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

1 (a)  $C_6H_5$ -COCH<sub>2</sub>OH or  $C_8H_8O_2$  and NaCl or Cl

(1) + (1) [2]

(1)

- (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]<sup>a</sup>)
  - (ii) from 1 and 2: rate increases by 50% as does [RCl], so rate  $\infty$   $[RCl]^1$  (1) from 1 and 3: rate  $\infty$   $[NaOH]^1$

(iii) (rate =) 
$$k[RCl][OH^-]$$
 (1)

(iv)

marking points:

- (+) or  $^{\delta+}$  on C and (–) or  $^{\delta-}$  on Cl (1)
- lone pair **and** charge on: OH<sup>-</sup> (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<sub>N</sub>1 alternative for last mark (only award mark if candidate's rate equation shows first order reaction): curly arrow breaking C-Cl bond and carbocation intermediate.

(c) (i) (add RC1 / RCOC1 to) (aq) Ag<sup>+</sup> / AgNO<sub>3</sub> 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-Cl or carbon is positive or RCOCl can react via addition-elimination (mention of electronegativity on its own is not enough for the mark)
 (1) [3]

[Total: 12]

[7]

Page	<u>ა</u>	Mark Scheme: Teachers' version	Syllabus	Paper	
		GCE AS/A LEVEL – May/June 2010	9701	42	
(a) le	ss solu	ble down group		(1)	
la	ttice er	ergy and hydration energies both decrease (i.e. becor	me less negative)	(1)	
bı	ut H.E.	decreases more (than L.E.) or change in H.E. outweig	hs L.E.	(1)	
so	ΔH <sub>sol</sub>	becomes more endothermic / less exothermic		(1)	[4]
(b) (i)	) for N	$\text{Mg:} \Delta H = 2993 - 1890 - (2 \times 550) = (+)3 \text{ (kJ mol}^{-1})$		(1)	
	for S	Sr: $\Delta H = 2467 - 1414 - (2 \times 550) = -47 \text{ (kJ mol}^{-1}\text{)}$		(1)	
(ii)		•	more exothermic	/ (1)	
	Assı	uming "other factors" (e.g. $\Delta$ S, $\emph{or}$ temperature etc.) are	the same	(1)	
(iii)	•	,	ΔH is negative	(1)	[5]
(c) (i	) K <sub>sp</sub> =	= [Ca <sup>2+</sup> ][OH <sup>-</sup> ] <sup>2</sup> (needs the charges) units: mol <sup>3</sup> dm <sup>-9</sup>	(	1) + (1)	
(ii)	<b>)</b> n(H <sup>⁺</sup>	) = $n(OH^{-}) = 0.05 \times 21/1000 = 1.05 \times 10^{-3} \text{ mol in } 25 \text{ cr}$	$m^3$		
	[OH	$[] = 1.05 \times 1000/25 = 4.2 \times 10^{-2} \text{ (mol dm}^{-3}\text{)}$		(1)	
	[Ca <sup>2</sup>	$^{+}$ ] = <b>2.1 × 10</b> <sup>-2</sup> (mol dm <sup>-3</sup> )		(1)	
	(a) le la bu so (iii (iii (iii) (iii (iii)	(a) less soluted lattice end but H.E. so ΔH <sub>sol</sub> less soluted lattice end but H.E. so ΔH <sub>sol</sub> less soluted lattice end but H.E. so ΔH <sub>sol</sub> less soluted lattice end but H.E. so ΔH <sub>sol</sub> less soluted lattice end	<ul> <li>(a) less soluble down group lattice energy and hydration energies both decrease (i.e. become but H.E. decreases more (than L.E.) or change in H.E. outweig so ΔH<sub>sol</sub> becomes more endothermic / less exothermic</li> <li>(b) (i) for Mg: ΔH = 2993 – 1890 – (2 × 550) = (+)3 (kJ mol<sup>-1</sup>) for Sr: ΔH = 2467 – 1414 – (2 × 550) = –47 (kJ mol<sup>-1</sup>)</li> <li>(ii) Sr(OH)<sub>2</sub> should be more soluble in water, and ΔH is negative Assuming "other factors" (e.g. ΔS, or temperature etc.) are (iii) Sr(OH)<sub>2</sub> should be less soluble in hot water, because exothermic</li> <li>(c) (i) K<sub>sp</sub> = [Ca<sup>2+</sup>][OH<sup>-</sup>]<sup>2</sup> (needs the charges) units: mol<sup>3</sup>dm<sup>-9</sup></li> </ul>	GCE AS/A LEVEL – May/June 2010  (a) less soluble down group lattice energy and hydration energies both decrease (i.e. become less negative) but H.E. decreases more (than L.E.) $or$ change in H.E. outweighs L.E. so $\Delta H_{sol}$ becomes more endothermic / less exothermic  (b) (i) for Mg: $\Delta H = 2993 - 1890 - (2 \times 550) = (+)3$ (kJ mol <sup>-1</sup> ) for Sr: $\Delta H = 2467 - 1414 - (2 \times 550) = -47$ (kJ mol <sup>-1</sup> )  (ii) Sr(OH) <sub>2</sub> should be <b>more</b> soluble in water, <b>and</b> $\Delta H$ is more exothermic negative Assuming "other factors" (e.g. $\Delta S$ , $or$ temperature etc.) are the same  (iii) Sr(OH) <sub>2</sub> should be <b>less</b> soluble in hot water, <b>because</b> $\Delta H$ is negative exothermic  (c) (i) K <sub>sp</sub> = [Ca <sup>2+</sup> ][OH <sup>-</sup> ] <sup>2</sup> (needs the charges) units: mol <sup>3</sup> dm <sup>-9</sup> (ii) $n(H^+) = n(OH^-) = 0.05 \times 21/1000 = 1.05 \times 10^{-3}$ mol in 25 cm <sup>3</sup> [OH <sup>-</sup> ] = 1.05 × 1000/25 = 4.2 × 10 <sup>-2</sup> (mol dm <sup>-3</sup> )	(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 $\Delta H_{sol}$ becomes more endothermic / less exothermic (1)  (b) (i) for Mg: $\Delta H = 2993 - 1890 - (2 \times 550) = (+)3$ (kJ mol <sup>-1</sup> ) (1) for Sr: $\Delta H = 2467 - 1414 - (2 \times 550) = -47$ (kJ mol <sup>-1</sup> ) (1)  (ii) Sr(OH) <sub>2</sub> should be more soluble in water, and $\Delta H$ is more exothermic / negative (1) Assuming "other factors" (e.g. $\Delta S$ , or temperature etc.) are the same (1)  (iii) Sr(OH) <sub>2</sub> should be less soluble in hot water, because $\Delta H$ is negative / exothermic (1)  (iv) Cr(OH) <sub>2</sub> should be less soluble in hot water, because $\Delta H$ is negative / exothermic (1)  (iv) $\Delta H_{sp} = [Ca^{2+}][OH^{-}]^{2}$ (needs the charges) units: mol <sup>3</sup> dm <sup>-9</sup> (1) + (1)  (iv) $\Delta H_{sp} = [Ca^{2+}][OH^{-}]^{2}$ (needs the charges) units: mol <sup>3</sup> dm <sup>-9</sup> (1) + (1)

