Cambridge Assessment International Education

Cambridge International AS & A Level

CHEMISTRY **9701/42**

Paper 4 A Level Structured Questions **May/June 2023**

MARK SCHEME

Maximum Mark: 100

Published

This mark scheme is published as an aid to teachers and candidates, to indicate the requirements of the examination. It shows the basis on which Examiners were instructed to award marks. It does not indicate the details of the discussions that took place at an Examiners' meeting before marking began, which would have considered the acceptability of alternative answers.

Mark schemes should be read in conjunction with the question paper and the Principal Examiner Report for Teachers.

Cambridge International will not enter into discussions about these mark schemes.

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Generic Marking Principles

These general marking principles must be applied by all examiners when marking candidate answers. They should be applied alongside the specific content of the mark scheme or generic level descriptors for a question. Each question paper and mark scheme will also comply with these marking principles.

GENERIC MARKING PRINCIPLE 1:

Marks must be awarded in line with:

- the specific content of the mark scheme or the generic level descriptors for the question
- the specific skills defined in the mark scheme or in the generic level descriptors for the question
- the standard of response required by a candidate as exemplified by the standardisation scripts.

GENERIC MARKING PRINCIPLE 2:

Marks awarded are always **whole marks** (not half marks, or other fractions).

GENERIC MARKING PRINCIPLE 3:

Marks must be awarded **positively**:

- marks are awarded for correct/valid answers, as defined in the mark scheme. However, credit is given for valid answers which go beyond the scope of the syllabus and mark scheme, referring to your Team Leader as appropriate
- marks are awarded when candidates clearly demonstrate what they know and can do
- marks are not deducted for errors
- marks are not deducted for omissions
- answers should only be judged on the quality of spelling, punctuation and grammar when these features are specifically assessed by the question as indicated by the mark scheme. The meaning, however, should be unambiguous.

GENERIC MARKING PRINCIPLE 4:

Rules must be applied consistently, e.g. in situations where candidates have not followed instructions or in the application of generic level descriptors.

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GENERIC MARKING PRINCIPLE 5: Marks should be awarded using the full range of marks defined in the mark scheme for the question (however; the use of the full mark range may be limited according to the quality of the candidate responses seen).
GENERIC MARKING PRINCIPLE 6: Marks awarded are based solely on the requirements as defined in the mark scheme. Marks should not be awarded with grade thresholds or grade descriptors in mind.

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Science-Specific Marking Principles

1	Examiners should consider the context and scientific use of any keywords when awarding marks. Although keywords may be present, marks should not be awarded if the keywords are used incorrectly.
2	The examiner should not choose between contradictory statements given in the same question part, and credit should not be awarded for any correct statement that is contradicted within the same question part. Wrong science that is irrelevant to the question should be ignored.
3	Although spellings do not have to be correct, spellings of syllabus terms must allow for clear and unambiguous separation from other syllabus terms with which they may be confused (e.g. ethane / ethene, glucagon / glycogen, refraction / reflection).
4	The error carried forward (ecf) principle should be applied, where appropriate. If an incorrect answer is subsequently used in a scientifically correct way, the candidate should be awarded these subsequent marking points. Further guidance will be included in the mark scheme where necessary and any exceptions to this general principle will be noted.
5	<u>'List rule' guidance</u> For questions that require ***n*** responses (e.g. State **two** reasons …): • The response should be read as continuous prose, even when numbered answer spaces are provided. • Any response marked *ignore* in the mark scheme should not count towards ***n***. • Incorrect responses should not be awarded credit but will still count towards ***n***. • Read the entire response to check for any responses that contradict those that would otherwise be credited. Credit should **not** be awarded for any responses that are contradicted within the rest of the response. Where two responses contradict one another, this should be treated as a single incorrect response. • Non-contradictory responses after the first ***n*** responses may be ignored even if they include incorrect science.

