Cambridge Assessment International Education
Cambridge International Advanced Subsidiary and Advanced Level

CHEMISTRY **9701/42**

Paper 4 A Level Structured Questions **February/March 2023**

MARK SCHEME

Maximum Mark : 100

March 2023

9701/42 [redacted] **FD**

Cambridge Assessment International Education – 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:

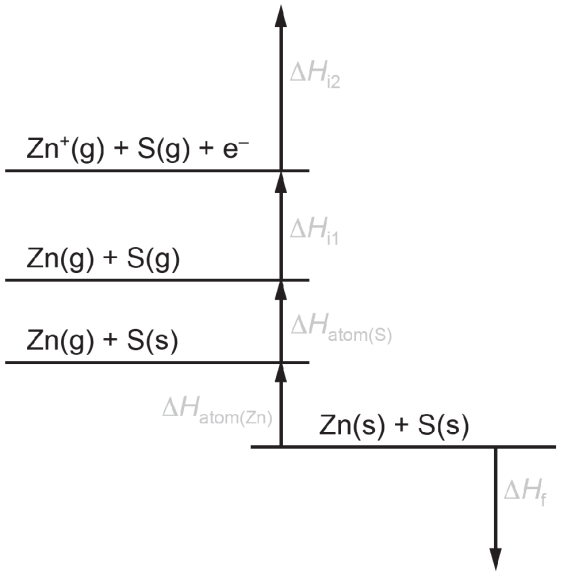
Rules must be applied consistently e.g. in situations where candidates have not followed instructions or in the application of generic level descriptors.

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).

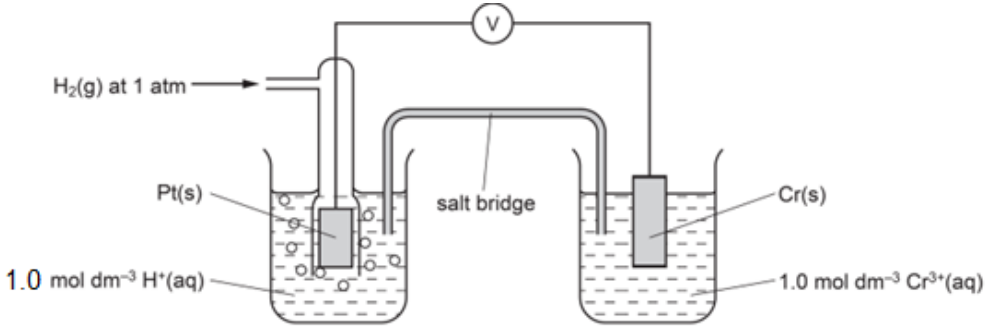
GENERIC MARKING PRINCIPLE 6:

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.

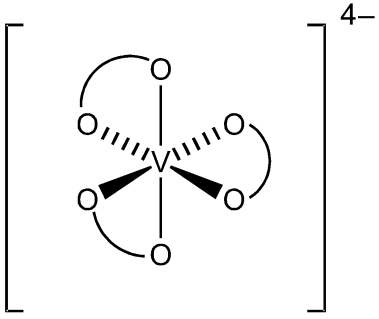
Question	Answer	Marks		Guidance
1 a i	[Ar] 1↓ 1↓ 1↓ 1↓ 1↓ ☐ ☐ ☐ ☐	1	1	
1 a ii		3	3	One ● for each species + state symbol ●●✔●●✔●●✔ **ALLOW** 1/8 S_8(s) for S(s)
1 a iii	• becomes less negative down group/S to Te • outer shell gets farther from nucleus/at higher energy level/more shielding of outer shells	2	2	●✔✔

