Q6.

The equation for the reaction between ammonia and oxygen is shown.

$$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g) \qquad \Delta H = -905 \text{ kJ mol}^{-1}$$

Some standard entropies are given in the table.

Gas	**S° / J K^{-1} mol^{-1}**
$NH_3(g)$	193
$O_2(g)$	205
$NO(g)$	211
$H_2O(g)$	189

(a) Calculate the entropy change for the reaction between ammonia and oxygen.

Entropy change ____________________ J K^{-1} mol^{-1}

(2)

(b) Calculate a value for the Gibbs free-energy change (ΔG), in kJ mol^{-1}, for the reaction between ammonia and oxygen at 600 °C

(If you were unable to obtain an answer to part (a), you should assume that the entropy change is 211 J K^{-1} mol^{-1}. This is not the correct answer.)

ΔG ____________________ kJ mol^{-1}

(2)

(c) The reaction between ammonia and oxygen was carried out at a higher temperature.

Explain how this change affects the value of ΔG for the reaction.

(2)

(d) Platinum acts as a heterogeneous catalyst in the reaction between ammonia and oxygen. It provides an alternative reaction route with a lower activation energy.

Describe the stages of this alternative route.

(3)

(e) Deduce the change in oxidation state of nitrogen, when NH_3 is oxidised to NO

(1)

(f) When ammonia reacts with oxygen, nitrous oxide (N_2O) can be produced instead of NO

Give an equation for this reaction.

(1)

(Total 11 marks)

Q7.

Titanium(IV) chloride can be made from titanium(IV) oxide as shown in the equation.

$$TiO_2(s) + 2C(s) + 2Cl_2(g) \rightarrow 2CO(g) + TiCl_4(l) \qquad \Delta H^\ominus = -60.0\ kJ\ mol^{-1}$$

Some entropy data are shown in the table.

Substance	$TiO_2(s)$	$C(s)$	$Cl_2(g)$	$CO(g)$	$TiCl_4(l)$
$S^\ominus$ / J K^{-1} mol^{-1}	50.2	5.70	223	198	253

Use the equation and the data in the table to calculate the Gibbs free-energy change for this reaction at 989 °C

Give your answer to the appropriate number of significant figures.

Use your answer to explain whether this reaction is feasible.

Gibbs free-energy change ____________________ kJ mol^{-1}

Explanation ____

____

(Total 6 marks)

Q8.

Anhydrous magnesium chloride, $MgCl_2$, can absorb water to form the hydrated salt $MgCl_2.4H_2O$

$$MgCl_2(s) + 4H_2O(l) \longrightarrow MgCl_2.4H_2O(s)$$

(a) Suggest **one** reason why the enthalpy change for this reaction cannot be determined directly by calorimetry.

____

____

(1)

(b) Some enthalpies of solution are shown in Table 1.

Table 1

Salt	**Enthalpy of solution / kJ mol^{-1}**
$MgCl_2(s)$	−155
$MgCl_2.4H_2O(s)$	−39

Calculate the enthalpy change for the absorption of water by $MgCl_2(s)$ to form $MgCl_2.4H_2O(s)$.

Enthalpy change ______________________________ kJ mol^{-1}

(2)

(c) Describe how you would carry out an experiment to determine the enthalpy of solution of anhydrous magnesium chloride.

You should use about 0.8 g of anhydrous magnesium chloride.

Explain how your results could be used to calculate the enthalpy of solution.

____

____

____

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____

____

____

____

(6)

(d) Anhydrous magnesium chloride can be formed by direct reaction between its elements.

$$Mg(s) + Cl_2(g) \longrightarrow MgCl_2(s)$$

The free-energy change, ΔG, for this reaction varies with temperature as shown in **Table 2**.