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6	<u>Calculation specific guidance</u> Correct answers to calculations should be given full credit even if there is no working or incorrect working, **unless** the question states ‘show your working’. For questions in which the number of significant figures required is not stated, credit should be awarded for correct answers when rounded by the examiner to the number of significant figures given in the mark scheme. This may not apply to measured values. For answers given in standard form (e.g. $a \times 10^n$) in which the convention of restricting the value of the coefficient (a) to a value between 1 and 10 is not followed, credit may still be awarded if the answer can be converted to the answer given in the mark scheme. Unless a separate mark is given for a unit, a missing or incorrect unit will normally mean that the final calculation mark is not awarded. Exceptions to this general principle will be noted in the mark scheme.
7	<u>Guidance for chemical equations</u> Multiples / fractions of coefficients used in chemical equations are acceptable unless stated otherwise in the mark scheme. State symbols given in an equation should be ignored unless asked for in the question or stated otherwise in the mark scheme.

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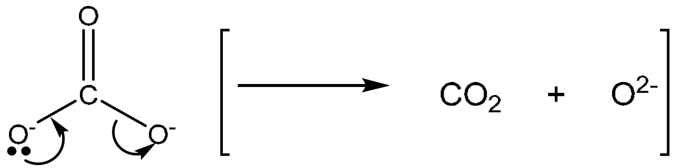
Question	Answer	Marks
1(a)(i)	 ARROW 1 starts from O^- to the C–O bond **AND** ARROW 2 starts at the C-O bond to other O^- ion	**1**
1(a)(ii)	**M1** increases (down the group) **M2** (cat)ionic radius / ion size **increases** (down the group) **OR** charge density of M^{2+} **decreases** **M3 less** polarisation / distortion of anion / carbonate ion / $CO_3^{(2)-}$	**3**
1(b)(i)	**M1** energy released when one mole of a ionic solid / compound is formed **M2** from gas (phase) ion(s) / gaseous ion(s) (under standard conditions)	**2**
1(b)(ii)	• (ΔH_{decomp} / it) becomes **more positive/less negative** (down the group) • size /(ionic) radii of oxide ion is **smaller** (than carbonate ion) **ORA** • so ΔH_{latt} of oxides becomes **ORA** less exothermic **faster OR** less negative **faster** **OR** changes **more OR** changes **faster** Any two [1], all three [2]	**2**
1(c)(i)	$2MnO_4^- + 6H^+ + 5SO_3^{2-} \rightarrow 2Mn^{2+} + 3H_2O + 5SO_4^{2-}$	**1**

Question	Answer	Marks
1(c)(ii)	**M1 M2** any two bullets [1] or all four [2] • moles MnO_4^- = 0.025 × 22.40 / 1000 = 5.6 × 10^{-4} • moles SO_3^{2-} = 5.6 × 10^{-4} × 5 / 2 = 1.4 × 10^{-3} (in 25 cm^3) ecf from **(c)(i)** and bullet 1 • moles SO_3^{2-} = 1.4 × 10^{-2} (in 250 cm^3) ecf bullet 2 • mass K_2SO_3 = 1.4 × 10^{-2} × 158.3 = 2.2162 g ecf bullet 3 **OR** moles K_2SO_3 (if 100% pure) = 3.40 ÷ 158.3 = 0.02148 **M3** % purity = 100 × 2.2162 / 3.40 = 65.2 / 65.3 % ecf min 2sf **OR** % purity = 100 × 0.014 / 0.02148 = 65.2 / 65.3 %	**3**
1(d)	S(α) tetrahedral	**1**

Question	Answer	Marks
2(a)	*Any two from:* • they have variable / multiple oxidation states OWTTE • they behave as catalysts • they form complex ions / complexes • they form coloured compounds/ions	**1**
2(b)(i)	(is a molecule or ion formed by a central) metal atom / metal ion bonded / surrounded by (one or more) ligands	**1**

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<table>
<tr><th>Question</th><th>Answer</th><th>Marks</th></tr>
<tr><td>2(b)(ii)</td><td>
<table>
<tr><td>reagent added</td><td>formula of species formed</td><td>colour / state of species formed</td><td>type of reaction</td></tr>
<tr><td>an excess of $NH_3(aq)$</td><td>$[Co(NH_3)_6]^{2+}$</td><td>brown solution
ALLOW yellow-brown solution</td><td>ligand exchange</td></tr>
<tr><td>an excess of concentrated HCl</td><td>$[CoCl_4]^{2-}$</td><td>blue solution</td><td>ligand exchange</td></tr>
<tr><td>NaOH(aq)</td><td>$Co(OH)_2$
OR
$Co(OH)_2(H_2O)_4$</td><td>blue ppt.
ALLOW pink ppt</td><td>precipitation</td></tr>
</table>

formula and colour / state: any two [1], any four [2], all six [3]
type of reaction: all three correct [1]</td><td>4</td></tr>
<tr><td>2(c)(i)</td><td>M1 (a species) that donates / uses two lone pairs
M2 to form a two dative / coordinate bond to a metal atom / metal ion</td><td>2</td></tr>
</table>

