UNIVERSITY OF CAMBRIDGE INTERNATIONAL EXAMINATIONS

GCE Advanced Subsidiary Level and GCE Advanced Level

MARK SCHEME for the May/June 2010 question paper

for the guidance of teachers

9701 CHEMISTRY

9701/42 Paper 4 (A2 Structured Questions), maximum raw mark 100

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International Examinations

Page 2	Mark Scheme: Teachers' version	Syllabus	Paper
	GCE AS/A LEVEL – May/June 2010	9701	42

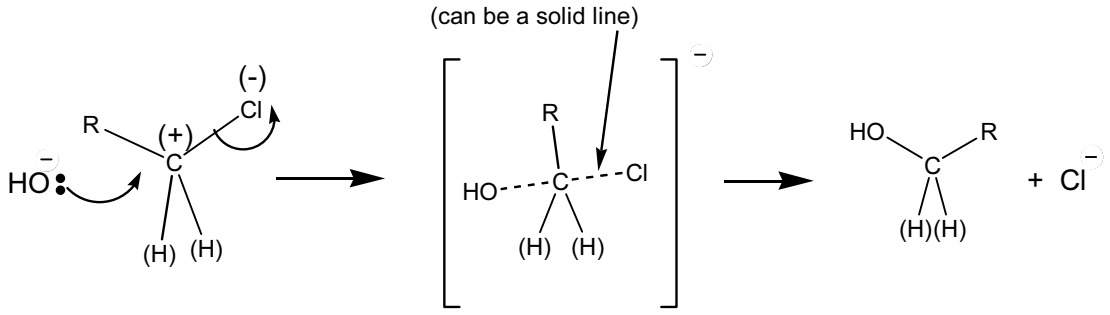
1 **(a)** C_6H_5-$COCH_2OH$ *or* $C_8H_8O_2$ **and** NaC*l* *or* C*l* (1) + (1) [2]

(b) **(i)** the exponent / power to which a concentration is raised in the **rate equation** (or in an equation, e.g. "[a]" in the equ: rate = $k[A]^a$) (1)

(ii) from 1 and 2: rate increases by 50% as does [RC*l*], so rate $\propto$ $[RCl]^1$ (1)
from 1 and 3: rate $\propto$ $[NaOH]^1$ (1)

(iii) (rate =) k[RC*l*][OH] (1)

(iv)



marking points:
- (+) or $^{\delta+}$ on C **and** (–) or $^{\delta}$ on C*l* (1)
- lone pair **and** charge on: OH (1)
- curly arrow from OH (lone pair) to $^{(\delta+)}$C, **and** *either* a curly arrow breaking C-C*l* bond *or* 5-valent transition state (ignore charge) (1)
- S_N1 alternative for last mark (only award mark if candidate's rate equation shows first order reaction): curly arrow breaking C-C*l* bond **and** carbocation intermediate. [7]

(c) **(i)** (add RC*l* / RCOC*l* to) (aq) Ag^+ / $AgNO_3$ *or* named indicator (e.g. MeOr) *or* use pH probe (1)

White ppt appears (faster with RCOC*l*) *or* turns acidic colour (e.g. red) *or* shows pH decrease (1)

if water is the only reagent, and no pH meter used: award only the second mark, for "steamy / white fumes"

(ii) (C=O is polarised /) carbon is more δ+ than in R-C*l* *or* carbon is positive *or* RCOC*l* can react via addition-elimination
(mention of electronegativity on its own is not enough for the mark) (1) [3]

[Total: 12]

2 **(a)** less soluble down group (1)

lattice energy and hydration energies both decrease (i.e. become less negative) (1)

but H.E. decreases more (than L.E.) *or* change in H.E. outweighs L.E. (1)

so ΔH_{sol} becomes more endothermic / less exothermic (1) [4]

(b) **(i)** for Mg: $\Delta H = 2993 - 1890 - (2 \times 550) =$ **(+)3** (kJ mol ^{1}) (1)

for Sr: $\Delta H = 2467 - 1414 - (2 \times 550) =$ **–47** (kJ mol ^{1}) (1)

(ii) $Sr(OH)_2$ should be **more** soluble in water, **and** ΔH is more exothermic / negative (1)