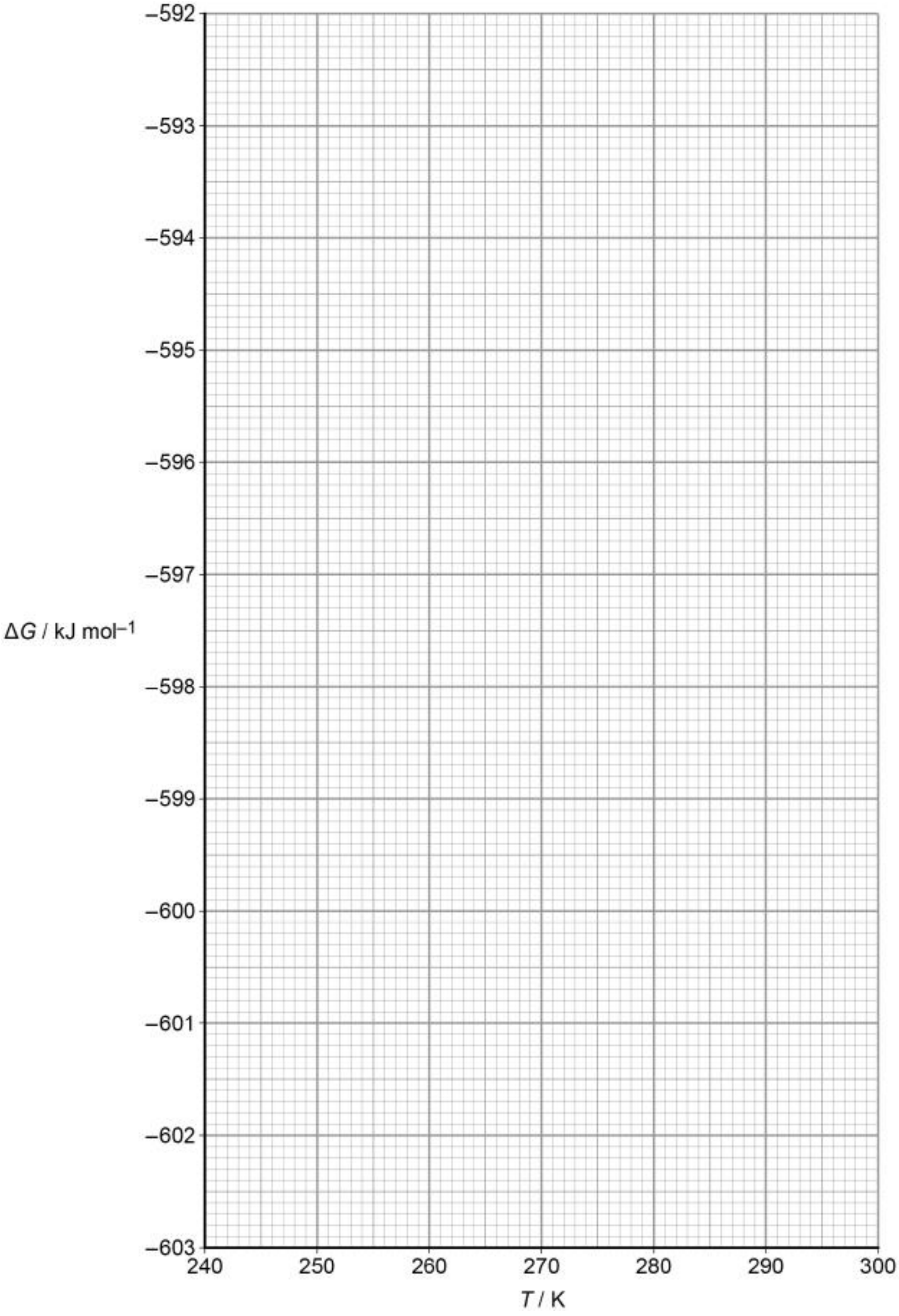
Table 2

T / K	**ΔG / kJ mol^{-1}**
298	−592.5
288	−594.2
273	−596.7
260	−598.8
240	−602.2

Use these data to plot a graph of free-energy change against temperature on the grid below.

Calculate the gradient of the line on your graph and hence calculate the entropy change, ΔS, in J K^{-1} mol^{-1}, for the formation of anhydrous magnesium chloride from its elements.

Show your working.



ΔS ______________________________________ J K^{-1} mol^{-1}

(5)

(Total 14 marks)

Q9.

A reaction is exothermic and has a negative entropy change.

Which statement is correct?

A The reaction is always feasible ○

B The reaction is feasible above a certain temperature ○

C The reaction is feasible below a certain temperature ○

D The reaction is never feasible ○

(Total 1 mark)

Q10.

Hydrogen can be manufactured by the reaction of methane with steam. An equilibrium is established as shown by the equation.