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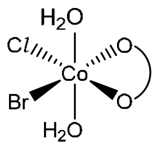
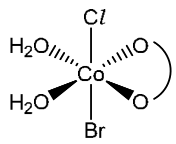
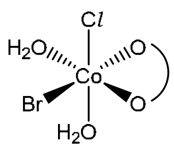
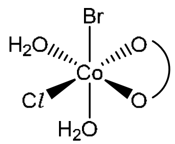
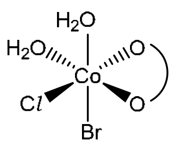
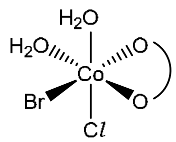
Question	Answer	Marks
2(c)(ii)	*Any four from:* isomer 1  isomer 2  isomer 3  isomer 4  isomer 5  isomer 6  Any two [1], any three [2], all four [3]	**3**
2(c)(iii)	oxidation state of cobalt (+)3 **AND** type of stereoisomerism cis-trans **OR** geometric(al) **OR** optical	**1**

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Question	Answer	Marks
3(a)	<table><tr><td>energy change</td><td>always positive</td><td>always negative</td><td>can be either negative or positive</td></tr><tr><td>bond energy</td><td>✓</td><td></td><td></td></tr><tr><td>enthalpy change of atomisation</td><td>✓</td><td></td><td></td></tr><tr><td>enthalpy change of formation</td><td></td><td></td><td>✓</td></tr></table>	1
3(b)	**M1** (enthalpy change) when one mole of gaseous atoms is produced **IGNORE** energy released **M2** from its element(s) in its standard state / standard conditions / 298 K **AND** 1 atm	2
3(c)	**M1** use of correct six numbers only –31 / 285 / 731 / –141 / 798 / 496 **M2** 2 × used correctly with Ag (2 × 285 (570) and 2 × 731 (1462)) **AND** 0.5 with O=O (496 (248)) **M3** correct signs and evaluation –31 = (2 × 285) + (2 × 731) + (–141) + (798) + x + (0.5 × 496) x = –2968 kJ mol^{-1}	3
3(d)	• Ag_2Se Ag_2S Ag_2O **OWTTE** *least exothermic* *most exothermic* • charge density of anion decreases down the group **ORA** / radius/size of anion increases down the group / Se^{2-} largest radius / O^{2-} smallest radius / O has smallest ionic radius • less attraction between the ions / ionic bond gets weaker (with Ag_2Se) **ORA** Any two [1], all three [2]	2
3(e)(i)	(K_{sp} =) $[Ag^+]^2[SO_3^{2-}]$ [1]	1

