# CAMBRIDGE INTERNATIONAL EXAMINATIONS GCE Advanced Level

# MARK SCHEME for the May/June 2013 series

## 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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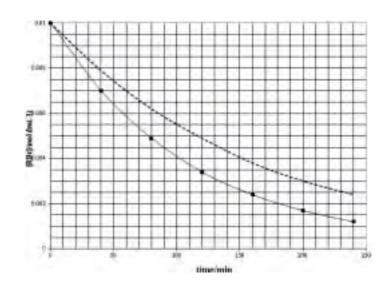
1 (a) (i) 
$$RBr + OH^- \longrightarrow ROH + Br^-$$

[1]

(ii) nucleophilic substitution

[1] **[2]** 

(b) (i)



plotting of all points (plotted to within ½ small square) [1]

good line of best fit [1]

(ii) 
$$t_{\frac{1}{2}} = 118 \text{ min or } 79 \text{ min } (\pm 5 \text{ min})$$

or

construction lines for two half-lives and mention that half-life is constant

or

calculate the ratio of two rates at two different concentrations

[1]

#### (iii) either ratio of initial rates (slopes)

or

ratio of t<sub>1/2</sub>

or

ratio of times for [RBr] to fall to the same level: all should be = 1.5

[1]

[1]

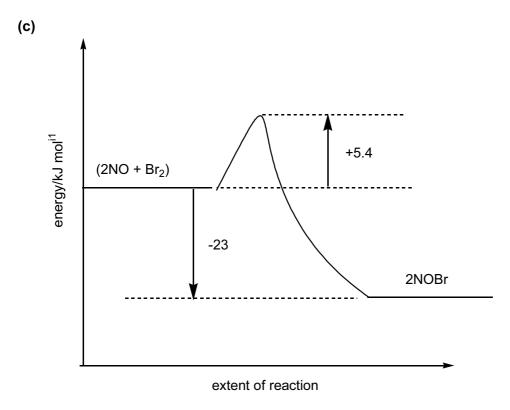
(iv) rate = 
$$k[RBr][OH^-]$$
 [1]

initial rate = 
$$0.01 / 185 = 5.4 \times 10^{-5} \text{ (mol dm}^{-3} \text{ min}^{-1}\text{)}$$
 [1]

$$k = 5.4 \times 10^{-5} / (0.01 \times 0.1) = 0.054 \text{ (mol}^{-1} \text{ dm}^3 \text{ min}^{-1})$$
 [1]

[8 max 7]

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four marking points: one activation "hump"

2NOBr (not just NOBr)

 $\Delta H$  labelled correctly (arrow down, or double headed, or just a line)  $E_a$  labelled correctly (arrow up, or double headed, or just a line)

all four points [2]

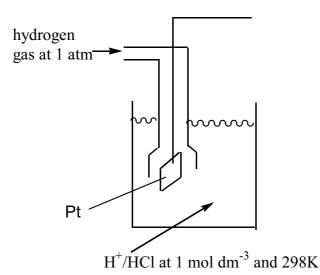
three or two points [1]

[2]

[Total: 11]

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## 2 (a) (i)



 $H_2(g)$  going in (i.e. not being produced) [1]

platinum electrode in contact with solution, with H<sub>2</sub> bubbling over it [1]

H<sup>+</sup> or HCl or H<sub>2</sub>SO<sub>4</sub> [1]

solution at 1 mol dm<sup>-3</sup>(or 0.5 M if  $H_2SO_4$ ) and T=298 K, p=1 atm [1]

(ii) 
$$E^{\circ} = 1.33 - (-0.41) = 1.74 \text{ V}$$
 [1]

$$Cr_2O_7^{2-} + 14H^+ + 6Cr^{2+} \longrightarrow 8Cr^{3+} + 7H_2O$$
 [1]

(iii) Colour would change from orange [1]

to green [1]

(b) there are two ways of calculating the ratio:

$$pK_a = -log_{10}(K_a) = -log_{10}(1.79 \times 10^{-5}) = 4.747 (4.75) \text{ or } [H^+] = 10^{-5.5} = 3.16 \times 10^{-6}$$
 [1]

$$\log_{10}([B] / [A]) = pH - pK_a = 0.753 (0.75) \text{ or [salt] / [acid]} = K_a / [H^{\dagger}]$$
 [1]

$$\therefore$$
 [B] / [A] =  $10^{0.753}$  = 5.66  
or = 1.79 x  $10^{-5}$  / 3.16 x  $10^{-6}$  = 5.66  
(or [A] / [B] =  $0.177$ )

