Mark Scheme (Results)

Summer 2014

IAL Chemistry (WCH05/01)

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Summer 2014
Publications Code IA038359*

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.
- Mark schemes will indicate within the table where, and which strands of QWC, are being assessed. The strands are as follows:

  i) ensure that text is legible and that spelling, punctuation and grammar are accurate so that meaning is clear
  ii) select and use a form and style of writing appropriate to purpose and to complex subject matter
  iii) organise information clearly and coherently, using specialist vocabulary when appropriate

Using the Mark Scheme

Examiners should look for qualities to reward rather than faults to penalise. This does NOT mean giving credit for incorrect or inadequate answers, but it does mean allowing candidates to be rewarded for answers showing correct application of principles and knowledge. Examiners should therefore read carefully and consider every response: even if it is not what is expected it may be worthy of credit.

The mark scheme gives examiners:
- an idea of the types of response expected
- how individual marks are to be awarded
- the total mark for each question
- examples of responses that should NOT receive credit.

/ means that the responses are alternatives and either answer should receive full credit.
( ) means that a phrase/word is not essential for the award of the mark, but helps the examiner to get the sense of the expected answer.
Phrases/words in **bold** indicate that the meaning of the phrase or the actual word is **essential** to the answer.
ecf/TE/cq (error carried forward) means that a wrong answer given in an earlier part of a question is used correctly in answer to a later part of the same question.

Candidates must make their meaning clear to the examiner to gain the mark. Make sure that the answer makes sense. Do not give credit for correct words/phrases which are put together in a meaningless manner. Answers must be in the correct context.

Quality of Written Communication

Questions which involve the writing of continuous prose will expect candidates to:
- write legibly, with accurate use of spelling, grammar and punctuation in order to make the meaning clear
- select and use a form and style of writing appropriate to purpose and to complex subject matter
- organise information clearly and coherently, using specialist vocabulary when appropriate.

Full marks will be awarded if the candidate has demonstrated the above abilities.
Questions where QWC is likely to be particularly important are indicated (QWC) in the mark scheme, but this does not preclude others.

Section A (multiple choice)

Question Number	Correct Answer	Reject	Mark
1	C		1

Question Number	Correct Answer	Reject	Mark
2	D		1

Question Number	Correct Answer	Reject	Mark
3(a)	D		1
(b)	A		1

Question Number	Correct Answer	Reject	Mark
4	B		1

Question Number	Correct Answer	Reject	Mark
5	B		1

Question Number	Correct Answer	Reject	Mark
6	A		1

Question Number	Correct Answer	Reject	Mark
7	B		1

Question Number	Correct Answer	Reject	Mark
8	C		1

Question Number	Correct Answer	Reject	Mark
9	A		1

Question Number	Correct Answer	Reject	Mark
10	C		1

Question Number	Correct Answer	Reject	Mark
11	C		1

Question Number	Correct Answer	Reject	Mark
12	D		1

Question Number	Correct Answer	Reject	Mark
13	D		1

Question Number	Correct Answer	Reject	Mark
14	A		1

Question Number	Correct Answer	Reject	Mark
15	B		1

Question Number	Correct Answer	Reject	Mark
16	D		1

Question Number	Correct Answer	Reject	Mark
17	D		1

Question Number	Correct Answer	Reject	Mark
18	C		1

Question Number	Correct Answer	Reject	Mark
19	B		1

Total for Section A = 20 marks

Section B

Question Number	Acceptable Answers	Reject	Mark
20(a)(i)	<table><tr><th>Ion</th><th>Oxidation number of vanadium</th></tr><tr><td>$V(H_2O)_6^{2+}$</td><td>+2</td></tr><tr><td>$V(H_2O)_6^{3+}$</td><td>+3</td></tr><tr><td>VO^{2+}</td><td>+4</td></tr><tr><td>VO_2^{+}</td><td>(+5)</td></tr></table> All three correct **(1)** IGNORE omission of '+'		1

Question Number	Acceptable Answers	Reject	Mark
20(a)(ii)	Electronic configuration of V: $[Ar]3d^3 4s^2$ ALLOW $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3\ 4s^2$ $[Ar]\ 4s^2 3d^3$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^3$ IGNORE Additional [Ar] **(1)** 5 electrons in valence shell / available for bonding ALLOW 5 electrons in outer shell (So max ON = +5) OR Uses the 2 4s and 3 3d electrons **(1)** ALLOW Lose 5 electrons (to form Ar structure) No TE on incorrect electronic configuration except $3d^5$ ($4s^0$) IGNORE Stability of +5 oxidation state	Gives electronic structure of Ar Loss of electrons from a (single) d orbital	2