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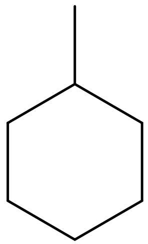
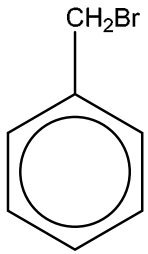
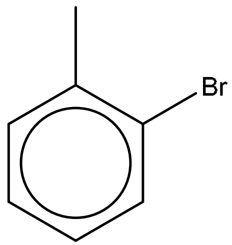
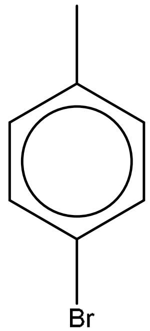
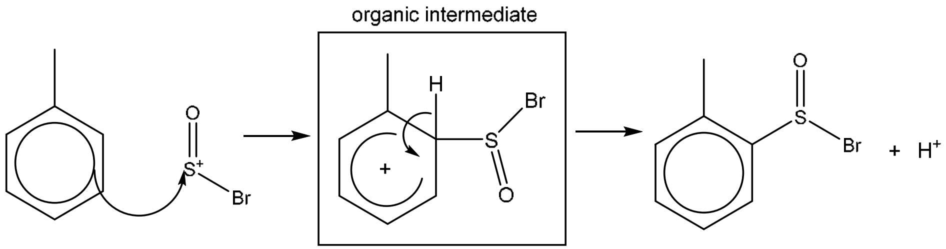
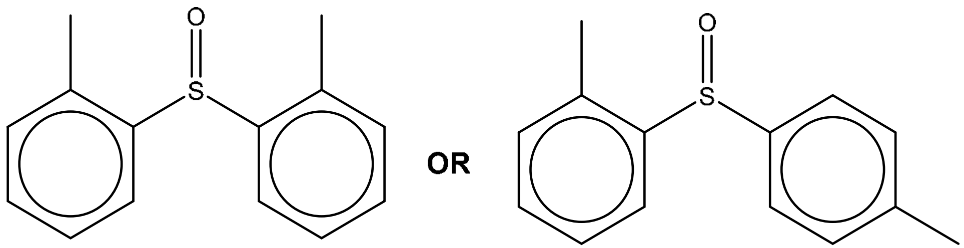
Question	Answer	Marks
3(e)(ii)	$x = \sqrt[3]{1.5 \times 10^{-14} / 4} = 1.55 \times 10^{-5}$ (mol dm^{-3}) $[Ag^+] = 1.55 \times 10^{-5} \times 2 = 3.11 \times 10^{-5}$ (mol dm^{-3}) min 2sf ecf (e)(i)	**1**
3(f)	• feasibility / it increases as temperature increases **ORA** • ΔS is positive / ΔS is >0 / entropy **change** is positive (and ΔH is positive) **OR** $-T\Delta S$ becomes more negative / $T\Delta S$ becomes more positive • as ΔG becomes / is negative / $\Delta G < 0$ Any two [1], all three [2]	**2**

Question	Answer	Marks
4(a)(i)	the sum/total of the power / exponent to which a concentration of a reactant is raised in the rate equation / law	**1**
4(a)(ii)	**M1** (expt 1 and 2) when $[Fe^{3+}] \times 3$, rate $\times$ 3 so first order w.r.t. Fe^{3+} **M2** (expt 1 and 3) when $[Fe^{3+}] \times 2$, $[I^-] \times 2$, rate $\times$ 8 so second order w.r.t. I^- **OR** (expt 2 and 3) when $[Fe^{3+}] \div 1.5$, $[I^-] \times 2$, rate $\times$ 2.7 so second order w.r.t. I^-	**2**
4(a)(iii)	(rate =) $k[Fe^{3+}][I^-]^2$ [1] ecf (a)(ii)	**1**
4(a)(iv)	k = rate / $[Fe^{3+}][I^-]^2$ = $(2.64 \times 10^{-4}) / (0.04 \times 0.02^2)$ k = 16.5 min 2sf ecf units = $mol^{-2}\,dm^6\,s^{-1}$ ecf	**2**
4(a)(v)	(k and rate of reaction) both increase	**1**

Question	Answer	Marks
4(b)(i)	step 1 as this has one mole of H_2O_2 and one mole of I^- **OR** step 1 as correct stoichiometry / coefficients of 1 H_2O_2 and 1 I^- **OR** step 1 as number of moles of each reactant are consistent with rate equation / their orders	1
4(b)(ii)	step 1 I oxid no –1 → +1 **AND** O oxid no –1 → –2 **OR** step 3 I oxid no –1 → 0 **AND** I oxid no +1 → 0	1
4(b)(iii)	intermediate **AND** formed (in step 2) and used up (in step 3) **ALLOW** oxidising agent (in step 3) **AND** oxidises I^- (to I_2)	1

Question	Answer	Marks
5(a)(i)	 reaction 1 **M1**  reaction 2 **M2**   reaction 3 **M3 BOTH**	3
5(a)(ii)	**M1** reaction 1: hydrogenation / reduction **M2** mechanism 2: (free) radical substitution	2
5(b)	the substitution product is stabilised by delocalization of π-electrons / by π-electrons in the ring **OR** the addition product is **not** stabilised by delocalisation (of π-)electrons **ALLOW** addition product will remove π-electron delocalised system	1

Question	Answer	Marks
5(c)(i)	 **M1** curly arrow from inside the hexagon to S atom **M2** structure of the intermediate **M3** curly arrow from C-H bond into the ring **AND** formation/loss of H^+	**3**
5(c)(ii)		**1**
5(d)(i)	$CH_3COOH + SOBr_2 \rightarrow CH_3COBr + HBr + SO_2$	**1**