Question	Answer	Marks		Guidance
	• less attraction for nucleus			
1 a iv	O^{2-} (has same charge but) **smaller** radius than S^{2-}	1	2	**ALLOW** O^{2-} has a higher charge density than S^{2-}
	stronger ionic bond /greater attraction between Zn^{2+} and O^{2-}	1		
1 b i	ΔS negative **AND** more moles of gaseous reactants than gaseous products	1	1	
1 b ii	ΔS = 50.8 + 197.7 – 43.7 – 5.7 = (+)**199.1** (J K^{-1} mol^{-1})	1	1	**TBD ALLOW ?** ΔS =(+)199
1 b iii	$\Delta G = \Delta H - T\Delta S$	1	2	
	= +733 – (800+273)×0.218 = (+)**499** (kJ mol^{-1}) min 3sf	1		calculator value 499.086 correct answer = 2 marks
1 c i	$Zn(NO_3)_2 \rightarrow ZnO + 2NO_2 + ½O_2$ **OR** $2Zn(NO_3)_2 \rightarrow 2ZnO + 4NO_2 + O_2$	1	1	
1 c ii	increases (in thermal stability down the group) **AND** (cat)ionic radius / ion size increases (down the group)	1	2	**ALLOW** increases **AND** charge density of cation decreases (down the group)
	less polarisation / less distortion of anion/ of nitrate ion/NO_3^- **OR** less weakening of N—O bond	1		
1 c iii	$Mg(NO_3)_2$ only	1	1	**ALLOW** Mg^{2+} / magnesium **IGNORE** $Be(NO_3)_2$ / Be^{2+} / beryllium

Question	Answer	Marks		Guidance
		16	**16**	

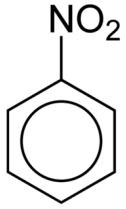
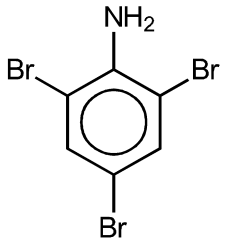
Question	Answer	Marks		Guidance
2 a	H_3PO_2	1	1	
2 b i	the electrode potential *E* would become **more positive** / **less negative** than $E^{\ominus}$ lower $[H_2PO_2^-]$ shifts equilibrium to the right hand side	1 1	2	**ALLOW** use of Nernst M1 equation M2 –1.53 V
2 b ii	+1.57 – 0.74 = (+)**0.83** (V)	1	1	
2 b iii	 • Pt(s) • Cr(s) • H^+(aq) • Cr^{3+}(aq) • H_2(g) • voltmeter • salt bridge • conditions of 1 atm **AND** 1 mol dm^{-3} • other liquid level and wire to electrode	3	3	••✔••✔••✔ state symbols not required
2 b iv	Pt electrode positive **AND** flow of electrons anticlockwise (to the SHE)	1	1	LINK to 2b(iii)

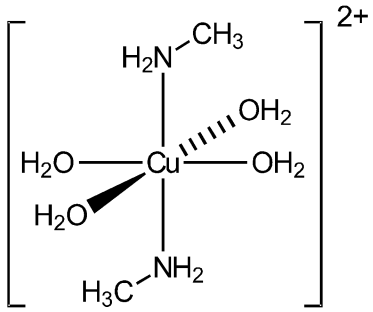
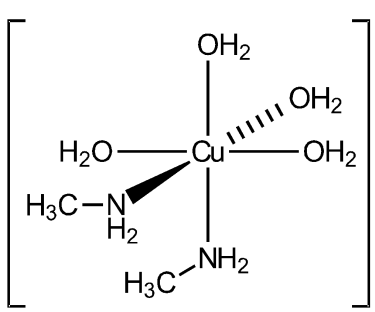
Question	Answer	Marks		Guidance
2 b v	$H_2PO_2^-$ + $3OH^-$ + Ni^{2+} → HPO_3^{2-} + $2H_2O$ + Ni	1	1	**any multiple**
2 c i	(6.4/24000) ÷ 60 **= 4.4 × 10^{-6}** (mol dm^3 s^{-1}) min 2sf	1	1	
2 c ii	$[H_2PO_2^-]$ doubles/ x2 from expts 1 to 2 volume of H_2 produced doubles/ x2 (∴ first order wrt $[H_2PO_2^-]$) $[H_2PO_2^-]$ trebles and $[OH^-]$ halves from expts 1 to 3 volume of H_2 produced falls to ¾ original (if first order wrt $[H_2PO_2^-]$ then must be second order wrt $[OH^-]$)	1 1	2	**ALLOW** M1 calculation M2 method for answering using experiments 2 & 3 **ALLOW ORA**
2 c iii	mol^{-2} dm^6 s^{-1}	1	1	
2 c iv	$t_{½}$ = 0.693 / 8.25 × 10^{-5} **= 8400** (s)	1	1	
2 c v	k_1 **increases** (with temperatures)	1	1	
2 d	• reactants **adsorb** to surface of catalyst • bonds (in reactant) weaken • (reaction occurs and the) **products** are desorbed • ✔ ✔	2	2	**IGNORE** lowers E_a etc / absorbed binds to the surface of the catalyst = adsorbed **ALLOW** "chemisorption" **TBD** **IGNORE** "bonds are broken" (happens in all reactions) deabsorbed or released / diffuse away = desorbed
		17	**17**	

