AQA A-LEVEL CHEMISTRY · 7405

CHEMISTRY



MARK SCHEME

3.2.5 TRANSITION METALS

SCORE	PERCENTAGE
/276	%

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Q1.

(a) (ΔS = Σ(*S products*) - Σ(*S reactants*))

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

1

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

1

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

If answer to (a) is incorrect, mark consequentially:
- 905 - (873 × (a) × 10^{-3})

1

ΔG = - 1063 / -1060 (kJ mol^{-1})

If alternative value of ΔS = 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 / Δ*S* is positive / *T*Δ*S* gets bigger / -*T*Δ*S* gets more negative.

Consequential on wrong (a)
*If candidate does a calculation in (a) to produce Δ*S* negative then allow Δ*G* 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]

Q2.

(a) Fe^{2+}

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

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

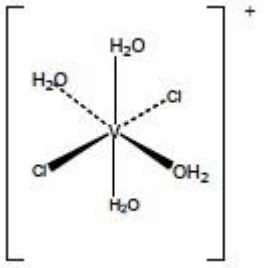
1

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

$V_2O_4 + ½\ O2 \rightarrow V_2O_5$

Both equations needed for 1 mark in this order

Allow multiples

1

[7]

Q3.

D

[1]

Q4.

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

1

or (2 × –395) – (2 × –297)

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= –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

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(iii) Surface area is increased

1

(iv) So that the catalyst is not poisoned

Allow correct reference to the blocking active sites

1

[14]

Q5.

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

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

M5 is for M4 ÷ 3

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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 250cm³

M6 n(complex) = 2.29/491.1 = 4.66×10^{-3} moles in 250cm³

M7 % = 0.0132/0.0140 × 100 = <u>94.3 or 94.4</u>%

1

(e) Make <u>some known</u> concentrations (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]

Q6.

(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:

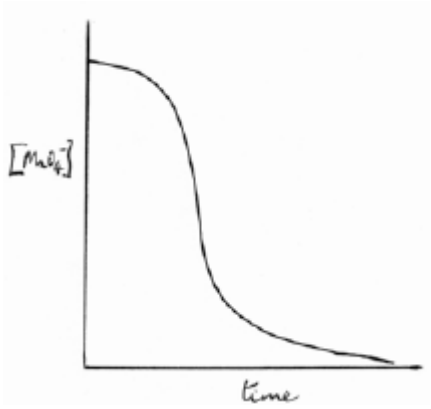
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$Mn^{3+} + C_2O_4^{2-} \rightarrow Mn^{2+}$

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

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

Slope / 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]

Q7.

(a) Negative ions repel one another

1

(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.

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^-

$S_2O_8^{2-} + 3I^- \longrightarrow 2SO_4^{2-} + I_3^-$

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1

[4]

Q8.

(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-----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 = <u>0.01015</u> mol

Allow 0.0101 to 0.0102

1

Moles of AgCl = 4.22/143.4 = 0.0294

Allow 0.029

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*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]

Q9.

(a) Stoppered flask or similar with side arm

Allow gas outlet through stopper.

1

Calibrated container for collection eg gas syringe

Allow collection over water, but must use calibrated vessel for collection.

Lose 1 mark if apparatus is not gas tight.

1

(b) Plot a graph of 'volume (of gas)' against 'time'

1

Determine the slope (gradient) at the beginning

1

(c) Repeat with same volume **or** concentration of hydrogen peroxide and at the same temperature

Ignore references to results.

Do not allow 'keep everything the same' or words to that effect. Must mention volume or concentration and temperature.

1

Add cobalt(II) chloride to one experiment

1

[6]

Q10.

(a) Variable / many oxidation states

1

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

Equations can be in either order
Allow multiples

1

$V_2O_4 + ½O_2 \rightarrow V_2O_5$

1

(c) (i) In a different phase / state <u>from reactants</u>

1

(ii) Impurities poison / deactivate the catalyst / block the active sites

Allow (adsorbs onto catalyst AND reduces surface area)

1

(d) (i) The catalyst is a reaction product

1

(ii) Mn^{2+} / Mn^{3+} ion(s)

1

(iii) $4Mn^{2+} + MnO_4^- + 8H^+ \rightarrow 5Mn^{3+} + 4H_2O$

Equations can be in either order

1

$2Mn^{3+} + C_2O_4^{2-} \rightarrow 2Mn^{2+} + 2CO_2$

1

[9]

Q11.

