Pearson Edexcel

Mark Scheme (Results)

January 2021

Pearson Edexcel International Advanced Level In Chemistry (WCH15)
Paper 1:Transition Metals and Organic Nitrogen Chemistry

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General Marking Guidance

- All candidates must receive the same treatment. Examiners must mark the first candidate in exactly the same way as they mark the last.
- Mark schemes should be applied positively. Candidates must be rewarded for what they have shown they can do rather than penalised for omissions.
- Examiners should mark according to the mark scheme not according to their perception of where the grade boundaries may lie.
- There is no ceiling on achievement. All marks on the mark scheme should be used appropriately.
- All the marks on the mark scheme are designed to be awarded. Examiners should always award full marks if deserved, i.e. if the answer matches the mark scheme. Examiners should also be prepared to award zero marks if the candidate's response is not worthy of credit according to the mark scheme.
- Where some judgement is required, mark schemes will provide the principles by which marks will be awarded and exemplification may be limited.
- When examiners are in doubt regarding the application of the mark scheme to a candidate's response, the team leader must be consulted.
- Crossed out work should be marked UNLESS the candidate has replaced it with an alternative response.

Section A (Multiple Choice)

Question number	Answer	Mark
1	**The only correct answer is B** (gains electrons, decreases) ***A*** *is incorrect because the oxidation number of manganese decreases* ***C*** *is incorrect because manganese gains electrons and its oxidation number decreases* ***D*** *is incorrect because manganese gains electrons*	**(1)**

Question number	Answer	Mark
2	**The only correct answer is A** (To increase the rate of the equilibrium between the hydrogen gas and the hydrogen ions) ***B*** *is incorrect because platinum black is chemically identical to shiny platinum* ***C*** *is incorrect because platinum black has the same electrical conductivity as shiny platinum* ***D*** *is incorrect because platinum black does not affect the conditions of the system*	**(1)**

Question number	Answer	Mark
3(a)	**The only correct answer is C** (Fe(s) | Fe^{2+}(aq) ‖ Sn^{2+}(aq) | Sn(s)) ***A*** *is incorrect because the oxidised part of Sn(s) | Sn^{2+}(aq) should be next to the cell junction* ***B*** *is incorrect because the oxidised part of Fe(s) | Fe^{2+}(aq) should be next to the cell junction* ***D*** *is incorrect because the oxidised part of both half-cells should be next to the cell junction*	**(1)**

Question number	Answer	Mark
3(b)	**The only correct answer is B** (−0.14 V) ***A*** *is incorrect because the* $E^{\ominus}_{cell}$ value *has been subtracted from the electrode potential of the* Fe/Fe^{2+} *electrode system rather than added.* ***C*** *is incorrect because the sign has been reversed.* ***D*** *is incorrect because the* $E^{\ominus}_{cell}$ value *has been subtracted from the electrode potential of the* Fe/Fe^{2+} *electrode system rather than added and the sign has been reversed.*	**(1)**

Question number	Answer	Mark
4	**The only correct answer is D** ($H_2(g) + 2OH^- \rightarrow 2H_2O(l) + 2e^-$) ***A*** *is incorrect because this is the cathode reaction* ***B*** *is incorrect because this is the reverse of the cathode reaction* ***C*** *is incorrect because hydrogen is the fuel and must be oxidised*	**(1)**

Question number	Answer	Mark
5	**The only correct answer is A** (chromium) ***B*** *is incorrect because an atom of iron has four unpaired electrons* ***C*** *is incorrect because an atom of manganese has five unpaired electrons* ***D*** *is incorrect because an atom of vanadium has three unpaired electrons*	**(1)**

Question number	Answer	Mark
6	**The only correct answer is C** ((nickel) forms stable ions with partially filled d orbitals) ***A*** *is incorrect because elements can be in the d block but not be transition metals* ***B*** *is incorrect because elements can have partially filled d orbitals but not be transition metals* ***D*** *is incorrect because elements can form stable compounds with different oxidation states but not be transition metals*	**(1)**

Question number	Answer	Mark
7(a)	**The only correct answer is D** ($Pt(NH_3)_2Cl_2$ is square planar and $CrCl_4^-$ is tetrahedral) ***A*** *is incorrect because* $CrCl_4^-$ *is tetrahedral* ***B*** *is incorrect because* $Pt(NH_3)_2Cl_2$ *is square planar* ***D*** *is incorrect because* $Pt(NH_3)_2Cl_2$ *is square planar and* $CrCl_4^-$ *is tetrahedral*	**(1)**