Question	Answer	Marks		Guidance
3 a	a d-block element forms (one or more) **stable** ions/compounds/oxidation states with incomplete / partially filled (3)d-orbital(s) / d-shell / d-subshell	1 1	1	**three components** **ALLOW** "stable complex ions"
3 b i	• they behave as catalysts • they form complex ions • they form coloured compounds	1	1	**IGNORE** insoluble hydroxides Any two ●✔
3 b ii	the **d** and **s** sub-shells/orbitals are close/similar in **energy** **ALLOW electrons** in **d** and **s** sub-shells/orbitals available for **bonding**	1	1	**ALLOW** 'same in energy' for 'similar in energy' **IGNORE** they can lose electrons from s and d orbitals
3 c i	0.02500 × 0.0300 = 7.50×10^{-4} mol VO_2^+ ½(28.15 + 28.10)/1000 × 0.0400 = 1.13×10^{-3} mol $C_2O_4^{2-}$ Use of ratio of VO_2^+ : $C_2O_4^{2-}$ = **1:1.5**	1 1	2	both for M1 Many methods exist
3 c ii	 3D structure charge	 1 1	2	**ALLOW** other optical isomer

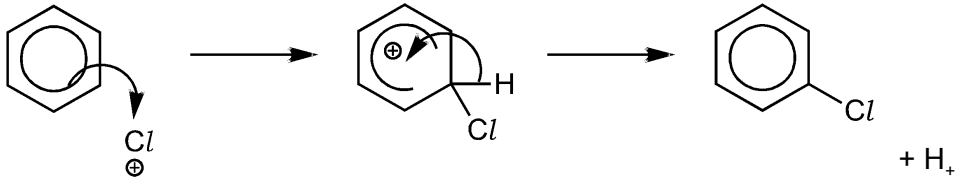
Question	Answer	Marks		Guidance
3 d i	VO_2^+ **AND** $E^{\ominus}$ of H_2O_2 is largest	1	1	**ALLOW** VO_2^+ **AND** E_{cell} = (+)0.77 V
3 d ii	(+)5/V	1	1	
		9	**9**	

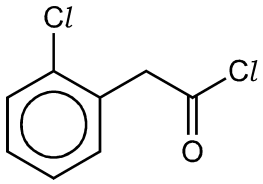
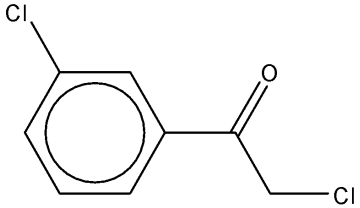
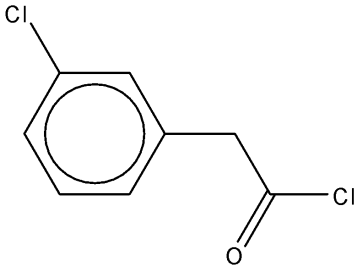
Question	Answer	Marks		Guidance
4 a i	$CH_3CONH_2 + 4[H] \rightarrow CH_3CH_2NH_2 + H_2O$	1	1	
4 a ii	nucleophilic substitution ethanol **AND** heat under pressure/heat in a sealed tube	1 1	2	
4 a iii	$(CH_3CH_2)_2NH$ **OR** $(CH_3CH_2)_3N$	1	1	diethylamine, triethylamine
4 b	(least) phenylamine < ammonia < ethylamine (most) **Phenylamine** lone pair/p-orbital from N delocalised/ overlaps with (π-)ring / benzene and decreases electron density on N **Ethylamine** alkyl/ ethyl group is electron donating group/ +I group and increases electron density on N (order of basicity) **ability of base** (linked to M1 **ALLOW** ecf) to **gain**/ **bond**/ **accept** a proton / **donate** its lone pair (to a proton)	1 1 1 1	4	Link to electron density needed once- **TBD** at **STM** **ECF** on absence of N for bullet 1 for bullet 3