Question Number	Acceptable Answers	Reject	Mark
20(a)(iii)	(3)d orbitals / (3)d subshell split (by the attached ligands) **(1)** Electrons are promoted (from lower to higher energy d orbital(s) / levels) OR Electrons move from lower to higher energy d orbital(s) / levels) ALLOW d—d transitions occur **(1)** Absorbing energy /photons of a certain frequency (in the visible region) ALLOW Absorbing light **(1)** Reflected / transmitted / remaining light is coloured / in the visible region ALLOW Complementary colour seen Reflected / transmitted / remaining light / frequency is seen **(1)** Penalise omission of (3)d once only. Ignore reference to electrons relaxing / dropping to the ground state	Orbital / shell is split Emitted	4

Question Number	Acceptable Answers	Reject	Mark
20(a)(iv)	V^{5+} is (small &) **high**ly charged /has a (very) **high** charge density **(1)** Would polarize / distort H_2O / H_2O electron clouds / O−H bond ALLOW O-H bond weakening / breaking OR Deprotonation **(1)** IGNORE References to ionization energy of V / highly electropositive	 Just 'Polarize' Ionic bonds	2

Question Number	Acceptable Answers	Reject	Mark
20(a)(v)	No. Because V^{5+} has no d electrons / d sub-shell is empty / d orbital**s** are empty. IGNORE Any mention of 4s V^{5+} has no partially filled d orbitals		1

Question Number	Acceptable Answers	Reject	Mark
20(b)(i)	Either **Method 1 (using equations)** $4H^+ + SO_4^{2-} + 2e^- \rightarrow H_2SO_3 + H_2O$ E^o = **+**0.17 (V) $VO^{2+} + 2H^+ + e^- \rightarrow V^{3+} + H_2O$ E^o = **+**0.34 (V) **(1)** $2VO^{2+} + H_2SO_3 \rightarrow 2V^{3+} + SO_4^{2-} + H_2O$ **(1)** E_{cell} (SO_2) = 0.34 – 0.17 = (+)0.17 (V) AND So reduces V(IV) to V(III) / reaction is feasible **(1)** **OR** **Method 2 (using anticlockwise rule)** When half reactions are placed in order (more negative first) $4H^+ + SO_4^{2-} + 2e^- \rightarrow H_2SO_3 + H_2O$ E^o = +0.17 V $VO^{2+} + 2H^+ + e^- \rightarrow V^{3+} + H_2O$ E^o = +0.34 V Required reaction 'goes' in anticlockwise direction Arrows on half equations and explanation **(2)** $2VO^{2+} + H_2SO_3 \rightarrow 2V^{3+} + SO_4^{2-} + H_2O$ **(1)**	Use of thiosulphate half cell =0 Uncancelled electrons Uncancelled electrons	3

Question Number	Acceptable Answers	Reject	Mark
20(b)(ii)	$2V^{3+} + H_2O \rightarrow V^{2+} + VO^{2+} + 2H^+$ ALLOW $V(H_2O)_6^{3+}$ and $V(H_2O)_6^{2+}$		1

Question Number	Acceptable Answers	Reject	Mark
20(b)(iii)	(Relevant electrode potentials are $VO^{2+} + 2H^+ + e^- \rightarrow V^{3+} + H_2O$ E^o = +0.34 V $V^{3+} + e^- \rightarrow V^{2+}$ $E^o = -0.26$ V) E_{cell} (disproportionation) =(−0.26 − 0.34) = **−0.6(**0) (V) **(1)** E_{cell} negative so disproportionation not (thermodynamically) feasible. **(1)** TE for second mark only if value given		2

Total for Question 20 = 16 marks

Question Number	Acceptable Answers	Reject	Mark
21(a)(i)	(pale) pink OR First permanent pink Ignore 'Colourless to'	purple	1

Question Number	Acceptable Answers	Reject	Mark
21(a)(ii)	$2MnO_4^- + 5C_2O_4^{2-} + \mathbf{16}H^+ \rightarrow \mathbf{2}Mn^{2+} + \mathbf{10}CO_2 + \mathbf{8}H_2O$		1

