Mark schemes

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

1

or (2 × −395) − (2 × −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 × 256) − 205 − (2 × 248)

= −189 $\underline{JK^{-1}\ mol^{-1}}$

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}
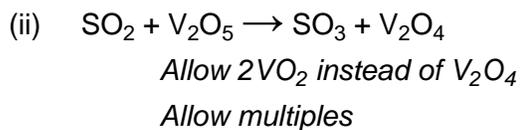
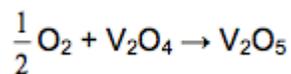*Allow alternative ΔH and/or alternative ΔS in calculation*

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]

2   (a)   [Ar] $4s^2\ 3d^7$ or $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$

        Allow 4s and 3d in either order

1

[Ar] $3d^7$ or $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7$

1

Any 3

Variable oxidation state

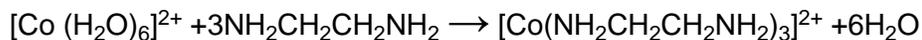Act as catalysts

Form complexes

Form coloured ions/compounds

3

(b) Two atoms that each donate a lone pair (of electrons) / coordinate
bonds from two atoms

1

Formula of ethane-1,2- diamine: $NH_2CH_2CH_2NH_2$

M2 gained from equation or structure

1

$[Co (H_2O)_6]^{2+} + 3NH_2CH_2CH_2NH_2 \longrightarrow [Co(NH_2CH_2CH_2NH_2)_3]^{2+} + 6H_2O$

Equation must be balanced inc charges

Allow en or $C_2H_8N_2$ in equation for ethane-1,2-diamine

1

There is an increase in the number of particles / the reaction goes
from 4 moles to 7 moles

*Allow increase number of molecules/moles. Allow numbers that
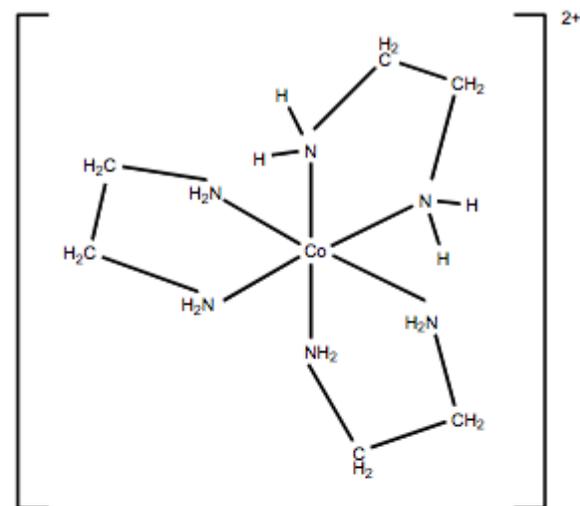match an incorrect equation*

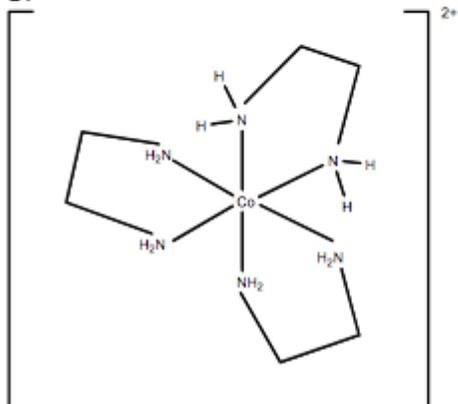**1**

Disorder/entropy increases / ΔS is positive

1

ΔG negative

1

Or

Mark for correct structure (ignore charges -even if wrong)

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NH$_2$ can be shown in either way – see structure

1

3 (a) A reaction that produces its own catalyst/ one of the products is the catalyst

1

Mn^{2+}

Allow Mn^{3+}

1

(b) H$_2$SO$_4$

1

(c) There is no/very little catalyst at the start OR the reaction only
speeds up when the catalyst is produced
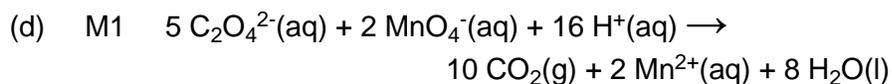
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Two negative ions (MnO$_4^-$ and C$_2$O$_4^{2-}$) <u>repel</u>