Question	Answer	Marks		Guidance
4 c		1	3	
	concentrated/conc./c. HNO_3 and H_2SO_4 (and 25–60 °C)	1		**CON** aqueous
	(reduction with) Sn and concentrated HC*l* (heat)	1		**CON** Sn catalyst **IGNORE** aqueous
4 d i		1	1	
4 d ii	HNO_2 **OR** $NaNO_2$ and dilute acid	1	1	**IGNORE** any temperature
4 d iii	phenol	1	1	**TBD ALLOW** sodium phenoxide
4 d iv	NaOH/alkali	1	1	**Maybe link to 4d(iii)**
4 d v	dyestuffs	1	1	
4 e i	species that contains a / one lone pair of electrons	1	2	
	that forms a (single) dative covalent bond to a central metal atom / ion	1		

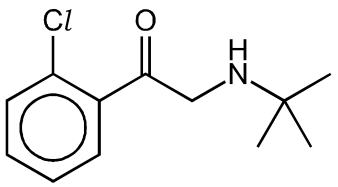
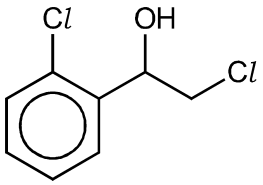
Question	Answer	Marks		Guidance
4 e ii	  correct 3D cis isomer correct 3D trans isomer	1 1	2	Any order CH_3NH_2 cis/trans
4 e iii	6	1	1	
4 f i	units = $mol^{-4}\ dm^{12}$	1	1	
4 f ii	$K_{stab} = \frac{\left[CdCl_4^{2-}(aq)\right]}{\left[Cd^{2+}(aq)\right]\left[Cl^{-}(aq)\right]^4}$	1	1	must use [ ] as outer most bracket all charges need to be inside [ ]
4 f iii	$[CdCl_4^{2-}] = K_{stab} \times 0.043 \times 0.072^4$ = **7.28×10^{-4}** ($mol\ dm^{-3}$) min 2sf	1	1	
4 f iv	CH_3NH_2 (is basic so) reacts with water to produce OH^-, which forms a complex with $Cd^{2+}(aq)$	1	1	**ALLOW** $CH_3NH_2 + H_2O \rightarrow CH_3NH_3^+ + OH^-$
4 f v	$Cd(OH)_4^{2-}$ = most stable **AND** $[Cd(H_2O)_6]^{2+}$ = least stable $Cd(OH)_4^{2-}$ has highest K_{stab} (and all K_{stab} values given > 1)	1 1	2	 **ORA**

Question	Answer	Marks		Guidance
		27	**27**	

Question	Answer	Marks		Guidance
5 a	any **three** points from: ● bond angle = 120° **and** shape is (hexagonal ring) planar / (trigonal) planar ● carbons are sp^2 hybridised ● contains delocalised electrons in the π bonds / system ● sp^2 orbitals between C–H / C–C overlap to form σ **bonds** ● a **p orbital** from each carbon atom overlap sideways with each other above and below the ring forming π **bonds**	3	3	**ALLOW** diagram to explain points STM to decide on ●✔ approach
5 b i	$Cl_2 + AlCl_3 \rightarrow Cl^+ + AlCl_4^-$	1	1	**ALLOW** formation of $^{\delta+}Cl$----$^{\delta-}Cl$—$AlCl_3$
5 b ii	 **M1** curly arrow from aromatic ring to Cl^+ **M2** intermediate	1 1	3	**M2** Intermediate rules: **centre of** + charge below and to the left of a line joining C2&C6, horseshoe includes C4 and C5, may include one or both of C2&C6 but must not include C1. horseshoe may be dots/dashes If the horseshoe has an arrow on one/both ends **CON**. Additional charges are **CON** but **IGNORE** additional partial charges **M3** Bond from C1 to H is needed. "H^+ formed / lost" may be inferred from formation of HCl but only if Cl^- or $AlCl_4^-$ already seen.