Assuming "other factors" (e.g. ΔS, *or* temperature etc.) are the same (1)

(iii) $Sr(OH)_2$ should be **less** soluble in hot water, **because** ΔH is negative / exothermic (1) [5]

(c) **(i)** $K_{sp} = [Ca^{2+}][OH^-]^2$ (needs the charges) units: mol^3dm^{-9} (1) + (1)

(ii) $n(H^+) = n(OH^-) = 0.05 \times 21/1000 = 1.05 \times 10^{-3}$ mol in 25 cm^3

$[OH^-] = 1.05 \times 1000/25 =$ **4.2×10^{-2}** (mol dm^{-3}) (1)

$[Ca^{2+}] =$ **2.1×10^{-2}** (mol dm^{-3}) (1)

$K_{sp} = 2.1 \times 10^{-2} \times (4.2 \times 10^{-2})^2 =$ **3.7×10^{-5}** (1)

(iii) **less** soluble in NaOH due to the common ion effect *or* equilibrium is shifted to the l.h.s. by high $[OH^-]$ (NOT just a mention of Le Chat^r on its own) (1) [6]

[Total: 15]

3 **(a)** SiF_4 is symmetrical *or* tetrahedral *or* bonds are at 109° *or* has no lone pair *or* 4 electron pairs shared equally *or* all Si-F dipoles cancel out, ***or*** SF_4 has a lone pair (on S). (1) [1]

(b)

compound	molecule has an overall dipole	molecule does not have an overall dipole
BCl_3		✓
PCl_3	✓	
CCl_4		✓
SF_6		✓

mark row-by-row, (2) [2]

(c) **(i)** Si **and** B have empty / available / low-lying orbitals *or* C does not have available orbitals (allow "B is electron deficient" but not mention or implication of d-orbital on B) (1)

(ii) $BCl_3 + 3H_2O \rightarrow H_3BO_3 + 3HCl$ *or* $2BCl_3 + 3H_2O \rightarrow B_2O_3 + 6HCl$ (1)

$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$ etc., e.g. $\rightarrow Si(OH)_4$, H_2SiO_3 (1) [3]

(d) **(i)** $Si_3Cl_8O_2$ (this has $M_r = 84 + 280 + 32 = 396$) *or* $Si4Cl_4O_9$ *or* $Si_8Cl_4O_2$ (1)

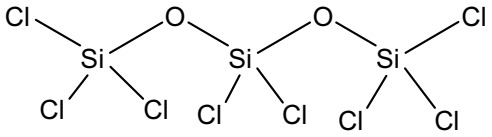
(ii)

mass number	structure
133	Cl_3Si
247	$Cl_3Si\text{-}O\text{-}SiCl_2$
263	$Cl_3Si\text{-}O\text{-}SiCl_2\text{-}O$

(3)

(if correct structures are **not** given for last 2 rows, you can award (1) mark for ***two*** correct molecular formulae:
either $Si_2Cl_5O + Si_2Cl_5O_2$ *or* $Si_3ClO_8 + Si_3ClO_9$ *or* $Si_7ClO + Si_7ClO_2$)

(iii)



allow ecf on the structure drawn in the third row of the table in **(ii)**
but any credited structure must show correct valencies for Si, C*l* and O. (1) [5]

[Total: 11]

4 **(a)** Cr^{3+}: $1s^2 2s^2 2p^6 ...$ **$3s^2 3p^6 3d^3$** (1)
Mn^{2+}: $1s^2 2s^2 2p^6 ...$ **$3s^2 3p^6 3d^5$** (1)
(allow (1) out of (2) for $3s^2 3p^6 4s^2 3d^1$ **and** $3s^2 3p^6 4s^2 3d^3$) [2]

(b) **(i)** **any three** of the following points:
- initial (pale) green (solution)
- fades to (almost) colourless (allow yellow)
- then (permanent faint) pink
- finally (deep) purple (3)

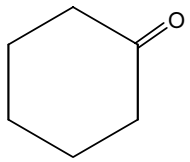
(ii) $MnO_4^- + 8H^+ + 5Fe^{2+} (+ 5e^-) \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+} (+ 5e^-)$ (1) [4]

