

Mark Scheme (Results)

Summer 2014

IAL Chemistry (WCH05/01)

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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.
- 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 <u>meaning</u> 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	С		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	В		1
Question Number	Correct Answer	Reject	Mark
5	В		1
Question Number	Correct Answer	Reject	Mark
6	A		1
Question Number	Correct Answer	Reject	Mark
7	В		1
Question Number	Correct Answer	Reject	Mark
8	C		1
Question Number	Correct Answer	Reject	Mark
9	Α		1
Question Number	Correct Answer	Reject	Mark
10	С		1
Question Number	Correct Answer	Reject	Mark
11	С		1
Question Number	Correct Answer	Reject	Mark
12	D		1

Question	Correct Answer	Reject	Mark
Number			
13	D		1
Question	Correct Answer	Reject	Mark
Number			
14	Α		1
		<u>.</u>	
Question	Correct Answer	Reject	Mark
Number			
15	В		1
Question	Correct Answer	Reject	Mark
Number			
16	D		1
		<u>.</u>	
Question	Correct Answer	Reject	Mark
Number			
17	D		1
		<u>.</u>	
Question	Correct Answer	Reject	Mark
Number			
18	С		1
	·	•	
Question	Correct Answer	Reject	Mark
Number			
19	В		1

**Total for Section A = 20 marks** 

# **Section B**

Question Number	Acce	eptable Answe	ers		Reject	Mark
20(a)(i)						1
		Ion	Oxidation number of vanadium			
		$V(H_2O)_6^{2+}$	+2			
		$V(H_2O)_6^{3+}$	+3			
		VO <sup>2+</sup>	+4			
		VO <sub>2</sub> <sup>+</sup>	(+5)			
	All t	hree correct		(1)		
	IGN	ORE omission	of `+'			

Question Number	Acceptable Answers	Reject	Mark
20(a)(ii)	Electronic configuration of V: [Ar]3d <sup>3</sup> 4s <sup>2</sup>		2
	ALLOW 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>3</sup> 4s <sup>2</sup> [Ar] 4s <sup>2</sup> 3d <sup>3</sup> 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 4s <sup>2</sup> 3d <sup>3</sup>		
	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)	Gives electronic structure of Ar	
	ALLOW Lose 5 electrons (to form Ar structure)  No TE on incorrect electronic	Loss of electrons from a (single) d orbital	
	configuration except 3d <sup>5</sup> (4s <sup>0</sup> )  IGNORE  Stability of +5 oxidation state		

Question Number	Acceptable Answers	Reject	Mark
20(a)(iii)	(3)d orbitals / (3)d subshell split (by the attached ligands) (1)	Orbital / shell is split	4
	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	Emitted	
	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		

Question Number	Acceptable Answers	Reject	Mark
20(a)(iv)	a (very) <b>high</b> charge density (1)		2
	Would polarize / distort $H_2O$ / $H_2O$ electron clouds / $O-H$ bond	Just 'Polarize' Ionic bonds	
	ALLOW O-H bond weakening / breaking OR		
	Deprotonation (1)		
	IGNORE		
	References to ionization energy of V / highly electropositive		

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

Question Number	Acceptable Answers	Reject	Mark
20(b)(i)	Either  Method 1 (using equations)	Use of thiosulphate half cell =0	3
	$4H^{+} + SO_{4}^{2-} + 2e^{-} \rightarrow H_{2}SO_{3} + H_{2}O E^{0} =$ +0.17 (V)		
	$VO^{2+} + 2H^{+} + e^{-} \rightarrow V^{3+} + H_{2}O E^{0}$ = $+0.34 (V)$ (1)		
	$2VO^{2+} + H_2SO_3 \rightarrow 2V^{3+} + SO_4^{2-} + H_2O$ (1)	Uncancelled electrons	
	$E_{\text{cell}}$ (SO <sub>2</sub> ) = 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)		
	$4H^{+} + SO_{4}^{2-} + 2e^{-} \rightarrow H_{2}SO_{3} + H_{2}O E^{0}$ = +0.17 V		
<b>4</b>	$VO^{2+} + 2H^{+} + e^{-} \rightarrow V^{3+} + H_{2}O E^{0}$ = +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)	Uncancelled electrons	

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

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

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
	$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$		1

Question Number	Acceptable Answers	Reject	Mark
21(a)(iii)	Amount $MnO_4^- = 24.55 \times .0205 \times 10^{-3}$		5
	$= 5.03275 \times 10^{-4} \text{ mol (ans *)}$		
	Amount $C_2O_4^{2-}$ in 25 cm <sup>3</sup> = ans. * x 5 /2 = 5.03275 x $10^{-4}$ x 5/2		
	$= 1.2581875 \times 10^{-3} \text{ mol}$		
	In 250 cm <sup>3</sup> = 1.2581875 x $10^{-2}$ mol (ans **)		
	$= amount Ca^{2+} = amount$ $CaCO_3$		
	Mass CaCO <sub>3</sub> = (ans**) x 100.1 = 1.2581875 x $10^{-2}$ x 100.1		
	( <b>1</b> ) = 1.2594457 g (ans***)		
	% CaCO <sub>3</sub> = 100 x (ans***) / 1.77 = 71.15512		
	= 71.2 ( % ) <b>(1)</b>		
	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 <sub>3</sub> > 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 )		

