

Mark Scheme (Results)
January 2012

GCE Chemistry (6CH05) Paper 01
General Principles of Chemistry II
Transition Metals and Organic Nitrogen
Chemistry
(including synoptic assessment)

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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. Questions labelled with an **asterix (*)** are ones where the quality of your written communication will be assessed.

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	Mark
1	A	1

Question Number	Correct Answer	Mark
2	D	1

Question Number	Correct Answer	Mark
3	A	1

Question Number	Correct Answer	Mark
4	B	1

Question Number	Correct Answer	Mark
5	D	1

Question Number	Correct Answer	Mark
6	B	1

Question Number	Correct Answer	Mark
7	C	1

Question Number	Correct Answer	Mark
8	D	1

Question Number	Correct Answer	Mark
9	B	1

Question Number	Correct Answer	Mark
10	B	1

Question Number	Correct Answer	Mark
11	C	1

Question Number	Correct Answer	Mark
12	A	1

Question Number	Correct Answer	Mark
13	C	1

Question Number	Correct Answer	Mark
14	B	1

Question Number	Correct Answer	Mark
15	C	1

Question Number	Correct Answer	Mark
16	D	1

Question Number	Correct Answer	Mark
17	C	1

Question Number	Correct Answer	Mark
18	D	1

Question Number	Correct Answer	Mark
19	D	1

Question Number	Correct Answer	Mark
20	A	1

TOTAL FOR SECTION A = 20 MARKS

Section B

Question Number	Acceptable Answers	Reject	Mark
21(a)	$3d^34s^2$ OR $4s^23d^3$ $3d^54s^1$ OR $4s^13d^5$ both must be correct. ALLOW Electron numbers could be on the line or as subscripts IGNORE case of letters		1

Question Number	Acceptable Answers	Reject	Mark
21(b)(i)	Variable/varying/different/several/ more than one oxidation state / number (1) Complex (ion formation) (1) Treat Physical properties (if correct) including catalytic activity as neutral	Each metal has a different oxidation number Ligand exchange	2

Question Number	Acceptable Answers	Reject	Mark
21(b)(ii)	The following metals scores (2) marks with correct E value: Mg 1.96, Ce 1.92, U 1.39, Al 1.25, Mn 0.78, V 0.77, Zn 0.35 NOTE: Positive sign/unit not needed, but penalise negative value The following metals score (1) mark with correct E value: Li 2.62, Rb 2.52, K 2.51, Ca 2.46, Na 2.30, Cr 0.33, Fe 0.03 NOTE: Positive sign/unit not needed, but penalise negative value	All other metals 0/2	2

Question Number	Acceptable Answers	Reject	Mark
21(b)(iii)	Not a redox process Chromate and dichromate both the same/no change in oxidation number (1) contain Cr(VI) 6/6+ (1) Mark independently OR Not redox and both contain Cr(VI) 6/6+ (2)		2

Question Number	Acceptable Answers	Reject	Mark
21(b)(iv)	Forms two (dative/covalent) bonds/has two lone pairs (to the Transition Metal/ion) OR donates two pairs of electrons (to the Transition Metal/ion) Check answer to (v) if mark not awarded here	'...to the molecule'	1

Question Number	Acceptable Answers	Reject	Mark
21(b)(v)	Any two from Both have two nitrogen atoms with lone pairs or implied (1) or Far enough apart/longer chain in between in en (but not in hydrazine)/too close in hydrazine/hydrazine is too short/not as long (1) or Dative bonds/lone pairs too close/repel in hydrazine (1) OR for two marks Forms 5-membered ring (with en with no angle strain/stable) (2) or Bond angles too acute/too much ring strain in hydrazine (2) Mark for iv can be awarded here.	N=N, or triple bond in hydrazine max 1 or if implies only en has lone pairs max 1	2

Question Number	Acceptable Answers	Reject	Mark
21(c)(i)	- 0.41 (V) +1.33 (V) Both answers needed, with number and sign, for 1 mark IGNORE additional words		1