Question number	Answer	Mark
7(b)	**The only correct answer is B** (the bonding in both complexes is dative covalent) ***A*** *is incorrect because the bonding is ionic in neither complex* ***C*** *is incorrect because the bonding in* $CrCl_4^-$ *is dative covalent* ***D*** *is incorrect because the bonding in* $Pt(NH_3)_2Cl_2$ *is dative covalent*	**(1)**

Question number	Answer	Mark
8	**The only correct answer is A** (anhydrous cobalt(II) chloride is blue and hydrated cobalt(II) chloride is pink) ***B*** *is incorrect because the colours are the wrong way round* ***C*** *is incorrect because the test does not involve a change of oxidation state* ***D*** *is incorrect because the test does not involve a change of oxidation state*	**(1)**

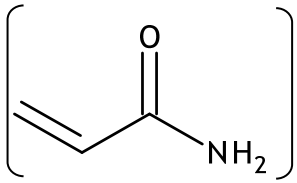
Question number	Answer	Mark
9	**The only correct answer is D** (Fe^{2+} is readily oxidised to Fe^{3+} which is then reduced to Fe^{2+}) ***A*** *is incorrect because* Fe^{2+} *does not react with iodide ions* ***B*** *is incorrect because the number of outer electrons is not a factor in homogeneous catalysis* ***C*** *is incorrect because the number of active sites is a factor in heterogeneous catalysis not in homogeneous catalysis*	**(1)**

Question number	Answer	Mark
10	**The only correct answer is D** ((the overlap of) p orbitals to form π bonds) ***A*** *is incorrect because the σ bonds are not delocalised* ***B*** *is incorrect because s orbitals do not form π bonds* ***C*** *is incorrect because the σ bonds are not delocalised*	**(1)**

Question number	Answer	Mark
11	**The only correct answer is B** (result in a kinetic barrier to intermediate formation) ***A*** *is incorrect because the delocalised electrons attract electrophiles* ***C*** *is incorrect because both ethene and benzene have endothermic enthalpies of formation and this is not a factor in their reactivity* ***D*** *is incorrect because catalysts have no effect on the thermodynamics of a reaction*	**(1)**

Question number	Answer	Mark
12	**The only correct answer is C** (2-methylbutanamide) ***A*** *is incorrect because the amide carbon is part of the main carbon chain* ***B*** *is incorrect because the amide carbon is part of the main carbon chain* ***D*** *is incorrect because the carbon chain is numbered from the amide end*	**(1)**

Question number	Answer	Mark
13	**The only correct answer is C** (phenylamine, ammonia, butylamine) ***A*** *is incorrect because butylamine has the highest pH and phenylamine the lowest* ***B*** *is incorrect because phenylamine has the lowest pH* ***D*** *is incorrect because phenylamine has a lower pH than ammonia*	**(1)**

Question number	Answer	Mark
14	**The only correct answer is A**  **B** *is incorrect because this monomer has four carbon atoms not three and would give a polymer with a methyl group on a different carbon to the amide group* **C** *is incorrect because this monomer has four carbon atoms not three and would give a polymer with a methyl group branched chain* **D** *is incorrect because this monomer has five carbon atoms not three and would give a polymer with two methyl group branched chains*	**(1)**

Question number	Answer	Mark
15	**The only correct answer is D** (a polyamide but not a polypeptide) **A** *is incorrect because polypeptides are formed from amino acids* **B** *is incorrect because it is a polyamide* **C** *is incorrect because it cannot be a polypeptide*	**(1)**

Question number	Answer	Mark
16	**The only correct answer is B** (five) ***A*** *is incorrect because the carbon with the two methyl groups attached has been omitted* ***C*** *is incorrect because the carbon with the two methyl groups attached has been omitted and the symmetry of the structure has been ignored* ***D*** *is incorrect because the symmetry of the structure has been ignored*	**(1)**

Question number	Answer	Mark
17	**The only correct answer is C** (C_4H_6) ***A*** *is incorrect because C_2H_3 cannot be a molecular formula* ***B*** *is incorrect because this formula is obtained without doubling the moles of water to give the moles of hydrogen* ***D*** *is incorrect because the moles of water has been halved instead of doubled*	**(1)**

Question number	Answer	Mark
18	**The only correct answer is C** (19.51 g) ***A*** *is incorrect because this is the mass of benzenecarboxylic acid that would be formed from 8.24 g of benzene in this sequence* ***B*** *is incorrect because this is the mass of benzene if both reactions have 100% yield* ***D*** *is incorrect because this value is calculated without using the M_r values*	**(1)**