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$

(a) Use Le Chatelier's principle to predict the effect on the equilibrium yield of hydrogen if the overall pressure is increased.
Explain your answer.

Effect on yield ______________________________

Explanation ______________________________

____

____

____

(3)

(b) Explain why the equilibrium yield of hydrogen is unchanged if a catalyst is used in the reaction.

____

____

____

____

____

(2)

(c) The table shows the standard enthalpy of formation and the standard entropy for each substance in this equilibrium reaction.

	$CH_4(g)$	$H_2O(g)$	$CO(g)$	$H_2(g)$
$\Delta_f H^\theta$ / kJ mol^{-1}	−75	−242	−111	0
S^θ / J K^{-1} mol^{-1}	186	189	198	131

Use data from the table to calculate the standard enthalpy change for this equilibrium reaction.

Standard enthalpy change _____________ kJ mol^{-1}

(2)

Use your answer from part **(c)** and the entropy data from the table above to calculate the minimum temperature, in °C, needed for this reaction to be feasible.
Give your answer to the appropriate number of significant figures.

(If you did not complete part **(c)** you should assume a value of 120 kJ mol^{-1} for the standard enthalpy change. This is **not** the correct value).

Minimum temperature _________ °C

(5)

(Total 12 marks)

Q11.

The table below contains some entropy data relevant to the reaction used to synthesise methanol from carbon dioxide and hydrogen. The reaction is carried out at a temperature of 250 °C.

Substance	$CO_2(g)$	$H_2(g)$	$CH_3OH(g)$	$H_2O(g)$
Entropy ($S^\ominus$) / J K^{-1} mol^{-1}	214	131	238	189

$$CO_2(g) + 3H_2(g) \rightleftharpoons CH_3OH(g) + H_2O(g) \quad \Delta H = -49 \text{ kJ mol}^{-1}$$

(a) Use this enthalpy change and data from the table to calculate a value for the free-energy change of the reaction at 250 °C.
Give units with your answer.

Free-energy change = _____________ Units = _____________

(4)

(b) Calculate a value for the temperature when the reaction becomes feasible.

Temperature = _______________ K

(2)

(c) Gaseous methanol from this reaction is liquefied by cooling before storage.

Draw a diagram showing the interaction between two molecules of methanol. Explain why methanol is easy to liquefy.

Diagram

Explanation ____

____

____

(4)

(Total 10 marks)

Q12.

(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)

Mark Scheme

Q6.

(a) ($\Delta S = \Sigma(S \text{ products}) - \Sigma(S \text{ reactants})$)

$= [(4 \times 211) + (6 \times 189)] - [(4 \times 193) + (5 \times 205)] = (1978 – 1797)$

1

181 (J K^{-1} mol^{-1})

1

(b) ($\Delta G = \Delta H – T\Delta S$) $= - 905 - (600 + 273) \times 181 \times 10^{-3}$

If answer to (a) is incorrect, mark consequentially:

$- 905 - (873 \times (a) \times 10^{-3})$

1

$\Delta G = - 1063$ / -1060 (kJ mol^{-1})

If alternative value of $\Delta S = 211$ used, answer $= -1089$ (kJ mol^{-1})

1

(c) ΔG becomes more negative/less positive

Ignore increase/decrease/larger/smaller ΔG

1

The entropy change / ΔS is positive / $T\Delta S$ gets bigger / $-T\Delta S$ gets more negative.

Consequential on wrong (a)

If candidate does a calculation in (a) to produce ΔS negative then allow ΔG becomes less negative or more positive

1

(d) Reactant(s) adsorbed onto the (platinum surface) / (platinum) provides a surface / active sites

1

Reaction (on the surface) or bond breaking(weakening) / bond making occurs (on the surface)

1

Desorption (of the product) or wtte

1

(e) (Oxidation state changes from) -3 to +2 OR (+) 5

1

(f) $2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O$

Allow multiples

Ignore state symbols

1

[11]

Q7.

$\Delta S = \Sigma_S$ products – ΣS reactants or
$253 + (2 \times 198) – (2 \times 223 + 2 \times 5.7 + 50.2)$ (= 649 – 507.6)

This expression could also score M1

1

$\Delta S = 141(.4)$ (J K^{-1}mol^{-1})

This scores M1 and M2

Allow ecf for M3, M4 and M5 from incorrect M2

1

$\Delta G = \Delta H - T\Delta S$

1

$\Delta G = -60 - (\underline{1262} \times 141(.4) \times 10^{-3})$

This expression also scores M3.