(a) *For reactions 1 to 3 must show complex ions as reactants and products*
Take care to look for possible identification on flow chart

Reaction 1

ammonia solution

1

W is $[Co(NH_3)_6]^{2+}$

1

$[Co(H_2O)_6]^{2+} + 6NH_3 \rightarrow [Co(NH_3)_6]^{2+} + 6H_2O$

Correct equation scores all 3 marks

1

Reaction 2

Allow oxygen, Do not allow air

H_2O_2

1

X is $[Co(NH_3)_6]^{3+}$

1

$2[Co(NH_3)_6]^{2+} + H_2O_2 \rightarrow 2[Co(NH_3)_6]^{3+} + 2OH^-$

Allow $2[Co(NH_3)_6]^{2+} + ½O_2 + H_2O \rightarrow 2[Co(NH_3)_6]^{3+} + 2OH^-$
Correct equations score all 3 marks

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1

Reaction 3

HCl

Do not allow Cl^- but mark on

1

Y is $[CoCl_4]^{2-}$

1

$[Co(H_2O)_6]^{2+} + 4Cl^- \rightarrow [CoCl_4]^{2-} + 6H_2O$/

Correct equation scores previous mark

$[Co(H_2O)_6]^{2+} + 4HCl \rightarrow [CoCl_4]^{2-} + 6H_2O + 4H_+$

This equation scores all three marks

1

Reaction 4

Na_2CO_3 Or $NaOH/NH_3$

Do not allow $CaCO_3$ as a reagent but mark on

1

Z is $CoCO_3$ $Co(OH)_2/Co(H_2O)_4(OH)_2$

1

$[Co(H_2O)_6]^{2+} + CO_3^{2-} \rightarrow CoCO_3 + 6H_2O$ $[Co(H_2O)_6]^{2+} + 2OH^- \rightarrow Co(H_2O)_4(OH)_2 + 2H_2O$ etc

Allow waters to stay co-ordinated to Co. This mark also previous mark

Or $[Co(H_2O)_6]^{2+} + Na_2CO_3 \rightarrow CoCO_3 + 6H_2O + 2Na^+$

Allow $Co^{2+} + CO_3^{2-} \rightarrow CoCO_3$

1

(b) $SO_3^{2-} + ½O_2 \rightarrow SO_4^{2-}$

Allow multiples

1

The activation energy is lower (for the catalysed route)

Or Co^{3+} attracts SO_3^{2-}/Co^{2+} attracts SO_3^{2-}/oppositely charged ions attract

1

$½O_2 + 2Co^{2+} + 2H^+ \rightarrow H_2O + 2Co^{3+}$

1

$2Co^{3+} + SO_3^{2-} + H_2O \rightarrow 2Co^{2+} + SO_4^{2-} + 2H^+$

Allow these equations in either order

1

[16]

Q12.

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

For all species correct / moles and species correct but

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charge incorrect

1

For balanced equation including all charges (also scores first mark)

1

(b) Manganate(VII) ions are coloured (purple)

1

All other reactants and products are **not** coloured (or too faintly coloured to detect)

Allow (all) other species are colourless

Allow Mn^{2+} are colourless / becomes colourless / pale pink

1

(c) The catalyst for the reaction is a reaction product

1

Reaction starts off slowly / gradient shallow

1

Then gets faster/rate increases / gradient increases

Allow concentration of MnO_4^- decreases faster / falls rapidly

1

(d) Mn^{2+} ions

Allow Mn^{3+} ions

1

(e) $MnO_4^- + 8H^+ + 4Mn^{2+} \longrightarrow 5Mn^{3+} + 4H_2O$

Allow multiples

1

$2Mn^{3+} + C_2O_4^{2-} \longrightarrow 2Mn^{2+} + 2CO_2$

1

[10]

Q13.

(a) $2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$

1

$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$

1

two negative ions repel / lead to reaction that is slow / lead to reaction that has high E_a

1

iron able to act because changes its oxidation state

allow iron has variable oxidation state

1

With iron ions have alternative route / route with lower activation energy

1

(b) (i) $[Fe(H_2O)_6]^{3+} \rightarrow [Fe(H_2O)_5OH]^{2+} + H^+$

can have H_2O on LHS and H_3O^+ on R

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do not penalise further hydrolysis equations
allow high charge density

1

Fe^{3+} ion has higher charge (to size ratio) (than Fe^{2+})

1

increases polarisation of co-ordinated water / attracts O
releasing an H^+ ion / weakens O–H bond

1

(ii) $Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$
or 6 mol Fe(II) react with 1 mol dichromate
If factor of 6 not used max = 3 for M2, M4 and M5
e.g. 1:1 gives ans= 8.93 to 8.98% (scores 3)

1

moles dichromate = $23.6 \times 0.218/1000 = 5.14 \times 10^{-4}$

1

moles iron = $5.14 \times 10^{-4} \times 6 = 0.00309$
M3 also scores M1

1

mass iron = $0.00309 \times 55.8 = 0.172$
Mark is for moles of iron × 55.8 conseq
Allow use of 56 for iron

1

% by mass of iron = $0.172 \times 100/0.321 = 53.7\%$
Answer must be to at least 3 sig figures allow 53.6 to 53.9
Mark is for mass of iron × 100/0.321 conseq

1

(c) brown precipitate / solid
Allow red-brown / orange solid
Not red or yellow solid

1

bubbles (of gas) / effervescence/ fizz
Allow gas evolved / given off
Do not allow just gas or CO_2 or CO_2 gas

1

$2[Fe(H_2O)_6]^{3+} + 3CO_3^{2-} \rightarrow 2Fe(H_2O)_3(OH)_3 + 3CO_2 + 3H_2O$
Allow
$2[Fe(H_2O)_6]^{3+} + 3CO_3^{2-} \rightarrow 2Fe(OH)_3 + 3CO_2 + 9H_2O$
Use of Na_2CO_3
e.g. … + $3Na_2CO_3 \rightarrow$ .. + .. + .. + $6Na^+$

1

[16]

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Q14.