(c) $E^\ominus$ values: $O_2 + 4H^+/2H_2O = +1.23V$ $Fe^{3+}/Fe^{2+} = +0.77$ V
$O_2 + 2H_2O/4OH^- = +0.40V$ $Fe(OH)_3/Fe(OH)_2 = -0.56V$ (2)

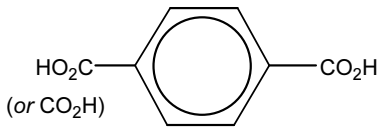
$E^\ominus_{cell}$ = +0.46V (allow –0.37) in acid, but +0.96V in alkali *or* $E^\ominus (OH^-) > E^\ominus (H^+)$ (1)

If **E_{cell}** is more positive it means a greater likelihood of reaction (1) [4]

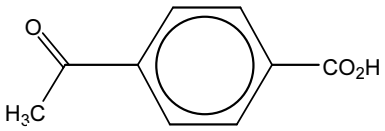
(d)



(1) and CH_3CO_2H (1)

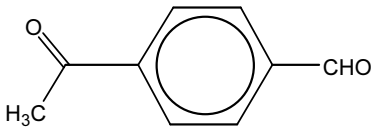


(1)



(1)

or



(1)

[5]

(e) **(i)** $(CH_3)_2C(OH)–CH_2OH$ (1)

(ii) reaction I: (cold dilute) $KMnO_4$ ("cold" not needed, but "hot" or "warm" negates) (1)
reaction II: $Cr_2O_7^{2-} + H^+ +$ **distil** (1) [3]

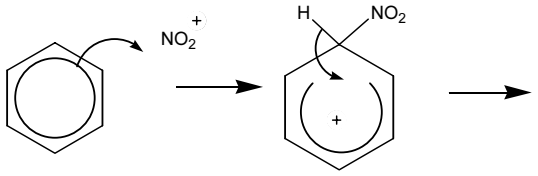
[Total: 18 max 17]

5 (a) (i) because the carbons are sp^2 / trigonal planar / bonded at 120° *or* are joined by π bonds / orbitals (1)

(ii) because the $\underline{\pi}$ electrons / double bonds are delocalised / in resonance *or* electrons are evenly distributed / spread out (1) [2]

(b) (i) $HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4$ (1)
or $HNO_3 + H_2SO_4 \rightarrow H_2NO_3^+ + HSO_4$ *or* $\rightarrow H_2O + NO_2^+ + HSO_4$

(ii) electrophilic substitution (1)
mechanism:



curly arrows from benzene to NO_2^+, **and** showing loss of H^+ (1)
correct intermediate (with "+" in the 'horse-shoe') (1) [4]

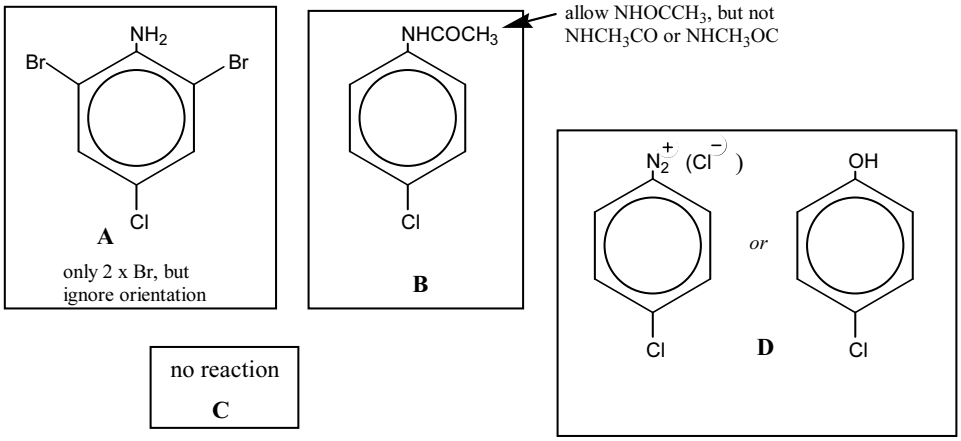
(c) C*l*$_2$ + A*l*C*l*$_3$ / FeC*l*$_3$ / Fe / A*l* / I_2 (aq or light negates this mark) (1) [1]