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 $n(MnO_4^{-}) = \dfrac{26.40 \times 0.02}{1000}$ OR $n(MnO_4^{-}) = 5.28 \times 10^{-4}$

1

M3 $n(C_2O_4^{2-}) = \dfrac{5}{2} \times 5.28 \times 10^{-4} = 1.32 \times 10^{-3}$

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

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

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

Answer must be to 3 s.f.

Correct answer scores 6 marks; mark equation separately

Alternative method using ratio by moles:

M5 $n(C_2O_4^{2-}) = 4.66 \times 10^{-3} \times 3 = 0.0140$ 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 × 100 = $\underline{94.3\ or\ 94.4}\%$

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]

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

All stages are covered and the explanation of each stage is generally correct and virtually complete.

Answer is communicated coherently and shows a logical progression from stage 1 to stage 2 then stage 3.

Level 3
5 – 6 marks

All stages are covered but the explanation of each stage may be incomplete or may contain inaccuracies OR two stages are covered and the explanations are generally correct and virtually complete.

Answer is mainly coherent and shows progression from stage 1 to stage 3.

Level 2
3 – 4 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 includes isolated statements but these are not presented in a logical order or show confused reasoning.

Level 1
1 – 2 marks

Insufficient correct chemistry to gain a mark.

Level 0
0 marks

Indicative chemistry content

Stage 1: Electrons round P
- P has 5 electrons in the outside shell
- With 3 electrons from 3 fluorine, there are a total of 8 electrons in outside shell
- so 3 bond pairs, 1 non-bond pair

Stage 2: Electron pair repulsion theory
- Electron pairs repel as far as possible
- Lone pair repels more than bonding pairs

Stage 3: Conclusions
- Therefore, tetrahedral / trigonal pyramidal shape
- With angle of 109(.5)° decreased to 107°

6

(b) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7$

Allow correct numbers that are not superscripted

1

(c) Too many electrons in d sub-shell / orbitals

1

(d) Tetrahedral (shape)

1

109.5°

Allow 109°

1

[10]

5 (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 = $(98\,000 \times 506 \times 10^{-6}) / (8.31 \times 293)$

= 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 $4.08 \times 10^{-2} / 4.00 \times 10 - 2 = 1$ mol
of electrons to the nearest integer, so new oxidation state is $5 - 1 = 4$

1

[11]

6 (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
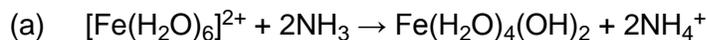
1

Therefore, the free-energy change is negative
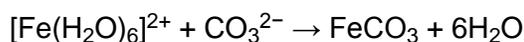   *M2 can only be awarded if M1 is correct*

1

     [11]

7 (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 NH₃ 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
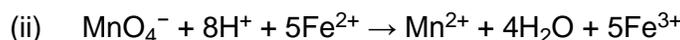
1

(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 cm³ = 10 × 1.91675 × 10⁻³ = 0.0191675 moles in 50 cm³
     Process mark for moles of iron in titration (M3) × 10

1

Original conc Fe^{2+} = 0.0191675 × 1000 / 50 = 0.383 <u>mol dm⁻³</u>
     Answer for moles of iron (M4) × 1000 / 50
     Answer must be to at least 2 sig. figs. (0.38)

1

     [11]

8 (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
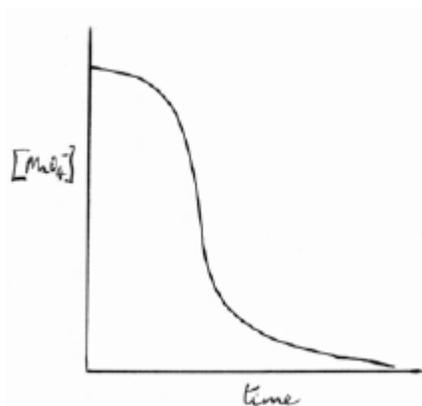
Mn^{2+} (oxidised (back)) to Mn^{3+} by MnO_4^- / equation

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

<u>Slope</u> / 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]

9 (a) <u>164.0</u>

Must be 1 decimal place

1

(b) 17.1(%) (= 28.0 × 100 / Qa)

Consequential on their (a)

Ignore precision but must be to at least 2 sig fig.