Question Number	Acceptable Answers	Reject	Mark
21(a)(iii)	Amount MnO_4^- = 24.55 x .0205 x 10^{-3} **(1)** = 5.03275 x 10^{-4} mol (ans *) Amount $C_2O_4^{2-}$ in 25 cm^3 = ans. * x 5 /2 = 5.03275 x 10^{-4} x 5/2 **(1)** = 1.2581875 x 10^{-3} mol In 250 cm^3 = 1.2581875 x 10^{-2} mol (ans **) **(1)** = amount Ca^{2+} = amount $CaCO_3$ Mass $CaCO_3$ = (ans**) x 100.1 = 1.2581875 x 10^{-2} x 100.1 **(1)** = 1.2594457 g (ans***) % $CaCO_3$ = 100 x (ans***) / 1.77 = 71.15512 = 71.2 (%) **(1)** ALLOW Final answer 71.1 / 71.2 / 71.3 scores 5 marks Final answer must be to 3 SF (max 4 if not) Until final answer ignore SF except 1 SF (penalise once) TE at each stage unless mass $CaCO_3$ > 1.77 NOTE Use of ethanedioate mass of 88 in step 4 gives final answer of 62.6% (max 4) Use of calcium ethanedioate mass of 128.1 / 128 in step 4 gives final answer of 91.0% (max 4)		5

Question Number	Acceptable Answers	Reject	Mark
21(b)(i)	Excess ethanedioate (ions in the solution) must be removed **(1)** ALLOW Remove ethanedioic acid Otherwise more $KMnO_4$ will be used (in the titration) / bigger titre **(1)** MP2 dependent on MP1	Impurities Acid	2

Question Number	Acceptable Answers	Reject	Mark
21 (b)(ii)			2

Apparatus	**Value**	**Maximum total error on the stated value**	**Percentage error on the stated value**
Balance	1.77 g	±0.01 g	0.56 (0.56497)
Volumetric flask	250 cm^3	±0.12 cm^3	0.048
Pipette	25 cm^3	±0.06 cm^3	0.24
Burette	24.55 cm^3	±0.10 cm^3	0.41 (0.40733)

All % calculations correct **(2)**
Any two or three calculations correct **(1)**

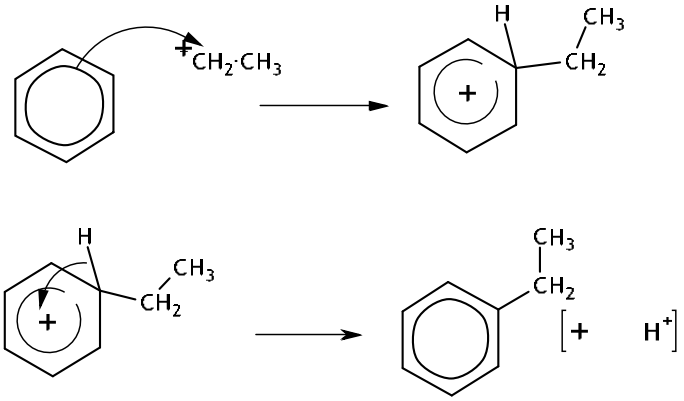
1 mark lost if 2 or more correct answers are not given to 2 SF

Question Number	Acceptable Answers	Reject	Mark
21(b)(iii)	**First mark** EITHER Max. mass of CaC_2O_4 precipitated = 0.015 x 128.1 = 1.9215 g OR 0.0067/2 = 0.00335 g remains in solution **(1)** **Second Mark** % error = 100 x 0.00335 / (1.9215 + 0.00335) = 100 x 0.00335 / 1.92485 = 0.174040 = 0.174 % ALLOW % error = 100 x 0.00335 / 1.9215 = 0.174343 = 0.174 % If M_r (CaC_2O_4) = 128 used = 0.174479 % **(1)** **Third Mark** Error comparable to / smaller than apparatus uncertainty / less than the worst / less than the balance / less than the total And so acceptable **(1)** IGNORE SF but penalise incorrect rounding once NOTE No TE for mark 2 from mark 1 BUT TE for mark 3. Accept reverse argument for large percentage.		3

Total for Question 21 = 14 marks

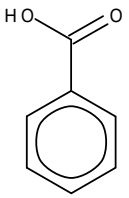
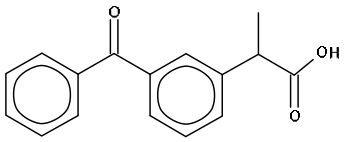
Question Number	Acceptable Answers	Reject	Mark
22(a)	**A** = PCl_5 / phosphorus(V) chloride / phosphorus pentachloride / PCl_3 / phosphorus(III) chloride / phosphorus trichloride / $SOCl_2$ / thionyl chloride / thionyl dichloride **(1)** **B** = benzene / C_6H_6 or ring structures **(1)** **C** = bromine / Br_2 **(1)**	Bromine water / Bromine and $FeBr_3$	3