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

Question Number	Acceptable Answers				Reject	Mark
21 (b)(ii)	Apparatu s	Value	Maximum total error on the stated value	Percentag e error on the stated value		2
	Balance	1.77 g	±0.01 g	0.56 (0.56497)		
	Volumetric flask	250 cm <sup>3</sup>	±0.12 cm <sup>3</sup>	0.048		
	Pipette	25 cm <sup>3</sup>	±0.06 cm <sup>3</sup>	0.24		
	Burette	24.55 cm <sup>3</sup>	±0.10 cm <sup>3</sup>	0.41		
				(0.40733)		
	All % calculat Any two or th	cions correct ree calculations	s correct	(2) (1)		
	1 mark lost if 2 SF	2 or more corr	ect answers ar	e not given to		

Question Number	Acceptable Answers	Reject	Mark
21(b)(iii)	First mark		3
	EITHER		
	Max. mass of $CaC_2O_4$ precipitated = 0.015 x 128.1 = 1.9215 g		
	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 <sub>2</sub> O <sub>4</sub> ) = 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.		

**Total for Question 21 = 14 marks** 

Question Number	Acceptable Answers		Reject	Mark
22(a)	A = PCl <sub>5</sub> / phosphorus(V) chloride / phosphorus pentachloride / PCl <sub>3</sub> / phosphorus(III) chloride / phosphorus trichloride / SOCl <sub>2</sub> / thionyl chloride / thi dichloride	onyl (1)		3
	$\mathbf{B}$ = benzene / $C_6H_6$ or ring structures			
	<b>C</b> = bromine / Br <sub>2</sub>	<ul><li>(1)</li><li>(1)</li></ul>	Bromine water / Bromine and FeBr <sub>3</sub>	

Question Number	Acceptable Answers	Reject	Mark
22(b)(i)	$CH_3CH_2Br + AlBr_3 \rightarrow CH_3CH_2^+ + AlBr_4^-$ (1)		2
	ALLOW $C_2H_5^+$ + sign anywhere on formula of electrophile (AlBr <sub>3</sub> is an) electron pair acceptor / lone pair acceptor / Lewis acid / Friedal-Crafts catalyst (1)	Accepts electrons Just 'catalyst'	
	ALLOW polarizes C-Br bond  IGNORE  Halogen carrier		

Question Number	Acceptable Answers	Reject	Mark
Number 22(b)(ii)	TE on incorrect electrophile in (b)(i)  Curly arrow from on or within the circle to positively charged carbon		3
	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 $AIX_4^-$ in the final step NOTE $C_2H_5^+$ as electrophile can score all 3 marks		

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

Question Number	Acceptable Answers	Reject	Mark
22(c)(ii)	Name / formula of any strong aqueous acid  OR named strong aqueous alkali followed by acidification	H <sup>+</sup> / H <sub>3</sub> O <sup>+</sup>	1
	Ignore heat / reflux / dilute / conc		

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

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

**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 <b>CO<sub>2</sub></b> OR <b>CO<sub>2</sub></b> reacts with potassium hydroxide / KOH		1
	OR CO <sub>2</sub> dissolves in potassium hydroxide / KOH		

Question Number	Acceptable Answers	Reject	Mark
23(c)	So $10x = 40$ x = 4 (1)		N
	So $10 + 10(x + (y/4)) - 10x = 20$		
	$     \begin{array}{r}       10(y/4) = 10 \\       y = 4     \end{array}   $ (1)		
	$C_{x}H_{y} = C_{4}H_{4} $ (1)	)	
	Correct formula with no working or explanation scores 3		

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

# **Section C**

Question Number	Acceptable Answers	Reject	Mark
24(a)(i)	HO C OH HO C H		1
	Circles around <b>both</b> asymmetric centres needed  ALLOW Any correct labelling		

Question Number	Acceptable Answers	Reject	Mark
24(a)(ii)	но о		1
	HO—C—H		
	H <b>—</b> C → OH		
	ОН		
	ALLOW  Any (correct) representation of carboxylic acid		
	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		

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		2
	(equally) in opposite directions		
	ALLOW Clockwise and anticlockwise / left and right / + and (1)		
	IGNORE Different directions		

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

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

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

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

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

Question	Acceptable Answers	Reject	Mark
Number			
24(c)(i)	CL NH3 CL NH3		1
	Cl NH <sub>3</sub> H <sub>3</sub> N Cl Both structures needed  Dative covalent bonds need not be shown.		

Question Number	Acceptable Answers	Reject	Mark
24(c)(ii)	One of: Only one isomer is (biochemically) active		1
	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		

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

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

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

Question Number	Acceptable Answers	Reject	Mark
24(d)(iii)	Fe <sup>3+</sup>	0 0 0 0 0 0	2
	1 mark for each structure		
	Penalise incorrect charges once only		
	ALLOW		
	Complexes with overall 3 <sup>-</sup>		
	For 1 mark 2 optical isomers with non ( $C_2O_4$ linked	displayed	

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

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