M1.(a) Reaction 1

## General principles in marking this question

Square brackets are not essential
Penalise charges on individual ligands rather than on the whole complex
Reagent and species can be extracted from the equation Ignore conditions such as dilute, concentrated, excess Reagent must be a compound NOT just an ion Equations must start from $\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$ except in part (b) Mark reagent, species and equation independently ammonia $\left(\mathrm{NH}_{3}\right)$ (solution) / NaOH
$\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}+2 \mathrm{NH}_{3} \rightarrow\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{4}(\mathrm{OH})_{2}\right]+2 \mathrm{NH}_{4}^{+} /$
$\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}+2 \mathrm{OH}^{-} \rightarrow\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{4}(\mathrm{OH})_{2}\right]+2 \mathrm{H}_{2} \mathrm{O}$
Do not allow $\mathrm{OH}^{-}$for reagent
Product 1, balanced equation 1
Allow either equation for ammonia
(b) Reaction 2

Ammonia (conc / xs)
$\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{4}(\mathrm{OH})_{2}\right]+4 \mathrm{NH}_{3} \rightarrow\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\left(\mathrm{NH}_{3}\right)_{4}\right]^{2+}+2 \mathrm{H}_{2} \mathrm{O}+2 \mathrm{OH}^{-}$
Product 1, balanced equation 1
Note that the equation must start from the hydroxide $\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{4}(\mathrm{OH})_{2}\right]$
(c) Reaction 3
$\mathrm{Na}_{2} \mathrm{CO}_{3} /$ any identified soluble carbonate / $\mathrm{NaHCO}_{3}$
Do not allow $\mathrm{NaCO}_{3}$ or any insoluble carbonate but mark on
$\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}+\mathrm{CO}_{3}{ }^{2-} \rightarrow \mathrm{CuCO}_{3}+6 \mathrm{H}_{2} \mathrm{O}$
$\mathrm{OR}\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}+\mathrm{Na}_{2} \mathrm{CO}_{3} \rightarrow \mathrm{CuCO}_{3}+6 \mathrm{H}_{2} \mathrm{O}+2 \mathrm{Na}^{+}$
OR $2\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}+2 \mathrm{CO}_{3}{ }^{2-} \rightarrow \mathrm{Cu}(\mathrm{OH})_{2} \cdot \mathrm{CuCO}_{3}+11 \mathrm{H}_{2} \mathrm{O}+\mathrm{CO}_{2}$
OR with $\mathrm{NaHCO}_{3}$
$\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}{ }^{2+}+\mathrm{HCO}_{3}^{-} \rightarrow \mathrm{CuCO}_{3}+6 \mathrm{H}_{2} \mathrm{O}+\mathrm{H}^{+}\right.$
Product 1, balanced equation 1
(d) Reaction 4

HCl (conc / xs) / NaCl
Allow any identified soluble chloride
$\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}+4 \mathrm{Cl}^{-} \rightarrow\left[\mathrm{CuCl}_{4}\right]^{2-}+6 \mathrm{H}_{2} \mathrm{O}$
Product 1, balanced equation 1
2
[12]

M2.(a) Cobalt has variable oxidation states
Allow exists as Co (II) and Co (III)
(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 $\mathrm{H}_{3} \mathrm{O}+$

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\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 $\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{~N}_{2}$

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 $\mathrm{AgCl}=4.22 / 143.4=0.0294$
Allow 0.029
If not AgCl (eg AgCl ${ }_{2}$ or $\mathrm{AgNO}_{3}$ ), 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
$\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6} \mathrm{Cl}_{3}\right.$ (square brackets not essential)

M3.(a) Water in the gaseous state from the precipitate absorbed by drying agent

## OR

Water vapour from the precipitate absorbed by drying agent
Allow 'water vapour reacts with drying agent'.
Do not allow 'absorb water' without qualification.
(b) (Blue to) pink / pink colour observed