For M4, allow $\Delta G = -60 - (\underline{1262} \times \text{their M2} \times 10^{-3})$

1

= –238 (kJ mol^{-1}) to 3 sig figs

If calculated in joules

M4: Allow $\Delta G = -60 \times 10^{3} - (\underline{1262} \times 141(.4))$

M5: Allow -238 000 J mol^{-1} providing units shown

1

feasible since ΔG is negative/less than zero

Allow consequential M6 from their ΔG

1

[6]

Q8.

(a) Not possible to prevent some dissolving

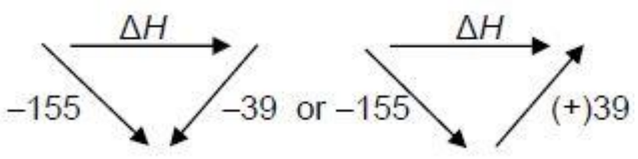
ALLOW It is soluble / dissolves / other hydrates may form / suggestions related to difficulty of measuring T (change) of a solid

1

(b) ($\Delta_{hyd}H$ =) –155 – (–39)

OR labelled cycle

Minimum needed for 'labelled cycle'



1

–116 (kJ mol^{-1})

1/2 for (+)116 or for –29 or for seeing –116 that has then be processed further

1

(c) This question is marked using levels of response. Refer to the Mark Scheme Instructions for examiners for guidance on how to mark this question

Level 3 (5 – 6 marks)

All stages are covered and the explanation of each stage is correct and virtually complete. Stage 2 must include use of a graphical method for Level 3 (i.e. ‘highest T reached’ method is max Level 2)

Answer communicates the whole explanation, including reference to enthalpy, coherently and shows a logical progression through all three stages.Answer is full and detailed and is supported by an appropriate range of relevant points such as those given below:
For the answer to be coherent there must be some indication of **how** the graph is used to find ΔT

Level 2 (3 – 4 marks)

All stages are covered (NB ‘covered’ means min 2 from each of stage 1 and 3) but the explanation of each stage may be incomplete or may contain inaccuracies
OR two stages covered and the explanations are generally correct and virtually complete

Answer is coherent and shows some progression through all three stages. Some steps in each stage may be out of order and incomplete

Level 1 (1 – 2 marks)

Two stages are covered but the explanation of each stage may be incomplete or may contain inaccuracies
OR only one stage is covered but the explanation is generally correct and virtually complete

Answer shows some progression between two stages

Level 0 (0 marks)

Insufficient correct Chemistry to warrant a mark

Indicative Chemistry Content

Stage 1 Method

(1a) Measures water with named appropriate apparatus
(1b) Suitable volume/mass / volume/mass in range 10 – 200 cm^3/g
(1c) Into insulated container / polystyrene cup (NOT just ‘lid’)
(1d) Add known mass of $MgCl_2(s)$
(1e) Use of ‘before and after’ weighing method. NOT ‘added with washings’

Stage 2 Measurements (could mark from diagram)

(2a) Record initial temperature (min 2 measurements)
(2b) Record T at regular timed intervals for 5+ mins / until trend seen
(2c) Plot T vs time

Stage 3 Use of Results (3a and 3b could come from diagram)