TOTAL FOR SECTION A = 20 MARKS

Section B

Question number	Answer	Additional guidance	Mark
19(a)	• **P** = copper / Cu (1) • **Q** = hexaaquacopper(II) / $[Cu(H_2O)_6]^{2+}$ (1) • **R** = copper(II) hydroxide / $Cu(OH)_2$ / $Cu(OH)_2(H_2O)_4$ (1) • **S** = copper(II) oxide / CuO (1) • **T** = tetraamminecopper(II) / $[Cu(NH_3)_4]^{2+}$ / $[Cu(NH_3)_4(H_2O)_2]^{2+}$ (1) • **V** = diamminecopper(I) / $[Cu(NH_3)_2]^{+}$(1) • **W** = hexaaquacopper(II) / $[Cu(H_2O)_6]^{2+}$ (1)	Ignore omission of brackets in complexes If name and formula are given, both must be correct Penalise omission of oxidation states twice Ignore state symbols even if incorrect Ignore charge vertically above the Cu Allow $Cu^{2+}(aq)$ / Cu^{2+} / copper(II) sulfate / $CuSO_4$ Ignore copper oxide Do not award $[Cu(NH_3)_6]^{2+}$ Allow 3 or 4 ammonia ligands Ignore water ligands Allow $Cu^{2+}(aq)$ / Cu^{2+} / copper(II) nitrate / $Cu(NO_3)_2$	**(7)**

Question number	Answer	Additional guidance	Mark
19(b)(i)	• complex(es)	Allow complex ions Allow ammine complexes Allow transition metal complexes Allow ligand complexes	(1)

Question number	Answer	Additional guidance	Mark
19(b)(ii)	An explanation that makes reference to the following • (the colour is due to) transition /promotion of **electrons** between (split) (3)d subshell / orbitals (1) • in Cu(II) the d orbitals are partially filled (so electron transitions are possible) (1) • in Cu(I) the d orbitals are full **and** so no (electron) transitions are possible (1)	Allow use of T and V **d** (subshell /orbitals) must be mentioned at least once penalise use of 'orbital' /shell rather than orbitals/ subshell once only Ignore detailed explanations of colour in transition metal compounds even if incorrect Allow d-d **electron** transitions Ignore just 'from lower to higher energy level' If M2 and M3 not scored, correct d subshell electronic configurations of Cu(I) and Cu(II) without explanation score (1) Allow no incompletely filled (3)d subshell / orbitals Do not award subshell not split light frequency outside visible region no electrons in d orbitals	(3)

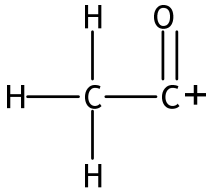
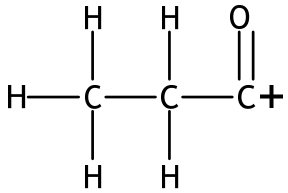
Question number	Answer	Additional guidance	Mark
19(b)(iii)	An explanation that makes reference to the following • Cu(I) is oxidised to Cu(II) (1) • by oxygen in the air (1)	 Allow Cu(I) is oxidised Allow Cu(I) forms Cu(II) Allow V is **oxidised** to T Allow just 'by oxygen' or 'by air'	**(2)**

Question number	Answer	Additional guidance	Mark
19(c)(i)	• a balanced ionic equation	<u>Example of equation</u> $2CuI \rightarrow Cu + Cu^{2+} + 2I^-$ Allow $2Cu^+ \rightarrow Cu + Cu^{2+}$ Do not award additional / spectator ions Ignore state symbols even if incorrect.	**(1)**

Question number	Answer	Additional guidance	Mark
19(c)(ii)	An answer that makes reference to the following points • identification of the appropriate half-equations and $E^{\ominus}$ values (1) • calculation of $E^{\ominus}_{cell}$ for the reaction **and** states (positive) so is feasible (1)	$Cu^{2+} + e^- \rightleftharpoons Cu^+$ $E^{\ominus} = +0.15$ V **and** $Cu^+ + e^- \rightleftharpoons Cu$ $E^{\ominus} = +0.52$ V Allow just $E^{\ominus}_{cell} = 0.52 - 0.15$ M2 dependent on M1 $E^{\ominus}_{cell}$ (= 0.52 − 0.15) = (+)0.37 (V) **and** therefore reaction is (thermodynamically) feasible No TE on incorrect half-equations / $E^{\ominus}_{cell}$ values	**(2)**