Question Number	Acceptable Answers	Reject	Mark
*21(c)(ii) QWC	<p>Combines the equations to obtain</p> $8\text{Cr}^{3+} + 7\text{H}_2\text{O} \rightarrow 6\text{Cr}^{2+} + \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+$ <p>ALLOW $6\text{Cr}^{3+} + 2\text{Cr}^{3+}$ instead of 8Cr^{3+}</p> <p>IGNORE state symbols even if wrong</p> <p>species (1), balance (1)</p> <p>$E^\ominus_{\text{reaction}} = -1.74\text{V}$ (1)</p> <p>So not feasible on condition of negative value (1)</p> <p>OR</p> $6\text{Cr}^{2+} + \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ \rightarrow 8\text{Cr}^{3+} + 7\text{H}_2\text{O}$ <p>If fully correct (1)</p> <p>$E^\ominus_{\text{reaction}} = +1.74\text{V}$ (1)</p> <p>Disproportionation not feasible on condition of positive value but reject 'reaction is spontaneous' (1)</p> <p>Other wrong equations</p> <p>IF $\text{Cr}_2\text{O}_7^{2-}$ or Cr^{2+} on left</p> <p>Then $+1.74\text{V}$ (1)</p> <p>If Cr^{3+} alone on the left</p> <p>Then -1.74V (1)</p> <p>and reaction not feasible (1)</p>	<p>1 max for the equation if electrons are shown balanced or unbalanced</p>	4

Question Number	Acceptable Answers	Reject	Mark
22(a)(i)	C $60/12 = 5$ H $8/1 = 8$ O $32/16 = 2$ ALLOW 1 mol = 100 g So 60 %C = C ₅ , etc		1

Question Number	Acceptable Answers	Reject	Mark
22(a)(ii)	<p>C=C</p> <p>Test : add bromine water/Br₂(aq) (1)</p> <p>Result: From yellow/brown/red-brown/orange to colourless/decolorises (1)</p> <p>OR</p> <p>Test : add (acidified) potassium manganate((VII)) (solution) (1)</p> <p>Result: goes from pink/purple to colourless/brown (1)</p> <p>Test : add alkaline potassium manganate((VII)) (solution) (1)</p> <p>Result: goes green (1)</p> <p>COOH:</p> <p>Test : add NaHCO₃/Na₂CO₃/sodium carbpnate (solution) (1)</p> <p>Result: Fizzes/bubbles/large volume neutralized (1)</p>	<p>Bromine/Br₂/Br₂(l)</p> <p>clear for colourless</p> <p>clear for colourless</p> <p>PCl₅ /LiAlH₄ as test</p> <p>NaOH/NaOH(aq)</p> <p>colourless gas evolved</p>	4

	<p>ALLOW gas given off that turns limewater cloudy</p> <p>OR</p> <p>Test : with blue litmus (1)</p> <p>Result: turns red (1)</p> <p>The test can be with any other indicator, including universal indicator, with the correct initial and final colour</p> <p>ALLOW pH meter (1)</p> <p>pH 4-6 (1)</p> <p>OR</p> <p>Test : add ethanol with conc H_2SO_4 (and warm) (1)</p> <p>Result: gives pleasant/fruity smell of ester (1)</p> <p>OR</p> <p>Test: add magnesium (1)</p> <p>Result: fizzing/bubbles etc (of hydrogen) (1)</p> <p>ALLOW gas given off that burns with a squeaky pop</p>	<p>Add sodium</p> <p>colourless gas evolved</p>	
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Question Number		Reject	Mark
22(b)(i)	<p>Explanation of precedence/priority in terms of atomic numbers/masses of the attached groups</p> <p>OR</p> <p>Highest-precedent/priority groups on each carbon are on opposite sides of the molecule (1)</p> <p><i>E</i>-/entgegen (1)</p> <p>Mark independently</p>	Both CH ₃ /methyl groups on the same side so Z (0/2)	2

Question Number	Acceptable Answers	Reject	Mark
22(b)(ii)	<p>45 COOH⁺ /CO₂H⁺ (1)</p> <p>55 C₄H₇⁺</p> <p>OR</p> <p>C₃OH₃⁺ (1)</p> <p>ALLOW Structural/displayed formulae of ions</p> <p>Absence of + charge (1 max)</p>		2

Question Number	Acceptable Answers	Reject	Mark
22(b)(iii)	<p>If they say yes (0)</p> <p>(No) (Cleavage of the C—COOH bond in) both compounds gives fragment(s) of the same mass OR Both give the same peak(s)/fragment(s)</p> <p>Both give CO₂H⁺/ C₄H₇⁺ fragments</p> <p>The mark can be scored by referring to just one of the fragments/peaks/masses.</p>	'No' on its own	1