(a) Incomplete (or partially filled) d orbitals/sub-shells

Do not allow d shell

1

(b) Variable oxidation states

1

(c) (i) $[H_3N–Ag–NH_3]^+$

Allow $[Cl–Ag–Cl]^-$ or similar Cu(I) ion

Allow compounds in (i), (ii) and (iii) (eg Cl-Be-Cl)

Allow no charge shown, penalise wrong charge(s)

1

(ii) Cis platin drawn out as square planar

Allow NiX_4^{2-} etc

1

(iii) $[CuCl_4]^{2-}$ drawn out as tetrahedral ion

Or $[CoCl_4]^{2-}$ drawn out

1

(d) (i) $SO_2 + 1/2O_2 \rightarrow SO_3$

Allow multiples

Allow $SO_2 + 1/2O_2 + H_2O \rightarrow H_2SO_4$

ignore state symbols

1

(ii) In a different phase/state (from the reactants)

1

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

can be in either order

1

$V_2O_4 + 1/2O_2 \rightarrow V_2O_5$

allow multiples

1

(iv) Surface area is increased

1

By use of powder or granules or finely divided

Allow suspending/spreading out onto a mesh or support

1

(e) (i) Forms two or more co-ordinate bonds

Allow more than one co-ordinate bond or <u>donates</u> more than 1 electron pair.

Do not allow "has more than one electron pair"

Allow uses more than one atom to bond (to TM)

1

(ii) Number of product particles > Number of reactant particles

Allow molecules/entities instead of particles

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Penalise incorrect numbers (should be 2→5)

1

Disorder increases or entropy increases
(or entropy change is positive)

Allow ΔG must be negative because ΔH = 0 and ΔS is +ve

1

(iii) 6

1

Cyanide strongly bound to Co (by co-ordinate/covalent bond)

1

[16]

Q15.

(a) Same phase/state

1

(b) Because only exist in one oxidation state

Allow do not have variable oxidation states

1

(c) $2I^- + S_2O_8^{2-} \rightarrow I_2 + 2SO_4^{2-}$

Ignore state symbols
Allow multiples

1

(d) Both (ions)have a negative charge

Or both have the same charge
Or (ions) repel each other
Do not allow both molecules have the same charge (contradiction)

1

(e) $2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$

1

$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$

1

Equations can be in any order

Positive and negative (ions)/oppositely charged (ions)

Mark independently

1

(f) Equations 1 and 2 can occur in any order

Allow idea of Fe^{3+} converted to Fe^{2+} then Fe^{2+} converted back to Fe^{3+}

1

[8]

Q16.

(a) $FeCl_3$ accepts electron pairs from water

1

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Hence acts as a Lewis acid

1

$[Fe(H_2O)_6]^{3+}$ donates protons

1

Hence acts as a Bronsted-Lowry acid

1

(b) The Fe^{2+} ion has a smaller charge to size ratio

1

Hence less polarising than Fe^{3+} or less weakening effect on O-H bonds

1

(c) (i) $V_2O_5 + SO_2 \rightarrow V_2O_4 + SO_3$

1

$V_2O_4 + O_2 \rightarrow V_2O_5$

1

(ii) Both ions are negative or ions repel

1

$2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$ Species

1

Balanced

1

$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$ Species

1

Balanced

1

[13]

Q17.

(a) Alternative route

Allow mechanism outlined
allow forms intermediate species

1

Lower activation energy

1

(b) Variable oxidation state

allow changes oxidation states

1

(c) (i) $SO_2 + V_2O_5 \rightarrow SO_3 + V_2O_4$

allow $2VO_2$ instead of V_2O_4

1

$O_2 + 2V_2O_4 \rightarrow 2V_2O_5$

1

(ii) Poison attaches to surface

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Allow blocks active site/surface
Decreases surface area

1

(iii) Purify reactants

Allow remove impurities

1

[7]

Q18.

C

[1]

Q19.