(d) (i) **Y** is chlorobenzene (1) **Z** is 4-chloronitrobenzene (1) (2)

(ii) Sn / Fe + (conc) HC*l* (1)

HC*l* is **conc**, **and** second step is to add NaOH(aq) (1)

(iii)



(4) [8]

[Total: 15]

6 (a) (i) Primary – the **amino acid** sequence / order / chain
or diag. e.g. NH-C-CO-NH-C-CO
or amino acids bonded by covalent / amide / peptide bonds (1)

(ii) Tertiary – the coiling / folding of the protein / polypeptide chain due to interactions between side-chains on the amino acids *or* the structure which gives the protein its 3-D / globular shape (1) [2]

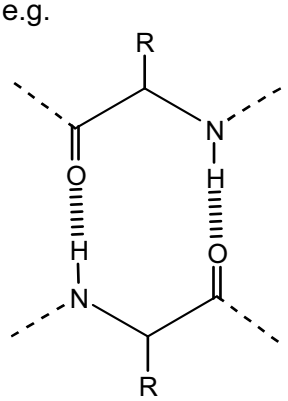
(b) (i) Diagram:
Minimum is $CH_2S\text{-}SCH_2$ (1)

(ii) Oxidation / dehydrogenation / redox (1)

(iii) Hydrogen / H bonds; ionic interactions / bonds *or* ion-dipole *or* salt bridges; van der Waals' *or* id-id *or* induced / instantaneous dipole forces
(ignore hydrophobic interactions) (2) [4]

(c) (i) Hydrogen bonds (1)

(ii) Correct new strand present (see below) needed
Diagram showing C=O bonding to N-H in new strand... ✓
...and N-H bonding to C=O in new strand ✓
e.g.



New strand must contain a minimum of two amino acid residues in a single chain. Deduct a penalty of –(1) for any wrong H-bond **only** if (2) marks have already been scored. (2) [3]

(d) There are bonds *or* S-S bridges / linkages **between the layers / sheets** (in β-keratin) (but only van der Waals interactions between the layers in silk) (1) [1]

[Total: 10]

7 **(a)** The amino acid is uncharged / neutral / a zwitterion *or* charges balance / are equal (NOT "is non-polar")

It is equally attracted by the anode / + and the cathode / – *or* attracted by neither

The pH of the buffer is at the isoelectric point/IEP of the amino acid *any two* ✓✓ (2) [2]

(b) (at pH 10), $H_2NCH_2CO_2$ *or* NH_2CH_2COO (1) [1]

(c)

amino acid	relative size	charge
A	small(est) (1)	–ve
B	large(st) (3)	–ve
C	middle (2)	+ve

(numbers are OK to show relative sizes)

Mark each row (3) [3]

(d) **(i)** lys – val – ser – ala – gly – ala – gly – asp (2)

(ii) gly – ala – gly (1)

(iii) aspartic acid (*or* lysine) (1) [4]

[Total: 10]

8 **(a)** Reaction II – since electrons are used up / required / gained / received (from external circuit) (1) [1]

(b) ($Pb^{2+} + 2e \rightarrow Pb$) $E^{\ominus} = -0.13V$
($PbO_2 + 4H^+ + 2e \rightarrow Pb^{2+} + 2H_2O$) $E^{\ominus} = +1.47V$
two correct $E^{\ominus}$ values (1)

Cell voltage is **1.6(0)** (V) (1) [2]

(c) **(i)** 3(+) (1)

(ii) They are less heavy / poisonous / toxic / polluting *or* are safer due to no (conc) H_2SO_4 within them (1) [2]

(d) **(i)** Platinum or graphite / carbon (1)

(ii) They need large quantities of **compressed** gases which take up space *or* the hydrogen would need to be **liquefied** *or* the reactant is (highly) **flammable / explosive / combustible** (1) [2]

(e) *Glass*: saves **energy** – the raw materials are easily accessible / cheap
or making glass is energy-intensive (1)

Steel: saves **energy** – extracting iron from the ore
or mining the ore is energy intensive
or saves a **resource** – iron **ore** (NOT just "iron") is becoming scarce
either one (1)

Plastics: saves a valuable / scarce **resource**: (crude) **oil / petroleum** (1) [3]

[Total: 10]

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