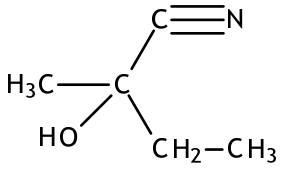
Question number	Answer	Additional guidance	Mark
19(d)	• calculation of moles of thiosulfate in mean titre (1) • determines ratio of Cu^{2+} to $S_2O_3^{2-}$ **and** gives moles of Cu^{2+} in 25 cm^3 (1) • calculation of moles of Cu^{2+} in 250 cm^3 (1) • calculation of M_r of mitscherlichite (1) • calculation of M_r of K_2CuCl_4 (1) • calculation of moles of water (1) Alternative M4 and M6 mass of K_2CuCl_4 in sample = $1.3325 \times 10^{-2} \times 283.7 = 3.7803$ g mass of water in sample = 4.26 − 3.7803 = 0.47970 (1) mol water in sample = 0.47970 ÷ 18 = 0.026650 **and** ratio H_2O : K_2CuCl_4 = 0.026650 ÷ 0.013325 = 1:2 (1)	<u>example of calculation</u> mol $S_2O_3^{2-} = \frac{26.65 \times 0.0500}{1000}$ $= 1.3325 \times 10^{-3} / 0.0013325$ Cu^{2+} in 25 cm^3 = $S_2O_3^{2-} = 1.3325 \times 10^{-3}$ $= 10 \times 1.3325 \times 10^{-3} = 1.3325 \times 10^{-2}$ $= 4.26 / 1.3325 \times 10^{-2} = 319.70$ $= 2 \times 39.1 + 63.5 + 4 \times 35.5 = 283.7$ mass of water = 319.7 − 283.7 = 36 moles of water = 36 / 18 = 2 (= n) correct answer with some working scores (6) TE at each stage but Do not award M4 or M6 if calculated value for M_r of (mitscherlichite) < M_r (K_2CuCl_4) Factor of 10 may be used at any point M1 to M3 Ignore SF in final answer	**(6)**

(Total for Question 19 = 22 marks)

Question number	Answer	Additional guidance	Mark
20(a)(i)	•  (1) •  (1)	Penalise omission of the positive charge or use of negative charges once only in 20(a)(i) and (ii) Penalise use of **just** molecular formulae once only in 20(a)(i) and (ii) Allow the positive charge anywhere on a structure or outside brackets covering a structure Allow structural formulae e.g. CH_3CO^+ Allow $C_2H_5CO^+$ Allow $CH_3COCH_2^+$ Ignore *m/z* values even if incorrect	**(2)**

Question number	Answer	Additional guidance	Mark
20(a)(ii)	• reasonable species	Allow only CH_3^+, $CH_3CH_2^+$, $C_2H_5^+$, $CH_3COCH_2CH_3^+$ Ignore *m*/*z* values even if incorrect Do not award species with *m*/*z* = 43 or 57	**(1)**

Question number	Answer	Additional guidance	Mark
20(b)	An answer that makes reference to the following points: • reaction of butanone with iodine in sodium hydroxide / NaOH (1) • to form sodium propanoate (1) • add dilute sulfuric acid / H_2SO_4 **and** to form propanoic acid / CH_3CH_2COOH (and distil off) (1) • (reflux propanoic acid with) lithium tetrahydridoaluminate(III) / $LiAlH_4$/ lithium aluminium hydride in dry ether (to give propan-1-ol) (1)	Score correct compounds / reagents even if preceding chemistry is incorrect) Allow unbalanced equations and reaction schemes Accept potassium hydroxide Allow alkali / alkaline / OH^- Accept $CH_3CH_2COO^-Na^+$ / CH_3CH_2COONa Allow propanoate (ion) Accept any identified strong acid. Ignore H^+ Allow 'lithal' Allow the use of $LiAlH_4$ in dry ether on propanoic acid or propanal (however these are obtained) to give propan-1-ol	**(4)**