(a) effect on reaction rate: catalyst provides an alternative reaction route.;

1

with a lower E_a;

1

more molecules able to react or rate increased;

1

equilibrium: forward and backward rates changes by the same amount;

1

hence concentration of reactants and products constant or yield unchanged;

1

(b) heterogeneous: catalyst in a different phase or state to that of the reactants;

1

active site: place where reactants adsorbed or attached or bond etc.;

1

reaction occurs or an explanation of what happens;

(allow absorbed)

1

reasons: large surface area;
reduce cost or amount of catalyst;

2

catalyst poison: lead adsorbed;
lead not desorbed or site blocked;

(lead adsorbed irreversibly scores both of these marks)

2

(c) reaction slow as: both ions negatively charged or ions repel;

1

$2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$ Species;
Balanced;

2

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$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$ Species ; Balanced;

2

[17]

Q20.

(a) Iron

1

Heterogeneous; catalyst in a different phase from that of the reactants

1

Poison; a sulphur compound (allow sulphur)

1

Poison strongly adsorbed onto active sites/ blocked

1

Poison not desorbed or reactants not adsorbed or catalyst surface area reduced

1

(b) Pale green solution 1

Green precipitate formed

1

Insoluble in excess ammonia

1

Equation:

e.g. $[Fe(H_2O)_6]^{2+} + 2NH_3 \rightarrow [Fe(H_2O)_4(OH)_2] + 2NH_4^+$ Species

1

Balance

1

NB Allow equations with H_2O and OH^- if reaction of H_2O with NH_3 also given

Max 4

[9]

Q21.

(a) A catalyst in the same phase/phase as the reactants

1

(b) (i) A reaction in which a product acts as a catalyst

1

(ii) Mn^{2+} or Mn^{3+}
"Self-catalysing" not allowed

1

(c) (i) $2CO + 2NO \rightarrow 2CO_2 + N_2$

or $4CO + 2NO_2 \rightarrow 4CO_2 + N_2$

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C not allowed as a product

1

Reducing agent CO

1

(ii) Pt, Pd or Rh

1

Deposited on a ceramic honeycomb or matrix or mesh or sponge

1

To increase surface area of catalyst

1

(d) (i) Reactants cannot move on surface or products not desorbed or
Active sites blocked

1

(ii) Reactants not brought together or
No increase in reactant concentration on catalyst surface or
Reactants not held long enough for a reaction to occur or
Reactant bonds not weakened

1

[10]

Q22.

(a) (i) Heterogeneous:- In a different phase to reactants **(1)**
Catalyst:- Increases reaction rate **(1)**
Alternative route or route described **(1)**
Lower E_a **(1)**
Unchanged at end of reaction **(1)** Max 4

(ii) Feature:- QoL Variable oxidation states shown by vanadium **(1)**
Equations $V_2O_5 + SO_2 \rightarrow V_2O_4 + SO_3$ **(1)**
$2V_2O_4 + O_2 \rightarrow 2V_2O_5$ **(1)**

7

(b) $VO_2^+ + 4H^+ + 3e^- \rightarrow V^{2+}(aq) + 2H_2O$ **(1)**

$Zn \rightarrow Zn^{2+} + 2e^-$ (given)

$2VO_2^+ + 8H^+ + 3Zn \rightarrow 3Zn^{2+} + 2V^{2+}(aq) + 4H_2O$ **(1)**

2

Mol $KMnO_4$ = mv/1000 = 0.0200 × 38.5/1000 = 7.70×10^{-4} **(1)**

Mole ratio MnO_4^- to V(II) = 3:5 deduced

or equation

$5V^{2+} + 3MnO_4^- + 4H^+ \rightarrow 2H_2O + 3Mn^{2+} + 5VO_2^+$ **(2)**

Mol V(II) = $7.70 \times 10^{-4} \times 5/3$ **(1)** = 1.283×10^{-3}

Mass V = $1.283 \times 10^{-3} \times 50.9$ **(1)** = 0.0653 g

% V in sample = 0.06532 × 100/0.160 = 40.8 **(1)**

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6

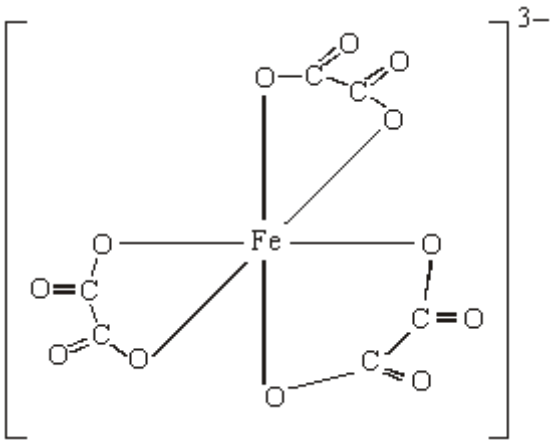
[15]

Q23.