(i.e. accept 17 or 17.07)

1

(c) (i) <u>*Absorption*</u> depends on (proportional to) path length / distance travelled through solution

Do not allow size.

1

(ii) To select the colour / frequency / wavelength that is (most strongly) absorbed (by the sample)

Allow the filter is chosen to complement the colour of the solution

1

(iii) Quicker to analyse extracted samples than by titration / uses smaller volumes of solution

1

[5]

10 (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

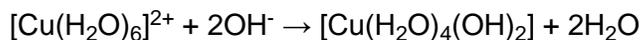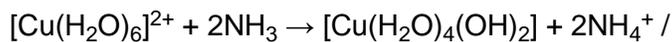*Ignore conditions such as dilute, concentrated, excess*

Reagent must be a compound NOT just an ion

Equations must start from $[Cu(H_2O)_6]^{2+}$ except in part (b)

Mark reagent, species and equation independently

ammonia (NH_3) (solution) / NaOH

1

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

$[Cu(H_2O)_6]^{2+} + 2OH^- \rightarrow [Cu(H_2O)_4(OH)_2] + 2H_2O$

Do not allow OH⁻ for reagent
Product 1, balanced equation 1
Allow either equation for ammonia

2

(b) **Reaction 2**

Ammonia (conc / xs)

1

$[Cu(H_2O)_4(OH)_2] + 4NH_3 \rightarrow [Cu(H_2O)_2(NH_3)_4]^{2+} + 2H_2O + 2OH^-$
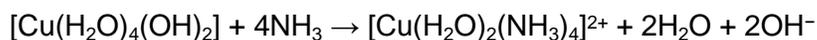
Product 1, balanced equation 1
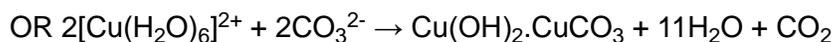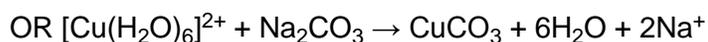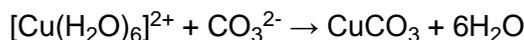*Note that the equation must start from the hydroxide*
[Cu(H₂O)₄(OH)₂]

2

(c) **Reaction 3**

Na_2CO_3 / any identified soluble carbonate / $NaHCO_3$

Do not allow NaCO₃ or any insoluble carbonate but mark on

1

$[Cu(H_2O)_6]^{2+} + CO_3^{2-} \rightarrow CuCO_3 + 6H_2O$

OR $[Cu(H_2O)_6]^{2+} + Na_2CO_3 \rightarrow CuCO_3 + 6H_2O + 2Na^+$

OR $2[Cu(H_2O)_6]^{2+} + 2CO_3^{2-} \rightarrow Cu(OH)_2.CuCO_3 + 11H_2O + CO_2$

OR with $NaHCO_3$

$[Cu(H_2O)_6]^{2+} + HCO_3^- \rightarrow CuCO_3 + 6H_2O + H^+$
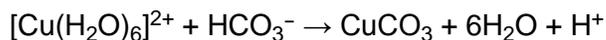
Product 1, balanced equation 1

2

(d) **Reaction 4**

HCl (conc / xs) / NaCl

Allow any identified soluble chloride

1

$[Cu(H_2O)_6]^{2+} + 4Cl^- \rightarrow [CuCl_4]^{2-} + 6H_2O$

Product 1, balanced equation 1

2

[12]