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

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.

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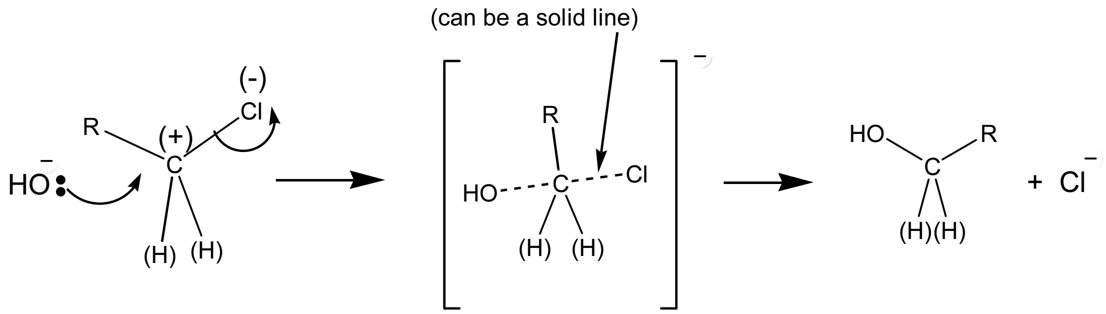
1 **(a)** C_6H_5-$COCH_2OH$ *or* $C_8H_8O_2$ **and** NaC*l* *or* C*l*$^-$ (1) + (1) [2]

(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 $\delta+$ 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)

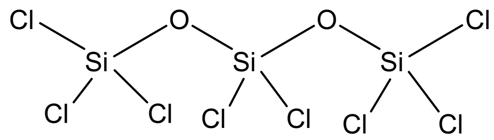
(ii)

mass number	structure
133	Cl_3Si
247	Cl_3Si-O-$SiCl_2$
263	Cl_3Si-O-$SiCl_2$-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, Cl and O. (1) [5]

[Total: 11]

4 **(a)** Cr^{3+}: $1s^2 2s^2 2p^6$... $\mathbf{3s^2 3p^6 3d^3}$ (1)
Mn^{2+}: $1s^2 2s^2 2p^6$... $\mathbf{3s^2 3p^6 3d^5}$ (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)

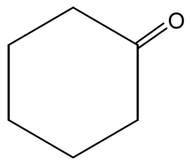
(ii) $MnO_4^- + 8H^+ + 5Fe^{2+}$ $(+ 5e^-)$ $\rightarrow$ $Mn^{2+} + 4H_2O + 5Fe^{3+}$ $(+ 5e^-)$ (1) [4]

(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)

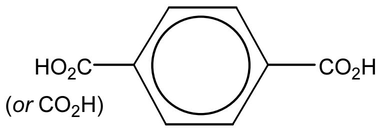
$\mathbf{E^\ominus_{cell}}$ = +0.46V (allow –0.37) in acid, but +0.96V in alkali *or* $E^\ominus (OH^-) > E^\ominus (H^+)$ (1)

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

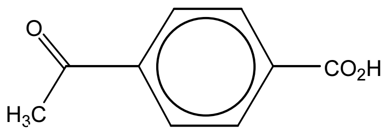
(d)



(1) and CH_3CO_2H (1)



(1)



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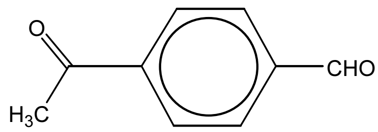


(1) (1)

[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]

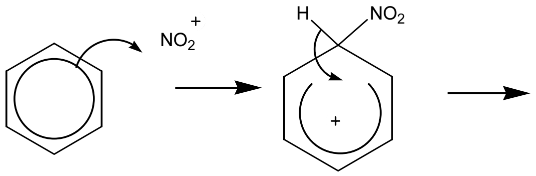
[Total: 18 max 17]

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]

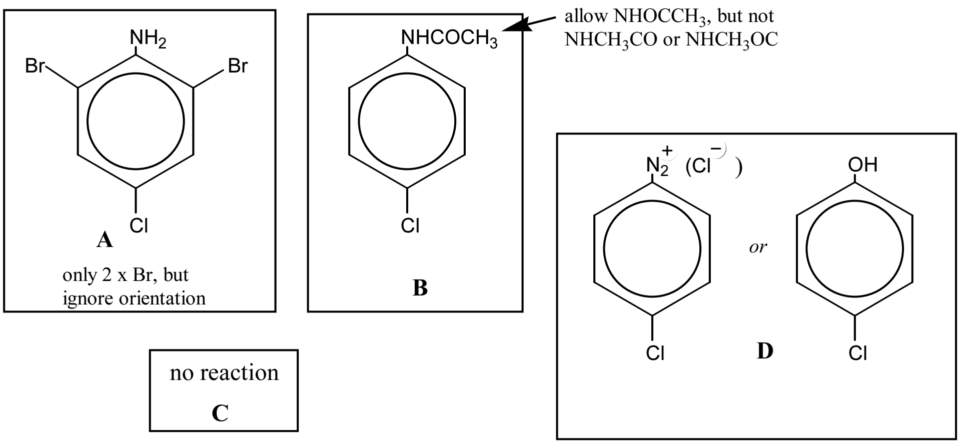
(c) Cl_2 + $AlCl_3$ / $FeCl_3$ / Fe / Al / I_2 (aq or light negates this mark) (1) [1]

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

(ii) Sn / Fe + (conc) HCl (1)

HCl 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]

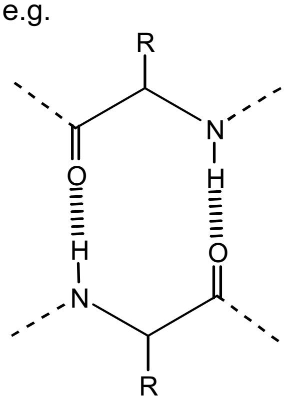
(b) **(i)** Diagram:
Minimum is $CH_2S\text{-}SCH_2$ (1)

(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]