Green precipitate
$\left[\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}+\mathrm{CO}_{3}{ }^{2-} \rightarrow \mathrm{FeCO}_{3}+6 \mathrm{H}_{2} \mathrm{O}$

Green precipitate
effervescence incorrect so loses M4
(b) (i) Colourless / (pale) green changes to pink / purple (solution)

Do not allow pale pink to purple

Just after the end-point $\mathrm{MnO}_{4}{ }^{-}$is in excess / present
(ii) $\mathrm{MnO}_{4}^{-}+8 \mathrm{H}^{+}+5 \mathrm{Fe}^{2+} \rightarrow \mathrm{Mn}^{2+}+4 \mathrm{H}_{2} \mathrm{O}+5 \mathrm{Fe}^{3+}$

Moles $\mathrm{KMnO}_{4}=18.7 \times 0.0205 / 1000=\left(3.8335 \times 10^{-4}\right)$
Process mark

Moles $\mathrm{Fe}^{2+}=5 \times 3.8335 \times 10^{-4}=1.91675 \times 10^{-3}$
Mark for M2 $\times 5$

Moles $\mathrm{Fe}^{2+}$ in $250 \mathrm{~cm}^{3}=10 \times 1.91675 \times 10^{-3}=0.0191675$ moles in 50 $\mathrm{cm}^{3}$

Process mark for moles of iron in titration (M3) $\times 10$

Original conc $\mathrm{Fe}^{2+}=0.0191675 \times 1000 / 50=0.383 \mathrm{~mol} \mathrm{dm}^{-3}$
Answer for moles of iron (M4) $\times 1000 / 50$
Answer must be to at least 2 sig. figs. (0.38)

M2.(a) Variable / many oxidation states
(b) $\mathrm{V}_{2} \mathrm{O}_{5}+\mathrm{SO}_{2} \rightarrow \mathrm{~V}_{2} \mathrm{O}_{4}+\mathrm{SO}_{3}$

Equations can be in either order
Allow multiples
$\mathrm{V}_{2} \mathrm{O}_{4}+1 / 2 \mathrm{O}_{2} \rightarrow \mathrm{~V}_{2} \mathrm{O}_{5}$
(c) (i) In a different phase / state from reactants
(ii) Impurities poison / deactivate the catalyst / block the active sites Allow (adsorbs onto catalyst AND reduces surface area)
(d) (i) The catalyst is a reaction product
(ii) $\mathrm{Mn}^{2+} / \mathrm{Mn}^{3+}$ ion(s)
(iii) $4 \mathrm{Mn}^{2+}+\mathrm{MnO}_{4}^{-}+8 \mathrm{H}^{+} \rightarrow 5 \mathrm{Mn}^{3+}+4 \mathrm{H}_{2} \mathrm{O}$

Equations can be in either order

$$
2 \mathrm{Mn}^{3+}+\mathrm{C}_{2} \mathrm{O}_{4}^{2-} \rightarrow 2 \mathrm{Mn}^{2+}+2 \mathrm{CO}_{2}
$$

M3.(a) Cobalt has variable oxidation states
(It can act as an intermediate that) lowers the activation energy
Allow (alternative route with) lower $E_{a}$
$\mathrm{CH}_{3} \mathrm{CHO}+2 \mathrm{Co}^{3+}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{CH}_{3} \mathrm{COOH}+2 \mathrm{Co}^{2+}+2 \mathrm{H}^{+}$
Allow multiples; allow molecular formulae
Allow equations with $\mathrm{H}_{3} \mathrm{O}+$

$$
\frac{1}{2} \mathrm{O}_{2}+2 \mathrm{Co}^{2+}+2 \mathrm{H}^{+} \rightarrow 2 \mathrm{Co}^{3+}+\mathrm{H}_{2} \mathrm{O}
$$

(b) (i) $\left[\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}+3 \mathrm{H}_{2} \mathrm{NCH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{2} \rightarrow\left[\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{NCH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{2}\right)_{3}\right]^{2+}+6 \mathrm{H}_{2} \mathrm{O}$

Do not allow en in equation, allow $\mathrm{C}_{2} \mathrm{H}_{8} \mathrm{~N}_{2}$

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

So the entropy change is positive / disorder increases / entropy increases
(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

Ligands need not have any atoms shown but diagram must show 6 bonds from ligands to Co, 2 from each ligand

Minimum for $\mathbf{M 2}$ is one ligand identified as $\mathrm{H}_{2} \mathrm{~N}----\mathrm{NH}_{2}$
Allow linkage as $-\mathrm{C}-\mathrm{C}$ - or just a line.