Allow lone pair donor
(b) $\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}+2 \mathrm{NH}_{3} \rightarrow \mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{4}(\mathrm{OH})_{2}+2 \mathrm{NH}_{4}^{+}$
(Blue solution) gives a (pale) blue precipitate/solid M2 only awarded if M1 shows Bronsted-Lowry reaction
(c) $\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{]^{2+}}+4 \mathrm{NH}_{3} \rightarrow\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\left(\mathrm{NH}_{3}\right)_{4}\right]^{2+}+4 \mathrm{H}_{2} \mathrm{O}\right.$ Allow formation in two equations via hydroxide
(Blue solution) gives a dark/deep blue solution
If (b) and (c) are the wrong way around allow one mark only for each correct equation with a correct observation (max 2/4)
M2 only awarded if M1 shows Lewis base reaction
(d) (Start with) green (solution)

Do not allow observation if compound incorrect or not given

Slowly changes to brown solid
Allow red-brown ppt
Allow turns brown or if precipitate implied
Can only score M3 if M2 scored
(Iron(II) hydroxide) oxidised by air (to iron(III) hydroxide)
Allow $\mathrm{Fe}(\mathrm{OH})_{2}$ oxidised to $\mathrm{Fe}(\mathrm{OH})_{3}$ by air / $\mathrm{O}_{2}$ Ignore equations even if incorrect
(e) (i) $2\left[\mathrm{Al}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}+3 \mathrm{H}_{2} \mathrm{NCH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{2} \rightarrow 2 \mathrm{Al}\left(\mathrm{H}_{2} \mathrm{O}\right)_{3}(\mathrm{OH})_{3}+3\left[\mathrm{H}_{3} \mathrm{NCH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{3}\right]^{{ }^{+}}$ For correct Al species

For correct balanced equation
Allow equation with formation of $3\left[\mathrm{H}_{2} \mathrm{NCH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{3}\right]+$ from 1 $\mathrm{mol}\left[\mathrm{Al}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}$

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

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Complex with 3 en showing 6 correct bonds from N to Co
Ignore charge
Accept $N-N$ for ligand
Ignore incorrect $H$
If $C$ shown, must be 2 per ligand

Co-ordinate bonds (arrows) shown from N to Co
Can only score M3 if M2 correct
$4\left[\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{NCH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{2}\right)_{3}\right]^{2+}+\mathrm{O}_{2}+2 \mathrm{H}_{2} \mathrm{O} \rightarrow 4\left[\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{NCH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{2}\right)_{3}\right]^{3+} 4 \mathrm{OH}^{-}$
For Co(III) species

For balanced equation (others are possible)
Allow $+\mathrm{O}_{2}+4 \mathrm{H}^{+} \rightarrow 2 \mathrm{H}_{2} \mathrm{O}$
If en used can score M4 and M5 only
If Cu not Co, can only score M2 and M3
Allow $\mathrm{N}_{2} \mathrm{C}_{2} \mathrm{H}_{8}$ in equations

M5.(a) (i) Two rings only around nitrogen or sulfur Lose this mark if more than 2 atoms are ringed.
Do not allow two atoms at the same end of the ion.
(ii) 275.8

Accept this answer only. Do not allow 276
(iii) Carboxylate / $\mathrm{COO}^{-}$

Allow salt of carboxylic acid or just carboxylic acid.
(b) $\quad(32.1 / 102.1)=31.4 \%$

Do not penalise precision but do not allow 1 significant figure.
(c) Zineb is mixed with a solvent / water Max=2 if M1 missed

Use of column / paper / TLC
Lose M1 and M2 for GLC

Appropriate collection of the ETU fraction

## OR Appropriate method of detecting ETU

Allow ETU is an early fraction in a column or collecting a range of samples over time, lowest retention time / travels furthest on paper or TLC (allow 1 mark for having the longest retention time in GLC).

Method of identification of ETU (by comparison with standard using chromatography)

If method completely inappropriate, only M1 is accessible