Question number	Answer	Additional guidance	Mark
20(c)	An answer that makes reference to the following points: • identification of a suitable halogenoalkane (1) • reaction with magnesium (powder) in dry ether (1) • to form the Grignard reagent CH_3MgBr / methyl magnesium bromide (1) • formation of 2-methylbutan-2-ol by reacting the Grignard reagent with butanone (1)  • reaction with concentrated phosphoric acid or concentrated sulfuric acid (to give 2-methylbut-2-ene (and some 2-methylbut-1-ene)) (1)	Allow names or formulae for reagents and intermediates. Score correct compounds and reagents even if preceding chemistry is incorrect) Equations need not balance CH_3Br Allow Cl or I, Ignore X for halogen Allow the use of dry ether with or without Mg in this reaction or halogen given for M1 Ignore just 2-methylbutan-2-ol If Grignard reagent not used (i.e. M1, M2, M3 & M4 not scored, reaction of butanone with HCN / KCN / CN^- to form 2-hydroxy-2-methylbutanenitrile scores (1) [ignore reaction conditions] Allow pass alcohol (vapour) over heated alumina / Al_2O_3 Allow correct reaction to form halogenoalkane **and** dehydrohalogenation with OH^- in ethanol Allow 1 mark for the dehydration of **any** alcohol by any of these reactions	**(5)**

(Total for Question 20 = 12 marks)

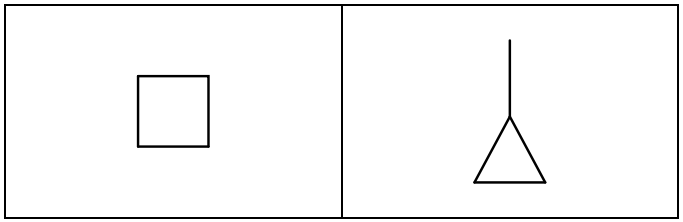
Question number	Answer	Additional guidance	Mark
21(a)	An answer that makes reference to the following points: • equation relating E^{o}_{cell} to half-cell values **and** determination of E^{o} for the right-hand electrode (1) • identification of **F** and **G** (1)	These are standalone marks $E^{o}_{cell} = E^{o}_{R} - E^{o}_{L}$ $1.94 = E^{o}_{R} - (-0.61)$ $E^{o}_{R} = 1.94 - 0.61 = (+)1.33$ (V) Allow (+)1.33 (V) with some working which relates 1.33 to 1.94 and −0.61 Allow (+)1.33 (V) with the $Cr_2O_7^{2-}$ / Cr^{3+} half-equation **F** = $Cr_2O_7^{2-}$ **and** **G** = Cr^{3+} Species must be clearly identified	**(2)**

Question number	Answer	Additional guidance	Mark
21(b)	• correct species on both sides of the equation and no electrons (1) • equation balanced (1)	<u>Example of equation</u> $3C_2H_5OH + Cr_2O_7^{2-} + 8H^+ \rightleftharpoons 2Cr^{3+} + 3CH_3CHO + 7H_2O$ Allow multiples uncancelled H^+ ions → or ⇌ Ignore state symbols even if incorrect Correct balanced equation with uncancelled electrons scores (1)	**(2)**

Question number	Answer	Additional guidance	Mark
21(c)	• correct equation	<u>Example of equation</u> $2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$ Allow multiples → or ⇌ Ignore state symbols even if incorrect Do not award uncancelled electrons	**(1)**

(Total for Question 21 = 5 marks)

Question number	Answer	Additional guidance	Mark
22(a)	• identification of correct algebraic equation for x **and** solves equation to obtain x (1) • identification of correct algebraic equation for x and y (1) • solves equation to obtain y and gives formula of the hydrocarbon (1)	<u>Example of calculation</u> {from the equation 1 mol of C_xH_y gives x mol of CO_2 so 25 mol will give 25x mol CO_2 and 25 cm^3 will give 25x cm^3CO_2 . Hence} 25x = 100 **and** x = 4 Allow just x = 4 with no working {change in volume is} (25 + 25(x+y/4) − 25x = 75 25y/4 = 50 therefore y = 8 **and** C_4H_8 correct formula with no working scores (1)	**(3)**

Question number	Answer	Additional guidance	Mark
22(b)	• structure of cyclobutane (1) • structure of methylcyclopropane(1)	<u>Examples of structures</u>  or displayed / semi-displayed structures Ignore names even if incorrect TE on 22(a) for cycloalkanes only If (a) is an alkane with C>3 2 correct isomers scores 1 mark	**(2)**

(Total for Question 22 = 5 marks)

<table>
<tr><th>Question number</th><th>Answer</th><th>Additional guidance</th><th>Mark</th></tr>
<tr>
<td>*23</td>
<td>
This question assesses the student's ability to show a coherent and logically structured answer with linkages and fully sustained reasoning.

Marks are awarded for indicative content and for how the answer is structured and shows lines of reasoning.