(a) (i) Two **(1)** lone pair donor / electron pair donor **(1)** atoms
Allow:– forms two co-ordinate bonds **(1)**

NOT atom with two lone pairs

(ii)



(O
C not essential)

*Correct ligand structure **(1)***
penalise any error
*Six correct O–Fe bonds **(1)***
*Correct charge **(1)***
N.B. Penalise the second mark if arrow from Fe shown
N.B. Ignore charges on atoms

5

(b) (Substitution of a monodentate ligand by a) bi or multidentate ligand **(1)** giving a more stable complex **(1)** or with an increase in entropy / disorder or forming a ring / cage complex / structure (crab like)

2

(c) (i) $[AgCl_2]^-$ or $AgCl_2^-$ **(1)**

(ii) Chloride or Cl^- big or large or repel **(1)**

NOT Cl_2 or Cl^+ or Cl
Allow 'chlorine ion'

2

(d) (i) (Both) ions are negative or ions repel or High E_a **(1)**

(ii) *Meaning of the term autocatalytic:* A product of the reaction acts as a catalyst **(1)**

NOT a self catalysing reaction (0)

Catalyst: Mn^{2+} or Mn^{3+} **(1)**

(iii) Mn^{2+} converted into Mn^{n+} or Mn^{2+} oxidised **(1)**

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Mn^{n+}/oxidised species then oxidises/reacts with $C_2O_4^{2-}$ **(1)**

5

[14]

Q24.

(a) reactants brought together / increased concentration on surface or increased collision frequency **(1)**
reactants must be correctly orientated **(1)**
reaction on the surface **(1)**
products desorbed **(1)**
example of a catalysed reaction (not a named process) **(1)**
a suitable catalyst for this reaction **(1)**

penalise incorrect second reactions and catalysts

If absorption too weak reactants not brought together **(1)**
e.g. silver **(1)**
If adsorption too strong products not desorbed **(1)**
e.g. tungsten **(1)**

max 8

(b) Equations:

$Cr_2O_7^{2-} + 14\ H^+ + 6\ Fe^{2+} \rightarrow 6\ Fe^{3+} + 2\ Cr^{3+} + 7\ H_2O$ **(1)**
$Zn + 2\ Fe^{3+} \rightarrow Zn^{2+} + 2\ Fe^{2+}$ **(1)**

Method

Titrate measured volume solution against $K_2Cr_2O_7$ **(1)**

Reduce same volume solution with zinc **(1)**

Filter off excess zinc **(1)**

Titrate total Fe^{n+} using $K_2Cr_2O_7$ **(1)**

Percentage Fe^{3+} = 100 × (titre2 - titre1) / titre 2
or equivalent **(1)**

7

[15]

Q25.

(a) High E_a: $S_2O_8^{2-}$ repels I^- **or** both ions negative **(1)**
$2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$ **(1)**
$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$ **(1)**

N.B. Ignore additional incorrect equations

Vanadium is a transition element **or** Magnesium is not a transition element **(1)**

Vanadium has variable oxidation states **(1)**

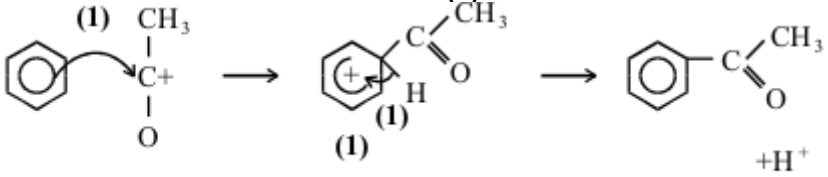
Magnesium only forms Mg^{2+}, **or** has only one oxidation state **(1)**

N.B. Score two marks for "Only vanadium has variable oxidation states"

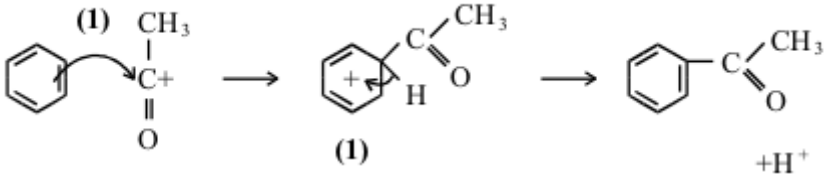
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(b) $AlCl_3 + Cl\text{-}COCH_3 \rightarrow AlCl_4^- + CH_3CO^+$ **(1)**



or



$H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl$ **(1)**
Lewis acid: $AlCl_3$ accepts electron pair

N.B. penalise incorrect acyl chloride by one
N.B. penalise chloroethane by two marks i.e. first equation mark, attack on benzene mark

NH_4Cl: Not a catalyst **(1)**

$FeCl_3$: A catalyst **(1)**
has a low energy vacant shell
or has spaces or vacancies in d shell
or has a partially filled d shell
or able to accept an electron pair
or can form $FeCl_4^-$ **(1)**

9

[15]

Q26.

D

[1]

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Q1.

(a) Nearly all students (91.1%) gained both marks here.

(b) Although 73.9% of students scored two marks, common errors here included a failure to convert temperature into kelvin or using inconsistent energy units.

(c) Students found the explanation in this part more challenging and many could not state that the Gibbs free-energy would become more negative. Many students, however, scored the second mark for a correct reference to a change in entropy.