Question Number	Acceptable Answers	Reject	Mark
*22(c)(i) QWC	<p>C is CH₃CHO (alone) (2)</p> <p>D is CH₃COCOOH (alone) (2)</p> <p>so tiglic acid must be B (1)</p> <p>tiglic acid mark can only be awarded if correct structures of either C or D are given.</p> <p>Any one of the following</p> <p>C must be an aldehyde (1)</p> <p>D is a ketone (1)</p> <p>Mention that CH₃CO present in either/both compounds (because of formation of iodoform) (1)</p> <p>If one or both of the structures are incorrect any of the last 3 marks can be awarded max 5</p> <p>If C and D are fully correct, but the wrong way round max 5</p>	CH ₃ COH 1 max	6

Question Number	Acceptable Answers	Reject	Mark
22(c)(ii)	<p>Doesn't distinguish <i>E</i>- isomer from <i>Z</i>- isomer/geometric isomers (so no)</p> <p>OR</p> <p>Doesn't distinguish which sides of C=C functional groups are on</p>	Just isomers/ stereoisomers/ enantiomers	1

Question Number	Acceptable Answers	Reject	Mark
22(d)(i)	<p>CH₃CHO (1)</p> <p>ACCEPT displayed or skeletal</p> <p>Step 1</p> <p>(heat)using acidified potassium dichromate/or H⁺/Cr₂O₇²⁻ (1)</p> <p>distil (product as formed) conditional on dichromate (1)</p> <p>Step 2</p> <p>HCN with KCN</p> <p>OR</p> <p>KCN with H⁺/acid</p> <p>OR</p> <p>KCN with (cold) NaOH(aq)/alkali (1)</p> <p>ALLOW HCN with NaOH/alkali</p> <p>For step 2 Ignore conditions e.g. any references to heat</p>	<p>CH₃COH</p> <p>Manganate VII/KMnO₄</p> <p>Reflux</p> <p>HCN alone</p>	4

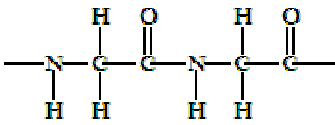
Question Number	Acceptable Answers	Reject	Mark
22(d)(ii)	<p>Nucleophilic addition</p> <p>Any recognisable spelling of 'philic' and addition, either order</p> <p>Both words needed</p>	<p>Nutrophilic addition</p> <p>Any other or additional words</p>	1

Question Number	Acceptable Answers	Reject	Mark
*22(d)(iii) QWC	<p>Ethanal is planar (at the reaction site)</p> <p>OR</p> <p>Ethanal is a planar molecule (1)</p> <p>Attack (from CN⁻ to give the cyanohydrin) is (equally likely) from either side/above or below/from both sides (of the molecule) (so a racemic mixture is formed) (1)</p> <p>Mark independently</p>	<p>Intermediate is planar</p> <p>Square planar</p> <p>Can attack carbocation from either side/any reference to SN1/SN2</p>	2

Question Number	Acceptable Answers	Reject	Mark
22(d)(iv)	<p>Receptors for the compound in the body are often stereospecific so only one stereoisomer is pharmacologically active</p> <p>OR</p> <p>Body recognises one (stereo)isomer</p> <p>ALLOW</p> <p>Only one (stereo)isomer is active</p> <p>OR</p> <p>One/the other isomer may be toxic/dangerous/harmful</p> <p>OR</p> <p>One isomer destroys body cells</p> <p>OR</p> <p>(Different) isomers have different biological/pharmacological/biochemical properties</p>		1

Question Number	Acceptable Answers	Reject	Mark
23(a)(i)	<p>Formula showing -NH_3^+ and -COO^- /-CO_2^-</p> <p>Charges can be anywhere on functional group</p> <p>Rest of the molecule must be correct</p> <p>ALLOW displayed/part displayed formula</p>		1

Question Number	Acceptable Answers	Reject	Mark
23(a)(ii)	<p>Any two from</p> <p>High energy needed (to overcome) (1)</p> <p>strong ionic/electrostatic forces OR strong forces between oppositely charged ions/between positive and negative (1)</p> <p>between different (zwitter)ions</p> <p>OR</p> <p>between -NH_3^+ and -COO^-</p> <p>OR</p> <p>between one molecule and another</p> <p>OR</p> <p>Chains of zwitterions/molecules (1)</p>	<p>any reference to intermolecular forces eg (strongly) polar/bond polarity</p> <p>if they state the ionic bond is within the same molecule</p>	2