The following table shows how the marks should be awarded for indicative content.
<table>
<tr><td>Number of indicative marking points seen in answer</td><td>Number of marks awarded for indicative marking points</td></tr>
<tr><td>6</td><td>4</td></tr>
<tr><td>5-4</td><td>3</td></tr>
<tr><td>3-2</td><td>2</td></tr>
<tr><td>1</td><td>1</td></tr>
<tr><td>0</td><td>0</td></tr>
</table>

The following table shows how the marks should be awarded for structure and lines of reasoning
<table>
<tr><td></td><td>Number of marks awarded for structure of answer and sustained lines of reasoning</td></tr>
<tr><td>Answer shows a coherent logical structure with linkages and fully sustained lines of reasoning demonstrated throughout</td><td>2</td></tr>
<tr><td>Answer is partially structured with some linkages and lines of reasoning</td><td>1</td></tr>
<tr><td>Answer has no linkages between points and is unstructured</td><td>0</td></tr>
</table>
</td>
<td>
Guidance on how the mark scheme should be applied.

The mark for indicative content should be added to the mark for lines of reasoning. For example, a response with five indicative marking points that is partially structured with some linkages and lines of reasoning scores 4 marks (3 marks for indicative content and 1 mark for partial structure and some linkages and lines of reasoning).

If there were no linkages between the points, then the same indicative marking points would yield an overall score of 3 marks (3 marks for indicative content and no marks for linkages).

In general it would be expected that
5 or 6 indicative points would get 2 reasoning marks
3 or 4 indicative points would get 1 reasoning mark
0, 1 or 2 indicative points would get 0reasoning marks.

If there is any incorrect chemistry, deduct mark(s) from the reasoning. If no reasoning mark(s) awarded do not deduct mark(s).

Comment: Look for the indicative marking points first, then consider the mark for the structure of the answer and sustained line of reasoning
</td>
<td></td>
</tr>
</table>

Question number	Answer	Additional guidance	Mark
***23 (cont)**	**Indicative content** **IP1** both platinum **and** V_2O_5 are heterogeneous catalysts **IP2** there is adsorption of reactants on the (catalyst) surface (this applies to both reactions) **IP3 (**in the catalytic converter) adsorbed reactant bonds are weakened / broken allowing reaction to occur more easily. (this applies only to the catalytic converter) **IP4** (in the catalytic converter there is) desorption of **products** from the surface (this applies to both reactions) **IP5 (**in the Contact Process the) V_2O_5 is reduced (to V(III) / V(IV)) **and** by sulfur dioxide / SO_2 **IP6** Vanadium species /V(III) / V(IV) is oxidised to V(V) **and** by oxygen	Allow (for **IP1**) both catalysts (provide an alternative path with) lower activation energy Do not award **IP1** if V_2O_5 is homogeneous or chemisorption / bond strongly Allow **IP2**, **IP3** and **IP4** for general description of heterogeneous catalysis penalise **ab**sorption once only Ignore **IP3** for the Contact Process Allow any indication of the **products** leaving the surface of the catalyst Equations showing reduction of V_2O_5 by SO_2 and the subsequent oxidation do **not** need to balance If neither **IP5** nor **IP6**scored Allow **IP6** for **Either** V_2O_5 first reduced then (V compound) oxidised **or** $2SO_2 + O_2 \rightleftharpoons 2SO_3$**and**$2CO + 2NO \rightarrow 2CO_2 + N_2$	**(6)**

(Total for Question 23 = 6 marks)

TOTAL FOR SECTION B = 60 MARKS

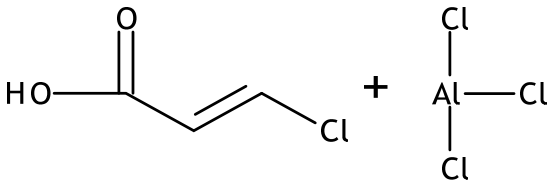
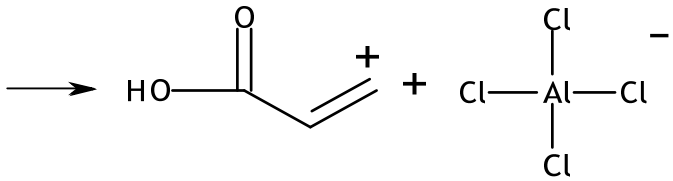
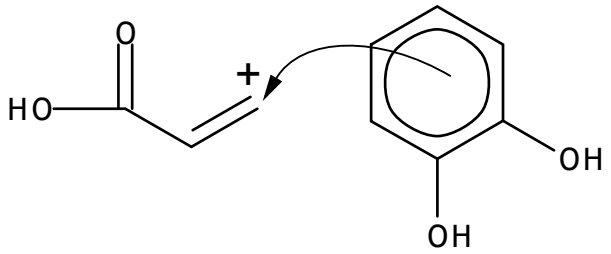
Section C