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Question	Answer	Marks
5(d)(ii)	**M1** acyl bromides (easiest) > acyl chlorides > alkyl chlorides (hardest) **M2 M3** *Any two from:* *Acyl bromides easiest* • in acyl bromides C–Br is much weaker **ORA AND** due to less orbital overlap / Br having a larger atomic radii *Acyl halides easier than alkyl chlorides* • carbon in C–C*l* / C–Br / C–X bond is more δ+/electron deficient **OR** C–C*l* / C–Br bond is weaker (than C-Cl in alkyl chlorides) **AND** attached to an oxygen atom / two electronegative atoms / electron withdrawing C=O group **ORA** *alkyl chlorides hardest* • in alkyl chlorides C–C*l* bond strengthened **AND** by positive inductive effect / electron donating effect of alkyl / R group	**3**

Question	Answer	Marks
6(a)(i)	5 / five	**1**
6(a)(ii)	**M1** benefit: higher biological efficiency / activity (of the drug) **OR** less side effects **OR** smaller dose required (as drug more potent) **M2** disadvantage: the need to separate (a racemic mixture into a single stereoisomer) **OR low**er **yield** (of biologically active molecule/product) **OR** need a chiral catalyst / enzyme (in the synthesis so expensive)	**2**
6(b)(i)	carboxylic acid/carboxyl, ester, amide, amine Any two [1], all four [2]	**2**

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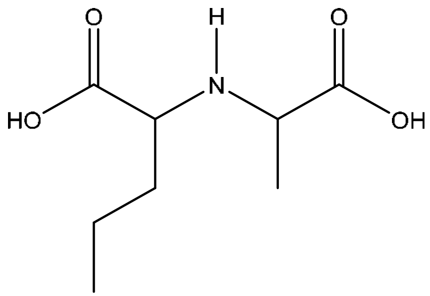
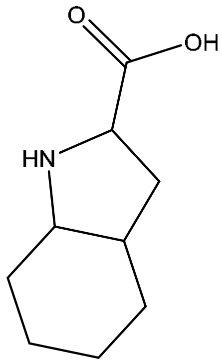
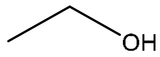
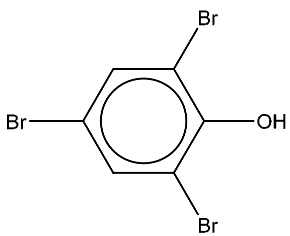
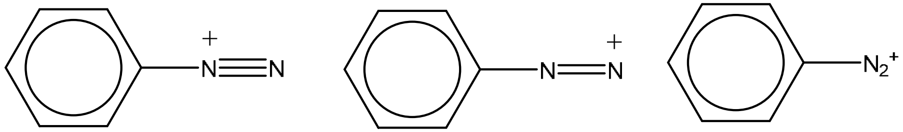
Question	Answer	Marks
6(b)(ii)	   3 × [1] for each structure	**3**

Question	Answer	Marks
7(a)	**M1** p-orbital / lone pair from **O** atom is overlaps / delocalised into the ring **M2** greater π electron density around the ring **OR** makes the ring more electron rich / positions 2,4,6 more electron rich **M3** polarises electrophiles **more** easily	**3**
7(b)	iodobenzene **AND** as Br is more electronegative (than I / $I^{\delta+}$/I^+ in the electrophile)	**1**
7(c)(i)	C_6H_6O / C_6H_5OH + Na → $C_6H_5O^-Na^+$ + ½H_2	**1**
7(c)(ii)		**1**

Question	Answer	Marks
7(c)(iii)	**M1** reaction 1: aqueous HNO_3 / dilute HNO_3 **M2** reaction 2: alkaline/ NaOH **AND** $C_6H_5N_2^+$ (Cl^-)  **OR** alkaline / NaOH **AND** benzene / phenyl diazonium ion / salt	**2**

Question	Answer	Marks
8(a)	• chlorobenzene is **less reactive** than chloroethane **OWTTE** • p-orbital / lone pair **on C*l*** will overlap / delocalise into the ring • due to partial double C-C*l* bond **OWTTE** **OR** C-C*l* bond strengthened (more) Any two [1], all three [2]	**2**
8(b)(i)	ethyl 3-chloropropanoate	**1**