Question Number	Acceptable Answers	Reject	Mark
23(a)(iii)	<div style="text-align: center;">  </div> <p>Correct peptide link (1)</p> <p>Minimum two residues and extension to the rest of the molecule (1)</p> <p>ALLOW -NHCH₂CONHCH₂CO- (2)</p> <p>Drawn the other way round, i.e. starting with the carbonyl group</p> <p>Brackets around outside with 'n' ie (.....)_n</p> <p>Second mark depends on first</p>		2

Question Number	Acceptable Answer	Reject	Mark
*23(b) QWC	<p>Key Points</p> <p>KP1 Spot (of hydrolysate) on paper/tlc/thin layer chromatogram (1)</p> <p>KP2 Marker spots of known amino-acids/measure R_f (1)</p> <p>KP3 Run in (suitable) solvent/discussion of comparative solubilities in phases (1)</p> <p>KP4 (Spray with) ninhydrin (and heat) [Stand alone mark] (1)</p> <p>KP 5 Marker spots and the unknown spots correspond ALLOW Compare R_f values of marker spots with hydrolysate spots (1)</p> <p>OR</p> <p>If 2-d chromatography used (2 different solvents run in two directions at right angles):</p> <p>KP1 Spot (of hydrolysate) on paper/tlc/thin layer chromatogram (1)</p> <p>KP2 Run in (suitable) solvent in one direction (1)</p> <p>KP3 Develop in suitable/different solvent at right angles OR discussion of comparative solubilities in phases (1)</p> <p>KP4 Spray with ninhydrin (and heat) (1)</p> <p>KP5 Compare hydrolysate spots with same experiment for known amino acids (1)</p> <p>OR</p>	<p>Spot one amino acid/protein</p> <p>Water alone as solvent</p> <p>Spot one amino acid</p>	5

	if column/GLC/GC used		
	KP1 Put amino acid mixture (Hydrolysate) into column (1)	Spot one amino acid	
	KP2 Separately known amino-acids into column (1)		
	KP3 Detect amino acids in effluent with Ninhydrin/mass spectrometry (1)		
	KP4 Measure retention times/discussion of comparative solubilities in phases (1)		
	KP 5 Compare retention times (1)		

TOTAL FOR SECTION B = 50 MARKS

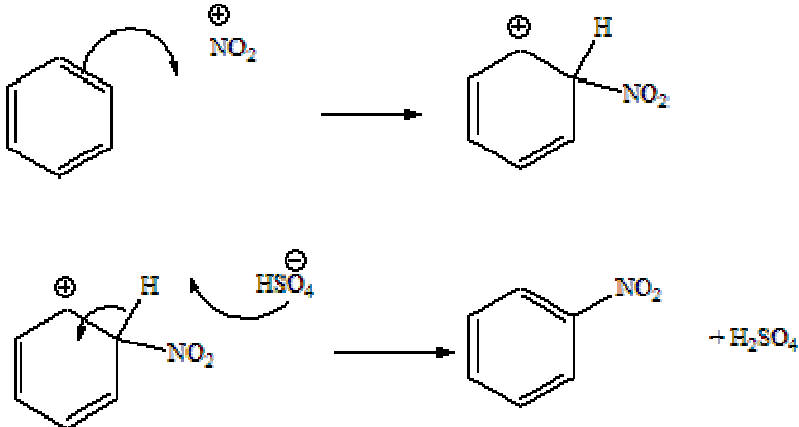
Section C

Question Number	Acceptable Answers	Reject	Mark
24(a)(i)	Not knowing the structure of the molecule (means that the reactions/reagents/reactants needed to make it are also unknown) ALLOW Structure not known		1

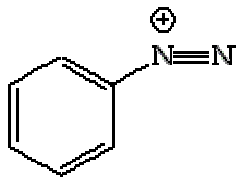
Question Number	Acceptable Answers	Reject	Mark
24(a)(ii)	Credit any reasonable arguments for example: First mark No longer any demand for madder/indigo OR Cheaper alternatives available (1) Second mark So the growing industries collapsed OR no market for crops OR farmers had to grow alternative crops OR decreased employment OR economic damage OR decreased GDP OR Loss of export (1)		2