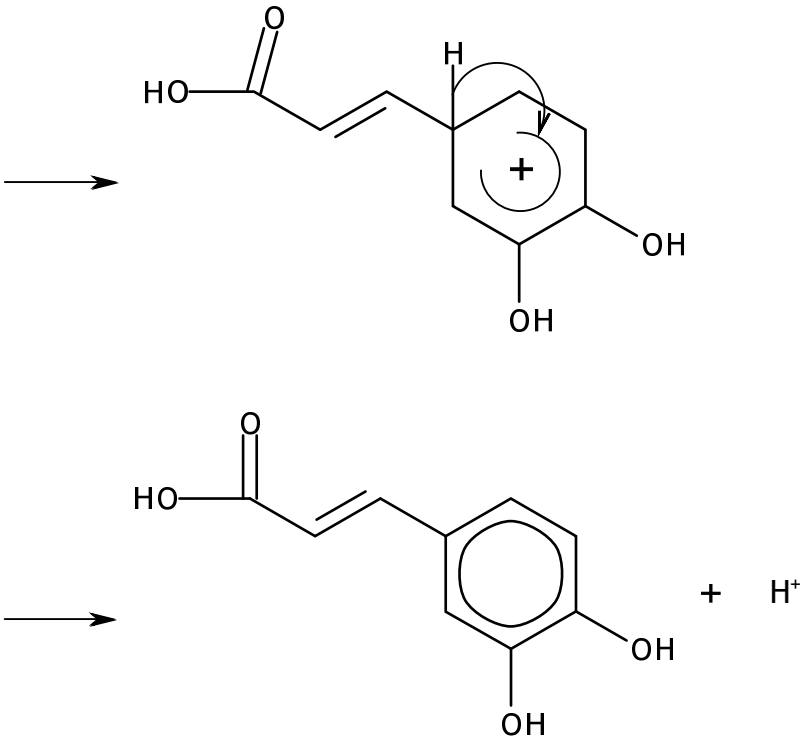
Question number	Answer	Additional guidance	Mark
24(a)(i)	An explanation that makes reference to the following points • (π) electron system (in the right-hand ring) is delocalised (1) M2 and M3 scored from any **two** of • the delocalisation involves the lone-pair(s) in the nitrogen (atom(s)) and the π electrons of the double bonds (1) • (the right-hand ring) will undergo substitution reactions rather than addition reactions (1) • caffeine has stabilisation / delocalisation energy(1) • all the C—N bonds (in the 5-membered ring) will be the same (length)(1)	Allow aromatic ring Ignore just 'form aπ bond' Do not award just it is a benzene ring Allow just 'the delocalisation involves the lone-pair(s) in the nitrogen (atom(s)) Allow electrophilic substitution (rather than addition) Ignore electrophilic reaction Allow caffeine / (delocalised) ring is more stable Allow all the bonds will be the same length Ignore C=C bonds will be the same length	**(3)**

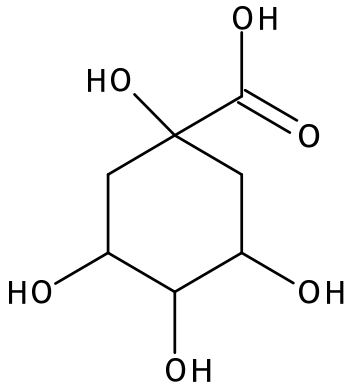
Question number	Answer	Additional guidance	Mark
24(a)(ii)	An explanation that makes reference to the following points • Description of basicity (1) • Effect of delocalisation(1)	 Either lone pair donation Or proton acceptor Nitrogen lone pair incorporated in delocalised system / overlaps with the π (electron) ring **and** reduces electron density / lone pair availability Do not award overlap with the benzene ring Ignore references to the amide even if incorrect. If no other mark is scored the positive inductive effect of alkyl groups increases availability of the lone pair in a primary amine scores (1)	**(2)**