(d) Many students discussed the general principles of homogeneous catalysis or the lowering of activation energy rather than the reaction on the platinum surface. The mark most commonly missed was the idea that the product desorbed from or left the surface of the catalyst. Surprisingly, over 10% of students made no attempt at this question.

(e) 74.4% of students answered this correctly, although a few students thought the oxidation state of N in ammonia was +3.

(f) Many students gave hydrogen as the other product or failed to balance an equation in which water was the other product.

Q2.

(a) Only 11.3% of students scored both marks here; sometimes Fe^{2+} was chosen but students could not explain their choice. The most common incorrect answer was Zn^{2+}.

(b) Just over three-quarters of students could give the oxidation state.

(c) The structure was often given, incorrectly, as a mirror image and the type of isomerism as optical; only 37.2% of students scored both marks.

(d) This was poorly answered, with only just over a third of students giving the correct equation.

(e) Over half of the students (55.6%) gave the correct equations; incorrect equations included charged vanadium species. Surprisingly, 12% of students were unable to make any attempt at this question.

Q4.

Most students scored highly in part (a). Incorrect units for entropy change were often seen in part (b). Students generally understood the concept of disorder and scored the mark in part (c). The majority of students could use their own values to calculate the free-energy change in part (d); common errors included incorrect units, failure to convert temperature into Kelvins and using a mixture of joules and kilojoules in their calculation. The relationship between ΔG and feasibility was well known in part (e). The meaning of heterogeneous was well known in part (f)(i) and the equations in part (f)(ii) were generally well known. Students answered part (f)(iii) well although in part (f)(iv) a few referred to impurities being produced without any reference to poisoning of the catalyst.

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Q5.

In part (a) most students could identify the autocatalyst in the reaction however some students thought that an autocatalyst was a reagent and identified the catalyst as MnO_4^-. Many students correctly identified the acid in part (b). Most students knew that two negative ions would repel in part (c) but did not link this to high activation energy. Some students did not state that the reaction was initially slow or would only speed up when the catalyst was produced. The equation in part (d) was generally well done. Some students had the correct ratio of reagents but missed charges on the ions or did not produce the correct amount of CO_2. Many students scored the first few marks but then failed to divide by 3 or multiplied by the wrong M_r. In part (e) many students described a colorimeter and the absorbance of visible light but did not answer the question as set and hence could not score the marks. Most students who used a series of concentrations knew that a calibration curve was used but often did not give correct labels for the axes. Those that did use a calibration curve mostly scored the last mark. A few very good students drew a diagram of the graph, with labelled axes, and showed how this would be used to find the concentration.

Q6.

This question proved to be difficult and discriminating. In part (a), only the best students could write a correct equation. The catalyst was usually identified correctly but the way in which the manganese(II) and manganese(III) ions were involved and regenerated in the reaction and the way in which contributed to the lowering of the activation energy were not understood by most students. In part (b) some excellent graphs were sketched although weaker students did not show the expected 'S' shaped curve. In the explanation of the shape of the curve, the increase in reaction rate caused by the increase in catalyst concentration was usually correct but fewer students explained correctly why the rate of reaction then decreased.

Q7.

Parts (a), (c) and (d) were generally very well answered. In part (b), the most common wrong answers referred to the catalyst providing a surface for the adsorption of reactants. Where students did talk about the opposite charges of the ions, they often did not specifically talk about attraction between these ions

Q8.

This stretch and challenge question proved testing for many students, particularly parts (a) and (c). The most frequent mark for part (a) was one out of four for stating that cobalt has variable oxidation states. Attempts at the two equations were poor. Equations should be balanced andshould not be half-equations with electrons. Despite the parallel with similar catalysed systems in the specification, students did not appreciate that the Co^{3+} ions would be the oxidising agents, reacting with ethanal and that Co^{2+} ions would be oxidised by oxygen back to Co^{3+}. In part (b)(i), weaker students did not know that the chelate effect is explained by entropy changes and they often, incorrectly, attempted to explain the effect in terms of the stability of a complex ion with bidentate ligands. Part (b)(ii) was answered well by most students. Part (c) proved to be very discriminating with only the very best students scoring more than three out of five marks. The most difficult marks to achieve were the formula of **Z**, $[Co(NH_3)_6]Cl_3$ and an explanation for the difference between the expected and the given ratio of cobalt ions to chloride ions in the complex. Many students lost marks because they did not use a correct formula for silver chloride–incorrectly using $AgCl_2$ or $AgNO_3$. Another common error was to ignore the precision of the data given in the question and to give the calculated molar ratio to only 1 significant figure whereas 3 significant figures were required, consistent with the data given.

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Q9.

The diagram in part (a) was well drawn by the majority of students. Most students were able to describe the graph needed in part (b) but many were unable to suggest an appropriate method for measuring the initial rate. In part (c), some students were allowed the first mark even though they did not describe the conditions to be kept constant.