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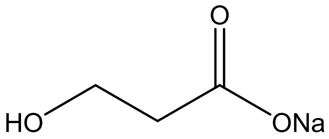
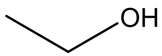
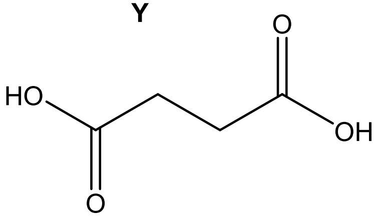
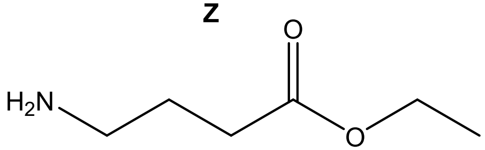
Question	Answer	Marks
8(b)(ii)	**W**  **X**  **Y**  **Z**  4 × [1] for each structure	**4**
8(b)(iii)	**M1** step 1 NaCN / KCN in ethanol (heat) **M2** step 2 H_2 + Ni / H_2 + Pt **ALLOW** $LiAlH_4$	**2**
8(c)(i)	(because solvent / D / $CDCl_3$) doesn't give a signal / peak / absorption **ORA**	**1**

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Question	Answer	Marks
8(c)(ii)	<table><tr><td>chemical shift δ / ppm</td><td>environment of proton</td><td>splitting pattern</td><td>number of ^{1}H atoms responsible for the peak</td></tr><tr><td>1.2</td><td>alkyl / alkane / (R-)$CH_{(3)}$</td><td>triplet</td><td>3</td></tr><tr><td>2.8</td><td>alkyl next to C=O / $CH_{(2)}$C=O</td><td>triplet</td><td>2</td></tr><tr><td>3.7</td><td>alkyl next to electronegative atom / $CH_{(2)}$-Cl</td><td>triplet</td><td>2</td></tr><tr><td>3.9</td><td>alkyl next to electronegative atom / $CH_{(2)}$-O</td><td>quartet / quadruplet</td><td>2</td></tr></table> Any three [1], any six [2], any nine [3], all twelve [4]	4
8(c)(iii)	(δ = 3.9) three H on neighbouring / adjacent C / it's next to a CH_3	1

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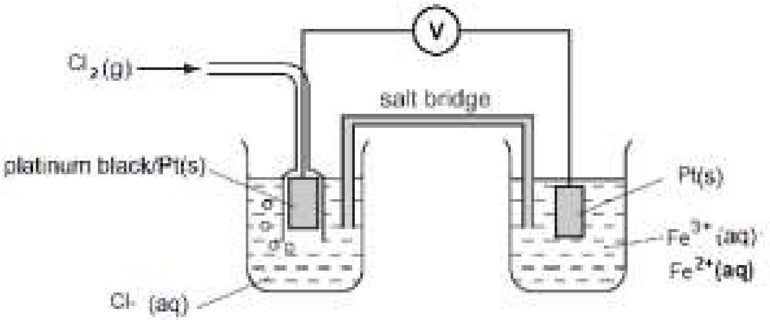
Question	Answer	Marks
9(a)	potential difference / voltage between the two half-cells / two electrodes (in a cell) under standard conditions	**1**
9(b)	 salt bridge / voltmeter / complete circuit [wires/salt bridge in/touching both solutions] Cl_2 / Cl^- / good delivery system (no arrow required) Pt / Pt / Fe^{2+} and Fe^{3+} Any three [1], any six [2], all nine [3]	**3**
9(c)	**M1** ($\Delta G^\ominus$) = – nF$E_{cell}^\ominus$ **OR** –2 × 96500 × 0.59 **M2** $\Delta G^\ominus$ = –2 × 96500 × 0.59 = –113870 J mol^{-1} $\Delta G^\ominus$ = –114 kJ mol^{-1} min 3sf ecf	**2**
9(d)(i)	E = 0.77 + (0.059 / 1) log (1/0.15) use of z = 1 E = 0.82 V	**1**
9(d)(ii)	E_{cell} = 0.59 + 0.77 – (answer to (d)(i)) = 0.54 V ecf	**1**