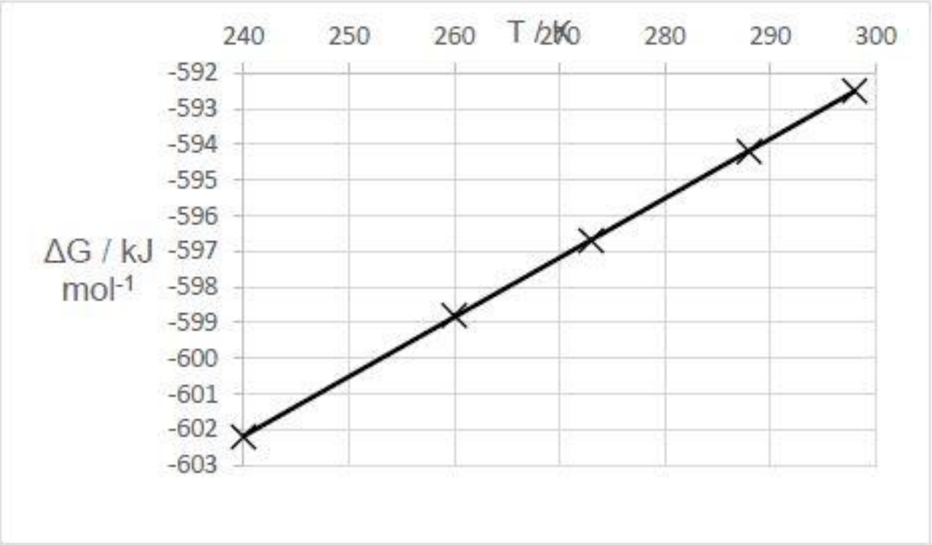
(3a) Extrapolate lines to when solid added (to find initial and final T)
(3b) $T_{final} - T_{initial} = \Delta T$ / idea of finding ΔT from graph at point of addition
(3c) $q = mc\Delta T$
(3d) amount = mass/Mr (0.80/95.3 = 8.39×10^{-3} mol)
(3e) $\Delta H_{soln} = -q/8.39 \times 10^{-3}$ or in words

This could all be described in words without showing actual calculations but describing stages

If method based on 'combustion' Max Level 1

6

(d)



M1 *= 5 points correctly plotted*

M2 *= line drawn correctly (NOT if curved, doubled or kinked)*

(Check line of best fit –

*if through 250, -600.5 and 280, -595.5 +/- one small square then award **M2**, if all crosses on line award **M1** as well)*

2

Gradient = $\Delta(\Delta G)/\Delta T$ = 0.167 (kJ K^{-1} mol^{-1})

1

($\Delta G = \Delta H - T\Delta S$ so gradient = $-\Delta S$)

ΔS = –167 (J K^{-1} mol^{-1})

M4 *= unit conversion i.e. **M3** × 1000; M5 = –sign (process marks)*

*Correct answer with sign gets **M3**, **M4** and M5*

ALLOW –163 to –171

1+1

[14]

Q9.

C

[1]

Q10.

(a) Decrease

1

Increasing pressure moves equilibrium to the side of least moles i.e. backward reaction

1

To oppose the increase in pressure or to decrease the pressure

1

(b) A catalyst speeds up the rate of the forward and backward reaction

1

By the same amount

1

(c) $\Delta H = -111 - (-75 - 242)$

1

206 (kJ mol^{-1})

1

(d) $\Delta S = 3 \times 131 + 198 - (186 + 189) = 216$ J K^{-1} mol^{-1}

1

$\Delta G = \Delta H - T\Delta S$

1

$0 = 206 - T\frac{216}{1000}$

1

T = 953.7 or 954 K

1

T = 681 (°C)

If the value given in the question is used then the answer is 283 (°C)

1

[12]

Q11.

(a) $\Delta S = 238 + 189 - 214 - 3 \times 131 = -180$ J K^{-1} mol^{-1}

1

$\Delta G = \Delta H - T\Delta S$

1

$= -49 - \frac{523 \times (-180)}{1000}$

1

= +45.1 kJ mol^{-1}

Units essential

1

(b) When $\Delta G = 0$, $\Delta H = T\Delta S$ therefore $T = \Delta H / \Delta S$

1

$= -49 \times 1000 / -180 = 272$ (K)

Mark consequentially to ΔS in part (a)

1

(c) Diagram marks

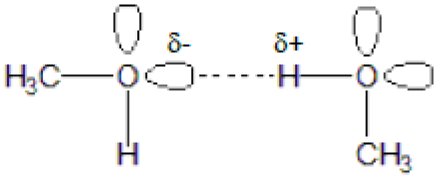


Diagram of a molecule showing O–H bond and two lone pairs on each oxygen **1**

Labels on diagram showing δ+ and δ- charges

Allow explanation of position of δ+ and δ- charges on H and O **1**

Diagram showing δ+ hydrogen on one molecule attracted to lone pair on a second molecule **1**

Explanation mark

Hydrogen bonding (the name mentioned) is a strong enough force (to hold methanol molecules together in a liquid) **1**

[10]

Q12.

(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]