Despite the long catalogue of points listed above, this was, overall, another very positive session in many schools and colleges. The teachers in these schools and colleges have successfully and securely delivered the practical assessment and have impressed with the accurate and consistent standard of their marking. In my last report as a Principal Moderator, I am grateful for the opportunity to salute these superb professionals and wish them well in the future.

Q10.

This question was answered well by most students. The most difficult part was part (d)(iii) where only the best students were able to write correct equations.

Q11.

Answers to part (a), a question that required recall of cobalt chemistry, produced a wide spread of marks. As always, a full identification of reagents was required and many students lost marks by failing to do so, specifying Cl^- (instead of HCl), carbonate (instead of sodium carbonate) and hydroxide (instead of NaOH). Missing or incorrect charges and inaccurate formulae were also common eg $CoCl_4$ and $C_o(OH_2)$. Reaction 1 was well known. Air was a common insufficient reagent for reaction 2. The equation mark for reaction 2 was often the missing mark from an otherwise perfect answer. Reaction 3 was the least well known of the four reactions. Many students did not recognise the blue solution to be $[CoCl_4]^{2-}$ and instead attempted to use an excess of NaOH to give a cobaltate(II) ion. In reaction 4, $NaCO_3$ and CO^{3-} were common wrong answers. In part (b), most students gained the first two marks. Although most students attempted the last two equations, very few were correct. Common wrong answers involved the wrong cobalt species being used. For example, students tried to oxidise sulfate(IV) ions with cobalt(II). They did not recognise that an oxidising agent must react with a reducing agent and they went on with an attempt to reduce cobalt(III) to cobalt(II) with oxygen.

Q12.

The equation required in part (a) is recognised to be discriminating and it proved to be so with only 34% of students giving a correct answer. Part (b) was a ‘how science works’ question and only 20% of students could explain that a spectrometer can be used because manganate(VII) ions are coloured but the products of the reaction are effectively colourless. Some students tried to use a mass spectrometer. Answers to parts (c) and (d) were pleasing. However, as expected, part (e) proved to be very discriminating and only the very best students could write balanced equations for the two reactions.

Q13.

Each part of this question discriminated very effectively between able and less able candidates. In part (a) a common omission was a failure to state that iron ions are able to catalyse redox reactions because they are able to change oxidation state. In this part, the most usual errors were to give an unbalanced equation for the reaction between iron (II) ions and persulfate ions and for the reaction between iron (III) ions and iodide ions. Candidates often used only one mole of iron ions, presumably because they omitted to check that charges, as well as numbers of moles, should balance. In part (b)(i), most candidates knew that the increased acidity of aqueous iron (III) ions could be attributed to

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their increased charge to size ratio compared with iron (II) ions. However, the reason why this high charge to size ratio caused an increase in ionisation of the $[Fe(H_2O)_6]^{3+}$ was less well understood. Very few correct equations were seen. Many did not show the release of one proton into the aqueous solution. They showed incorrectly the formation of Fe(H2O)3(OH)3 often by reaction with hydroxide or carbonate ions. There were many good answers to part (b)(ii) with about 40% of candidates scoring full marks. Answers to part (c) were not so impressive. Although a brown precipitate was usually described, evolution of a gas was often missing and the difficult equation was not balanced correctly.

Q14.

This question proved to be discriminating with a facility for most parts of only about 50%. In part (c), as expected, the hardest example to recall was that of a square planar complex but it was also surprising to find that a common error in part (c)(iii) was to show an octahedral complex. In part (d)(i), many candidates gave an incorrect equation using O instead of O_2 but other parts were answered quite well. It was disappointing to find that in part (e)(i) about one third of candidates could not give the correct meaning of the term multidentate. In part (e)(ii), it was pleasing to note that about half of candidates scored full marks. In part (e)(iii), only the best candidates were able to explain clearly that the cyanide ion is bound strongly to the cobalt so it is not toxic when complexed in vitamin B_{12}.

Q15.

Part (a) was answered well but part (b) was more difficult and weak candidates confused ions with atoms. In part (c) it was disturbing to note the large number of candidates who gave a wrong formula for the sulfate ion produced, usually showing only a single negative charge. Part (d) was answered well. Part (e) proved to be challenging, especially the equations. Only the best candidates could write balanced equations, the most common error being to use only one mole of iron ions, despite requiring two moles of electrons for reaction of the $S_2O_8^{2-}$ ion and for the formation of I2. In part (f) most candidates attempted to answer in general terms by mentioning activation energy rather than giving an answer specific to iron(II) and iron(III) ions.

Q17.

This question produced a range of answers. Parts (a), (b) (c)(i) and (c)(ii) were answered well by most candidates. The answer to part (c)(iii) was less well known and only 54% of candidates could suggest how to minimise poisoning of the catalyst by removing impurities from the reactants.

Q19.