## Minimum for M3 is one bidentate ligand showing two arrows from separate nitrogens to cobalt

(c) Moles of cobalt $=(50 \times 0.203) / 1000=\underline{0.01015} \mathrm{~mol}$

Allow 0.0101 to 0.0102

```
Moles of AgCl = 4.22/143.4 = 0.0294
    Allow 0.029
    If not AgCl (eg AgCl2 or AgNO})\mathrm{ ), lose this mark and can only
    score M1, M4 and M5
```

Ratio $=\mathrm{Cl}^{-}$to $\mathrm{Co}=2.9: 1$
Do not allow 3 : 1 if this is the only answer but if 2.9:1 seen somewhere in answer credit this as M3
$\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right] \mathrm{Cl}_{3}$ (square brackets not essential)

Difference due to incomplete oxidation in the preparation
Allow incomplete reaction.
Allow formation $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{5} \mathrm{Cl}^{2} \mathrm{Cl}_{2}\right.$ etc.
Some chloride ions act as ligands / replace $\mathrm{NH}_{3}$ in complex.
Do not allow 'impure sample' or reference to practical deficiencies

M4.(a) $\quad \mathbf{Y}$
(b) X
(c) Jump in trend of ionisation energies after removal of fifth electron Fits with an element with 5 outer electrons $\left(4 s^{2} 3 d^{3}\right)$ like $V$
(d) Explanation: Two different colours of solution are observed

Because each colour is due to vanadium in a different oxidation state
(e) Stage 1: mole calculations in either order

Moles of vanadium $=50.0 \times 0.800 / 1000=4.00 \times 10^{-2}$
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.

Moles of $\mathrm{SO}_{2}=\mathrm{pV} / \mathrm{RT}=\left(98000 \times 506 \times 10^{-6}\right) /(8.31 \times 293)$
$=2.04 \times 10^{-2}$

Stage 2: moles of electrons added to $\mathrm{NH}_{4} \mathrm{VO}_{3}$
When $\mathrm{SO}_{2}$ (sulfur(IV) oxide) acts as a reducing agent, it is oxidised to sulfate $(\mathrm{VI})$ ions so this is a two electron change

Moles of electrons released when $\mathrm{SO}_{2}$ is oxidised $=2.04 \times 10^{-2} \times 2$
$=4.08 \times 10^{-2}$

Stage 3: conclusion
But in $\mathrm{NH}_{4} \mathrm{VO}_{3}$ vanadium is in oxidation state 5
$4.00 \times 10^{-2} \mathrm{~mol}$ vanadium has gained $4.08 \times 10^{-2} \mathrm{~mol}$ of electrons therefore 1 mol vanadium has gained $4.08 \times 10^{-2} / 4.00 \times 10-2=1 \mathrm{~mol}$ of electrons to the nearest integer, so new oxidation state is $5-1=4$

M5.(a) Negative ions repel one another
(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.
(c) $\mathrm{S}_{2} \mathrm{O}_{8}{ }^{2-}+2 \mathrm{e}^{-} \longrightarrow 2 \mathrm{SO}_{4}{ }^{2-}$

Allow multiples including fractions. Ignore state symbols.
(d) $\mathrm{S}_{2} \mathrm{O}_{8}{ }^{2-}+2 \mathrm{I}^{-} \longrightarrow 2 \mathrm{SO}_{4}{ }^{2-}+\mathrm{I}_{2}$ Allow multiples including fractions. Ignore state symbols. Allow the correct equation involving $I_{3}^{-}$ $\mathrm{S}_{2} \mathrm{O}_{8}{ }^{2-}+3 \mathrm{H}^{-} \longrightarrow 2 \mathrm{SO}_{4}^{2-}+\mathrm{I}_{3}^{-}$


M6.(a) moles of $\mathrm{Cr}_{2} \mathrm{O}_{7}^{2-}$ per titration $=21.3 \times 0.0150 / 1000=\underline{3.195 \times 10^{-4}}$

$$
\begin{gathered}
\left(\mathrm{Cr}_{2} \mathrm{O}_{7^{2-}}+14 \mathrm{H}^{+}+6 \mathrm{Fe}^{2+} \rightarrow 2 \mathrm{Cr}^{3+}+7 \mathrm{H}_{2} \mathrm{O}+6 \mathrm{Fe}^{3+}\right) \mathrm{Cr}_{2} \mathrm{O}_{7}^{2-} \cdot \mathrm{Fe}^{2+}=1: 6 \\
\text { If 1:6 ratio incorrect cannot score M2 or M3 }
\end{gathered}
$$

```
moles of \(\mathrm{Fe}^{2+}=6 \times 3.195 \times 10^{-4}=1.917 \times 10^{-3}\)
    Process mark for M1 \(\times 6\) (also score M2)
```

original moles in $250 \mathrm{~cm}^{3}=1.917 \times 10^{-3} \times 10=1.917 \times 10^{-2}$
Process mark for M3 $\times 10$
mass of $\mathrm{FeSO}_{4} .7 \mathrm{H}_{2} \mathrm{O}=1.917 \times 10^{-2} \times 277.9=5.33(\mathrm{~g})$
Mark for answer to M4 $\times 277.9$
(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)
(b) (Impurity is a) reducing agent / reacts with dichromate / impurity is a version of $\mathrm{FeSO}_{4}$ with fewer than 7 waters (not fully hydrated)

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

Such that for a given mass, the impurity would react with more dichromate than a similar mass of $\mathrm{FeSO}_{4} .7 \mathrm{H}_{2} \mathrm{O}$

OR for equal masses of the impurity and $\mathrm{FeSO}_{4} \cdot 7 \mathrm{H}_{2} \mathrm{O}$, the impurity would react with more dichromate.

Must compare mass of impurity with mass of $\mathrm{FeSO}_{4} \cdot 7 \mathrm{H}_{2} \mathrm{O}$