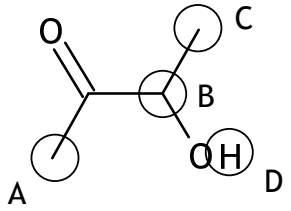
Question number	Answer	Additional guidance	Mark
24(b)(i)	• determination of M_r(from molecular formula)(1) • calculation of amount of caffeine(1) • calculation of concentration of caffeine (1) • final answer to 1 or 2 SF (1)	<u>Example of calculation</u> ($C_8H_{10}N_4O_2$) M_r = 194 $\frac{85}{1000 \times 194}$ (= 4.3814 x 10^{-4}/ 0.00043814) (mol) $= \frac{1000 \times 85}{200 \times 1000 \times 194} / \frac{1000 \times 0.00043814}{200}$ = 2.1907 x 10^{-3}/ 0.0021907 (mol dm^{-3}) = 2 x 10^{-3} /2.2 x 10^{-3} / 0.002 /0.0022(mol dm^{-3}) Do not award > 2 SF TE at each stage correct answer with no working scores (1)	**(4)**

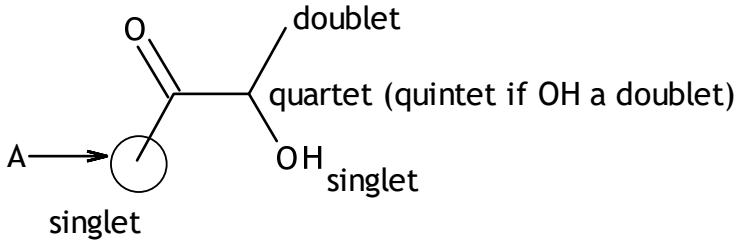
Question number	Answer	Additional guidance	Mark
24(b)(ii)	• calculation of number of half-lives (1) • applies half-lives to three hours (1)	<u>Example of calculation</u> $\frac{20}{160}=\frac{1}{8}=\left(\frac{1}{2}\right)^{n}$ n = 3 or 160⟶80 ⟶ 40 ⟶ 20 (3 half lives) time = 3 x 3 = 9 hours TE on number of half lives calculated correct answer with some working scores (2)	**(2)**

Question number	Answer	Additional guidance	Mark
24(c)(i)	A mechanism showing the following • structure of 3-chloropropenoic acid (1) • structure of the electrophile **and** balanced equation involving $AlCl_3$ and $AlCl_4^-$ (1) • curly arrow from on or within the circle to the positively charged carbon (1) **Allow any electrophile for M3, M4 and M5**	M1 and M2 are for the electrophile formation M3, M4 and M5 are for the electrophilic substitution Example of mechanism  Allow Br or I for Cl and Fe for Al Penalise errors in structure of 3-chloropropenoic acid / electrophile in M1 or M2 only   Allow curly arrow from anywhere in the hexagon Allow dotted horseshoe	**(5)**

Question number	Answer	Additional guidance	Mark
24(c)(i) cont	• intermediate structure including charge with horseshoe covering at least 3 carbon atoms **and** facing the tetrahedral carbon **and** with some part of the positive charge within the horseshoe (1) • curly arrow from C—H bond to anywhere in the benzene ring reforming delocalised structure with phenol groups in the 3 and 4 positions(1)	 penalise incorrect position / omission of the phenol groups at final marking point. Ignore omission of H^+ in final step correct Kekulé structures score full marks Ignore structure of substituents apart from the position of the OH groups in final structure	

Question number	Answer	Additional guidance	Mark
24(c)(ii)	• 	or displayed structure Allow COOH and CO_2H Ignore all connectivity errors to 'OH' Only penalise O−H−C	(1)

Question number	Answer	Additional guidance	Mark
24(d)(i)	• 	Allow any labelling sequence Do not award any other labelling	(1)

<table>
<tr><th>Question number</th><th>Answer</th><th>Additional guidance</th><th>Mark</th></tr>
<tr><td>24(d)(ii)</td><td>
<table>
<tr><th>Proton environment (labelled as in (i))</th><th>Splitting pattern</th></tr>
<tr><td>A</td><td>singlet</td></tr>
<tr><td>B</td><td>quartet</td></tr>
<tr><td>C</td><td>doublet</td></tr>
<tr><td>D</td><td>singlet</td></tr>
</table>
OR


</td><td>all four correct (2)

three correct (1)

Allow non-standard terms such as ‘two splits’ or just ‘2’ for doublet

If D (OH proton) is given as a doublet, allow B as a quartet or as a quintet

Ignore carbonyl carbon labelled as a proton environment</td><td>(2)</td></tr>
</table>

(Total for Question 24 = 20 marks)
TOTAL FOR SECTION C = 20 MARKS

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