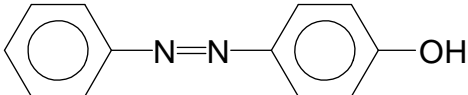
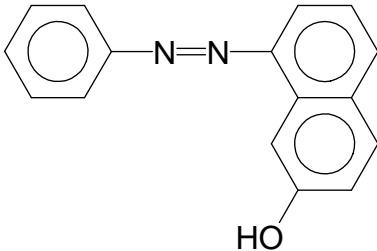
Question Number	Acceptable Answers	Reject	Mark
24(b)(i)	<p>First mark Double bonds expected to react with bromine water turning it colourless</p> <p>OR</p> <p>Bromine water remained yellow/orange/red/brown (1)</p> <p>Second mark So benzene does not contain double bonds</p> <p>OR</p> <p>Double bonds not normal/not simply double bonds/any indication that double bonds are different</p> <p>OR</p> <p>His representation incorrect (1)</p>		2

Question Number	Acceptable Answers	Reject	Mark
24(b)(ii)	<p>The p/pi-/π/6 electrons (of carbon)</p> <p>OR</p> <p>π system (1)</p> <p>Electrons are delocalised around the ring (1)</p> <p>Which gives the molecule greater stability/need more energy to break the bonds in benzene (and hence a less exothermic hydrogenation enthalpy)</p> <p>Allow it is more stable (1)</p>	Harder to break/disrupt [alone]	3

Question Number	Acceptable Answers	Reject	Mark
24(c)	<p>$2\text{H}_2\text{SO}_4 + \text{HNO}_3 \rightarrow \text{NO}_2^+ + \text{H}_3\text{O}^+ + 2\text{HSO}_4^-$ (1)</p> <p>OR</p> <p>$\text{H}_2\text{SO}_4 + \text{HNO}_3 \rightarrow \text{NO}_2^+ + \text{H}_2\text{O} + \text{HSO}_4^-$</p> <p>OR</p> <p>$\text{H}_2\text{SO}_4 + \text{HNO}_3 \rightarrow \text{H}_2\text{NO}_3^+ + \text{HSO}_4^-$ and $\text{H}_2\text{NO}_3^+ \rightarrow \text{NO}_2^+ + \text{H}_2\text{O}$</p> <p>Charges are needed for first mark</p>  <p>Attack on nitronium ion arrow must start on or in the benzene (1)</p> <p>Wheland intermediate Can be a part, but not complete circle, in correct place inside ring BUT part circle must cover minimum of 3 carbon atoms AND must not include where nitro group is attached and must positive charge somewhere (1)</p> <p>Either but only one of first two marks can be lost if bond is clearly to oxygen</p> <p>Arrow from H bond into the ring to produce either H^+ or H_2SO_4 and return to aromaticity (1)</p>		4

Question Number	Acceptable Answers	Reject	Mark
24(d)(i)	<p>< 0° C/temperature too low: reaction too slow/insufficient energy to overcome activation energy (1)</p> <p>> 10° C/temperature too high: diazonium ion decomposes/produces phenol (1)</p>	Will not take place	2

Question Number	Acceptable Answers	Reject	Mark
24(d)(ii)	 <p>Positive charge can be on either N</p> <p>Cl⁻ may be given as well</p> <p>ALLOW circle in benzene ring and hydrogens/carbons displayed</p> <p>OR</p> <p>---N=N⁺ Is acceptable providing charge is on the end N</p>	Positive charge on wrong N	1

Question Number	Acceptable Answers	Reject	Mark
24 (d)(iii)	<p>Adds phenol in sodium hydroxide/OH^-/alkali</p> <p>ALLOW 2-naphthol in sodium hydroxide/OH^- /alkali (1)</p> <p>Correct structure for the $-\text{N}=\text{N}-$ bond between 2 benzene rings (1)</p> <p>Remainder of molecule (1)</p> <p>which is either:</p>  <p>ALLOW anionic form of $-\text{OH}$</p> <p>OR if 2-naphthol is used it is:</p> 	<p>Ignore position of $-\text{OH}$ group on the ring</p>	3

Question Number	Acceptable Answers	Reject	Mark
24 (e)	<p>First mark</p> <p>—SO_3^- are solvated / hydrated</p> <p>Can be drawn with polar H of water</p> <p>OR</p> <p>Negative ion bonds with/attracted to water (1)</p> <p>Second mark</p> <p>Nitrogen/oxygen atoms hydrogen-bonded (to water)</p> <p>Can be drawn (1)</p>	<p>Just sodium ions attracted to water</p>	2

TOTAL FOR SECTION C = 20 MARKS

TOTAL FOR PAPER = 90 MARKS

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