Question Number	Acceptable Answers	Reject	Mark
22(b)(i)	$CH_3CH_2Br + AlBr_3 \rightarrow CH_3CH_2^+ + AlBr_4^-$ **(1)** ALLOW $C_2H_5^+$ + sign anywhere on formula of electrophile ($AlBr_3$ is an) electron pair acceptor / lone pair acceptor / Lewis acid / Friedal-Crafts catalyst **(1)** ALLOW polarizes C-Br bond IGNORE Halogen carrier	Accepts electrons Just 'catalyst'	2

Question Number	Acceptable Answers	Reject	Mark
22(b)(ii)	 TE on incorrect electrophile in (b)(i) Curly arrow from on or within the circle to positively charged carbon ALLOW Curly arrow from anywhere within the hexagon Arrow to **any** part of the electrophile including to the + charge **(1)** 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 ALLOW dotted horseshoe **(1)** Curly arrow from C—H bond to anywhere in the benzene ring reforming delocalized structure **(1)** Correct Kekulé structures score full marks Ignore any involvement of AlX_4^- in the final step NOTE $C_2H_5^+$ as electrophile can score all 3 marks	Curly arrow on or outside the hexagon Partial bonds to H and CH_3	3

Question Number	Acceptable Answers	Reject	Mark
22(c)(i)	KCN / potassium cyanide / NaCN / sodium cyanide **(1)** In ethanol (dependent on mark 1) ALLOW alcohol / aqueous ethanol / aqueous alcohol **(1)** ethanolic or alcoholic KCN (etc) scores both marks BUT CN^- / HCN in ethanol scores second mark	cyanide / CN^- HCN	2

Question Number	Acceptable Answers	Reject	Mark
22(c)(ii)	Name / formula of any strong aqueous acid OR named strong aqueous alkali followed by acidification Ignore heat / reflux / dilute / conc	H^+ / H_3O^+	1

Question Number	Acceptable Answers	Reject	Mark
22(d)(i)	1700-1680 (cm^-  benzenecarboxylic acid 1700-1680 (cm^-  ketoprofen 1725-1700 1 mark for each correct range / reverse range Single numbers within range = max 2 marks		3

Question Number	Acceptable Answers	Reject	Mark
22(d)(ii)	Only (the carboxylic acid group in) ketoprofen will give a peak at 1725 – 1700 cm^{-1} ALLOW Ketoprofen has 2 absorptions whilst benzenecarboxylic acid has one Correct TE identifying a unique range	 Just ketoprofen has more peaks	1

Total for Question 22 = 15 marks

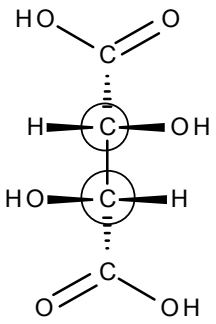
Question Number	Acceptable Answers	Reject	Mark
23(a)	Volume of CO_2 is less than volume of oxygen (and only other product is water). OR Fewer moles / molecules of gaseous products (than reactants).		1

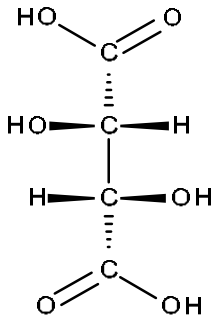
Question Number	Acceptable Answers	Reject	Mark
23(b)	Potassium hydroxide / KOH absorbs **CO_2** OR **CO_2** reacts with potassium hydroxide / KOH OR **CO_2** dissolves in potassium hydroxide / KOH		1

Question Number	Acceptable Answers	Reject	Mark
23(c)	So $10x = 40$ $x = 4$ **(1)** So $10 + 10(x + (y/4)) - 10x = 20$ $10(y/4) = 10$ $y = 4$ **(1)** $C_xH_y = C_4H_4$ **(1)** Correct formula with no working or explanation scores 3		3

Total for Question 23 = 5 marks
Total for Section B = 50 marks

Section C

Question Number	Acceptable Answers	Reject	Mark
24(a)(i)	 Circles around **both** asymmetric centres needed ALLOW Any correct labelling		1

Question Number	Acceptable Answers	Reject	Mark
24(a)(ii)	 ALLOW Any (correct) representation of carboxylic acid groups (e.g. COOH / CO_2H) Any orientation of carboxylic acid groups Fischer diagrams ONLY if labelled as such		1