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

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

[Total: 15]

[6]

(1)

(1)

Page 4	Mark Scheme: Teachers' version	Syllabus	Paper
	GCE AS/A LEVEL – May/June 2010	9701	42

(a) SiF<sub>4</sub> 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<sub>4</sub> 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 <sub>4</sub>		✓
SF <sub>6</sub>		<b>√</b>

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) 
$$BCl_3 + 3H_2O \rightarrow H_3BO_3 + 3HCl \text{ or } 2BCl_3 + 3H_2O \rightarrow B_2O_3 + 6HCl$$
 (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  $Si_4Cl_4O_9$  or  $Si_8Cl_4O_2$  (1)

(ii)

mass number structure	
133	Cl₃Si
247	$Cl_3Si-O-SiCl_2$
263	Cl <sub>3</sub> Si-O-SiCl <sub>2</sub> -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]

Page 5	Mark Scheme: Teachers' version	Syllabus	Paper
	GCE AS/A LEVEL – May/June 2010	9701	42

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

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

(c) 
$$E^{\theta}$$
 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)

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

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

(d)

$$HO_2C$$
  $CO_2H$   $CO_2H$   $CO_2H$ 

[5]

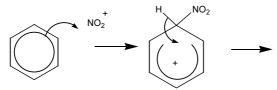
(e) (i) 
$$(CH_3)_2C(OH)-CH_2OH$$
 (1)

(ii) reaction I: (cold dilute) KMnO<sub>4</sub> ("cold" not needed, but "hot" or "warm" negates) (1) reaction II:  $Cr_2O_7^{2-} + H^+ + distil$  (1) [3]

[Total: 18 max 17]

Page 6	Mark Scheme: Teachers' version	Syllabus	Paper
	GCE AS/A LEVEL – May/June 2010	9701	42

- 5 (a) (i) because the carbons are  $sp^2$  / trigonal planar / bonded at 120° or are joined by  $\pi$  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)  $Cl_2 + A/Cl_3 / FeCl_3 / Fe / Al / I_2$  (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)
    - HC1 is **conc**, **and** second step is to add NaOH(aq) (1)

allow NHOCCH<sub>3</sub>, but not NHCH<sub>3</sub>CO or NHCH<sub>3</sub>OC

NHCOCH<sub>3</sub>

A Cl

only 2 x Br, but ignore orientation

B

no reaction

C

` , - -

[8]

(4)

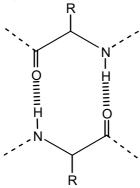
[Total: 15]

Page 7	Mark Scheme: Teachers' version	Syllabus	Paper
	GCE AS/A LEVEL – May/June 2010	9701	42

- 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  $CH_2S-SCH_2$  (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)

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

[Total: 10]

[3]

Page 8	Mark Scheme: Teachers' version	Syllabus	Paper
	GCE AS/A LEVEL – May/June 2010	9701	42

**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* ✓ ✓

**(b)** (at pH 10),  $H_2NCH_2CO_2^-$  or  $NH_2CH_2COO^-$ 

(1) [1]

(2) [2]

(c)

amino acid	relative size	charge
Α	small(est) (1)	-ve
В	large(st) (3)	-ve
С	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]

Page 9	Mark Scheme: Teachers' version	Syllabus	Paper
	GCE AS/A LEVEL – May/June 2010	9701	42

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

[1]

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

two correct E<sup>o</sup> values

Cell voltage is 1.6(0) (V)

(1) [2]

(1)

- (c) (i) 3(+) (1)
  - (ii) They are less heavy / poisonous / toxic / polluting or are safer due to no (conc) H<sub>2</sub>SO<sub>4</sub> 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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