Question	Answer	Marks		Guidance
	M3 curly arrow from C—H to centre of ring **AND** H^+	1		
5 c i	electrophilic substitution	1	1	**ALLOW/ IGNORE** Friedel-Crafts acylation **??**
5 c ii	 **OR** 4-substituted acyl/alkyl derivative  	1	1	**CON** di/trisubstituted products – isomer of **Q** **ALLOW** 3- & 4-substituted products

Question	Answer	Marks	Guidance
5 c iii	(most) acyl chloride > alkyl chloride > aryl chloride (least)	1	
	any two from: ● acyl chlorides carbon in C—C*l* bond is more electron deficient since it is also attached to an oxygen atom **OR** C—C*l* bond is weakest / weakened in acyl chlorides since it is also attached to an oxygen atom / two electronegative atoms ● aryl chlorides (no hydrolysis) C—C*l* bond is part of delocalised system / partially double bond character (so C—C*l* bond is stronger) **OR** lone pair / p-orbital on Cl delocalises with π ring (so C—C*l* bond is stronger) ● alkyl chlorides C—C*l* bond strengthened by electron donating effect / positive inductive effect of alkyl / R group (as compared to acyl chlorides) **OR** carbon atom has a smaller δ+ and the C—C*l* bond is stronger (than the C—C*l* bond in COC*l*) due to (the carbon) being only attached to one electronegative atom	2 3	
5 d	$(CH_3)_3CNH_2$ (in ethanol)	1	} in either order
	$NaBH_4$	1 3	} **ALLOW** $LiAlH_4$/dry ether or other viable reducing agents

Question	Answer	Marks		Guidance
	 **OR** 	1		**depending** on order of M1 and M2
5 e i	molecules that have identical physical and chemical properties but rotate the plane of plane polarised light differently / in the opposite direction	1	1	
5 e ii	reduced/different biological activity of "other" enantiomer **OR** lower yield of biologically active molecule **OR** need to separate the optical isomers to form the pure active isomer	1	1	
5 e iii	chiral catalyst	1	1	**ALLOW** enzyme **ALLOW** any chiral chromatography
5 f i	ten / 10	1	1	
5 f ii	δ = 6.0–9.0 4H multiplet **H**–Ar / attached to aromatic ring δ = 0.9–1.7 9H singlet –C**H**$_3$ / alkane	1 1	3	**IGNORE** data referring to O<u>H</u> or N<u>H</u> peaks **SALVAGE** mark **TBD** at **STM** for example • all chemical shifts linked to correct splitting • all chemical shifts linked to correct no. of H in each environment

Question	Answer	Marks		Guidance
	δ = 3.2–4.0 1H triplet –C**H**O / alkyl next to electronegative atom	1		
		22	**22**	

Question	Answer	Marks		Guidance
6 a i	SiO_2 **OR** Al_2O_3	1	1	
6 a ii	Cd^{2+} **AND** R_f = 2/5 = 0.40	1	1	
6 b	Metal cations are less soluble in butanol (than in water)	1	1	**ALLOW** Metal cations are insoluble in butanol
6 c	H_2O **AND** SCN^-	1	1	**ALLOW** names
6 d i	$C_8H_5O_4K + KOH \rightarrow C_8H_4O_4K_2 + H_2O$	1	1	**ALLOW** ionic equation (ignoring K^+)
6 d ii	initially: moles of KOH = 0.150 × 20.0 ÷ 1000 = 3.0×10^{-3} **AND** moles of acid HA = 0.100 × 50.0÷1000 = 5.0×10^{-3} at equilibrium: moles of salt KA = 3.0×10^{-3} **AND** moles of acid HA = 5.0×10^{-3} – moles of NaOH = 2.0×10^{-3} pH = pK_a – log[HA]/[A^-] = 5.40 – log $\frac{0.0020 / 0.070}{0.0030 / 0.070}$ = 5.40 + 0.18 = 5.58 min 2sf	1 1 1 1 1	4	$C_8H_4O_4K_2$ = KA; $C_8H_5O_4K$ = HA **ALLOW** ECF from M1 calculator value 5.576… *Alternative calculation* M3 recall of Henderson-Hasselbalch equation M4 Use of H-H equation with calculated values
		9	**9**	