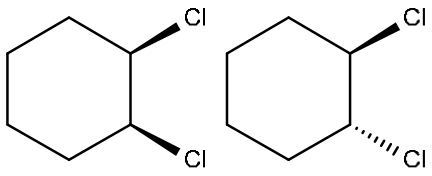
Question Number	Acceptable Answers	Reject	Mark
24(a)(iii)	The enantiomers will rotate the plane of plane-polarized light **(1)** Mark 1 must see rotate, plane and polarized (equally) in opposite directions ALLOW Clockwise and anticlockwise / left and right / + and **(1)** IGNORE Different directions		2

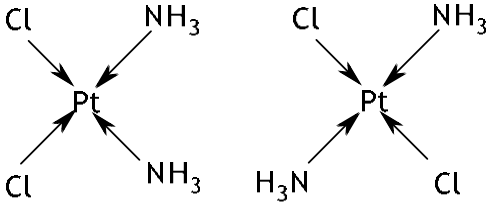
Question Number	Acceptable Answers	Reject	Mark
24(a)(iv)	No because the proton / H environments are the same (in both enantiomers) ALLOW No, the same peaks / spectrum		1

Question Number	Acceptable Answers	Reject	Mark
24(a)(v)	(S_N2) Because nucleophile must **attack** only from one side (of the molecule) / from the opposite side (to the leaving group) **OR** (Not S_N1) Because nucleophile would **attack** on both sides (of the intermediate) (and form a racemic mixture) **(1)** Substitution must be S_N2 **OR** Substitution cannot be S_N1 **(1)** NOTE For mark 1 IGNORE references to structure of intermediate		2

Question Number	Acceptable Answers	Reject	Mark
24(a)(vi)	Superimposable on its mirror image (allow enantiomer / isomer) / it has a plane of symmetry ALLOW The molecule is identical to its mirror image (Two chiral centres produce) equal but opposite rotation (of plane polarized light)	Centre of symmetry	1

Question Number	Acceptable Answers	Reject	Mark
24(b)(i)	Rotation (about the bond) reduces (lateral) overlap **(1)** to an energetically less favourable alignment OR so bond weaker OR (π) bond breaks **(1)**	π bond restricts rotation Double bond breaks	2

Question Number	Acceptable Answers	Reject	Mark
24(b)(ii)	 Both structures needed ALLOW Hydrogens to be shown Perspective diagrams		1

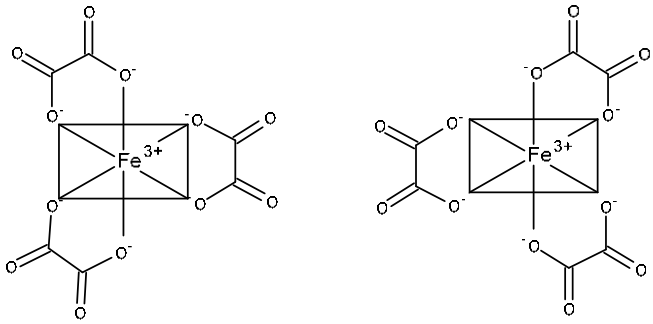
Question Number	Acceptable Answers	Reject	Mark
24(c)(i)	 Both structures needed Dative covalent bonds need not be shown.		1

Question Number	Acceptable Answers	Reject	Mark
24(c)(ii)	One of: Only one isomer is (biochemically) active One isomer is more active than the other One isomer is beneficial but the other has a negative effect Different isomers have different (biochemical) properties		1

Question Number	Acceptable Answers	Reject	Mark
24(c)(iii)	Any **three** from: 1. Avoids waste of substances (compounds, solvents etc) (used in the synthesis) ALLOW No waste product(s). 2. Avoids any need to separate enantiomers. 3. Unwanted enantiomer(s) might have negative effects / be toxic / harmful. 4. (Synthesising specific isomers results in) more effective / lower dosage of medicines. IGNORE Cost / yield / atom economy / (harmful) side effects	Just 'easier to prepare'	3

Question Number	Acceptable Answers	Reject	Mark
24(d)(i)	A bidentate ligand occupies two coordination positions (around a central ion) OR Can donate / has two lone pairs that can bond (separately) (to the central ion) OR Can form two dative bonds		1

Question Number	Acceptable Answers	Reject	Mark
24(d)(ii)	(Conversion of a monodentate ligand complex to a bidentate ligand complex) increases the number of particles so ΔS_{tot} / ΔS_{sys} / entropy increases	Bidentate complexes have higher entropy	1

Question Number	Acceptable Answers	Reject	Mark
24(d)(iii)	 1 mark for each structure Penalise incorrect charges once only ALLOW Complexes with overall 3 $^-$ For 1 mark 2 optical isomers with non displayed C_2O_4 linked		2

Total for Question 24 = 20 marks
Total for Section C = 20 marks