Parts (a) and (b) were both well answered and many candidates scored full, or nearly full, marks. Almost all candidates stated that the reaction between I^- and $S_2O_3^{2-}$ was slow as they were both negative and would repel each other, few gave correct equations showing the involvement of iron(II) and iron(III) ions in the reaction. Sadly some candidates, who gave correct species, lost a mark as they failed to balance the equations.

Q20.

In answer to part (a), most candidates identified iron as the heterogeneous catalyst in the Haber process and explained the term *heterogeneous* correctly. Although poisoning of the

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iron catalyst by sulphur is clearly stated in the Specification, many other elements and compounds were stated incorrectly to poison this catalyst. The method by which the poison works was well known and well explained. Only the best candidates gave a correct equation for the reaction of an aqueous iron(II) salt with an excess of aqueous ammonia as required in part (b). Candidates who gave equations involving the reaction of either water or hydroxide ions were allowed to score full marks provided that they also gave an equation showing the equilibrium reaction of ammonia with water. Correct observations were given by most of the good candidates but others either failed to state any observations or gave incorrect answers.

Q21.

Parts (a) and (b) were generally well done but part (c) proved to be surprisingly difficult. Incorrect and unbalanced equations were common errors in section (i) and many candidates failed to identify the reducing agent in the reaction. Although most candidates gave a correct transition element used as a catalyst in section (ii) there were numerous other incorrect answers. The chemistry tested in part (d) was generally well known but candidates whose answers merely restated the question lost marks.

Q22.

Although some candidates confused the terms *homogenous* with *heterogeneous*, the terms *heterogeneous* and *catalyst* were generally well known and most candidates gave correct explanations of how, in general terms, a catalyst works. The role of vanadium(V) oxide in the Contact Process was also well known and many candidates scored full marks for their answers to part (a). Part (b) proved, as expected, to be more difficult. Many candidates were able to use half-equations to construct an overall equation for the reduction of VO_2^+ to V^{2+} by zinc in acidic solution. Almost all were also able to calculate correctly the number of moles of potassium manganate(VII) used to oxidise the vanadium(II) ions back to vanadium(V) ions. However, in order to calculate the number of moles of vanadium(II) in the solution, it was necessary to deduce the mole ratio MnO_4^-: V^{2+}. The best students made this deduction and went on to determine the percentage of vanadium in the sample. Candidates who failed to make this deduction were able to score an additional mark if they used the correct A_r of vanadium when calculating the mass of vanadium in the sample from their value for moles of V^{2+} in the solution.

Q23.

The term ‘bidentate ligand’ was well understood and most candidates were able to sketch the structure of the required complex in (a)(ii). The term ‘chelate effect’ was less well understood but many candidates were able to score both marks. In part (c) almost all explained correctly that chloride ions do not usually form octahedral complexes with metal(II) ions because of their relatively large size. Most were able to deduce correctly the formula of the linear complex formed when silver chloride dissolves in concentrated hydrochloric acid. Section 1 (i) and (ii) of part (d) were well answered but, having recognised Mn^{2+} as the catalyst for the reaction between the negative ions, MnO_4^- and $C_2O_4^{2-}$, the suggestions of how the catalyst might be involved in the reaction were sometimes given in general terms rather than by specific reference to the involvement of the Mn^{2+} ion.

Q24.

Most candidates gave good explanation of how a heterogeneous catalyst works and high marks were scored in part (a). By contrast, few gave a good outline plan for the experiment to determine the percentage of iron as iron(III) in a solution containing Fe^{3+} (aq) and Fe^{2+} (aq) ions. Most stated correctly that the concentration of Fe^{2+} (aq) in solution

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can be determined by a titration using potassium dichromate(VI) but few clearly stated that the volumes of both solution would need to be measured. Although most used the fact that zinc can reduce Fe^{3+} (aq) to Fe^{2+} (aq), very few stated that, after the reduction, excess zinc would need to be removed by filtration. Marks were awarded for correct equations but many candidates did not give them.

Q25.

The reaction between persulphate ions and iodide ions was well known and almost all candidates stated correctly that the reaction has a high activation energy as these ions are both negative and repel each other. Good candidates gave correct equations explaining the catalytic action of iron(II) ions but a significant number of weaker candidates lost marks when they failed to balance these equations.
Many candidates completed their answer to part (a) by predicting correctly that the variable oxidation states of the transition element vanadium would enable V^{3+}(aq) to function as a catalyst for the reaction whilst Mg^{2+}(aq) would not. The role of $AlCl_3$ in the reaction between benzene and ethanoyl chloride was well known by many candidates. Some, however, lost marks when they failed to show the involvement of $AlCl_3$ in the formation of the acylium intermediate and the reformation of $AlCl_3$ at the end of the reaction. Marks were lost by candidates who drew inaccurate structures in the organic reaction mechanism. The link between the ability of $AlCl_3$ to behave as a Lewis acid and accept a lone electron pair was made by good students who then predicted correctly that $FeCl_3$ would function as a catalyst but NH_4Cl would not. Marks in this section were not awarded to candidates who made vague predictions.

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