[1]

(correct ratio = [3] marks)

since B + A = 100, 
$$\therefore$$
 (100–A) / A = 5.66  $\Rightarrow$  vol of acid = 15 cm<sup>3</sup> vol of salt = 85 cm<sup>3</sup> [1]

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(c) (i) 
$$CH_3CO_2Na + HCl \longrightarrow CH_3CO_2H + NaCl$$

[1]

(ii) 
$$CH_3CO_2H + NaOH \longrightarrow CH_3CO_2Na + H_2O$$

[1] **[2]** 

(d) e.g. hydrolysis of esters  $RCO_2R'$  (+  $H_2O$ )  $\longrightarrow$   $RCO_2H$  + R'OH or its reverse

or hydrolysis of amides: RCONH<sub>2</sub> (+ 
$$H_3O^+$$
)  $\longrightarrow$  RCO<sub>2</sub>H + NH<sub>4</sub><sup>+</sup>

hydrolysis of nitriles: RCN (+  $H_3O^+ + H_2O$ )  $\longrightarrow$  RCO<sub>2</sub>H +  $NH_4^+$ 

nitration of benzene (or any arene):  $C_6H_6 + HNO_3 \longrightarrow C_6H_5NO_2$  (+  $H_2O$ )

dehydration of alcohols, e.g. :  $CH_3CH(OH)CH_3 \longrightarrow CH_3CH=CH_2 + H_2O$  (or the reverse)

halogenation of ketones, e.g. :  $CH_3COCH_3 + X_2 \longrightarrow CH_3COCH_2X$  (+ HX)

[3]

[Total: 17]

3 (a) (i) 
$$HNO_3 + H_2SO_4$$
 conc (both acids) and  $30^{\circ}C < T < 60^{\circ}C$  or warm

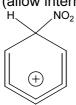
[1]

[1]

(ii) dilute HNO<sub>3</sub> or HNO<sub>3</sub>(aq) and room temp. (allow T ≤ 30°C)

[1] **[3]** 

**(b)** (allow intermediate from methylbenzene)



[1]

[1]

(c) Sn/tin (or SnC $l_2$ , Fe) + HCl (NOT H<sub>2</sub>SO<sub>4</sub> or H<sup>+</sup>, Zn, or LiAlH<sub>4</sub>.)

[1] **[1]** 

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(d) (i)

[1] + [1]

(ii) NaNO<sub>2</sub> + HCl or H<sub>2</sub>SO<sub>4</sub> or H<sup>+</sup> or HNO<sub>2</sub> [1]

 $T \le 10^{\circ}C$  [1] [4 max 3]

(e) (i) amide [1]

(ii)  $M_r = 108+11+14+16 = 149$ 

 $%N = (14 \times 100)/149 = 9.4\%$  [1]

(iii) NHCOC<sub>2</sub>H<sub>5</sub>

[1] **[3]** 

[Total: 11]

4. (a) (i) Many electrons of similar energy in a valence-shell orbital

or

successive ionisation energies rise steadily (no big jumps)

or

ability to form bonds with ligands can stabilise very low or very high oxidation states or

4s + 3d orbitals/shells/energy levels have similar / same energies

[1]

(ii)  $VO_2^+$ : +5  $CrF_6^{2-}$ : +4  $MnO_4^{2-}$ : +6

[3 × 1]

[4]

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(b)

- (colour due to) absorption of light/photons/frequencies/wavelengths or colour seen is complement of colour absorbed.
- d-orbitals/d-subshell split (by ligand field)
- (when photon is absorbed), electron is promoted *or* moves (from lower) to higher (d–)orbital
- energy difference/gap  $or \Delta E$  or splitting corresponds to photon/frequency/wavelength in visible region
- in s-block elements the energy gap is too large (to be able to absorb visible light)

[any four  $4 \times 1$ ]

[4]

- (c) (i)  $2MnO_4^- + 2H_2O + 5SO_2 \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 4H^+$  [1]
  - (ii) solution will go from purple [1]

to colourless [1]

(d) (pale) blue solution [1]

gives a (pale) blue ppt. [1]

which re-dissolves, *or* forms a solution, which is dark/deep blue *or* purple [1]

[3]

[3]

[Total: 14]

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(a) (i) 5

two or three centres correctly identified [1] four centres correctly identified [2]

(ring subst. allow 2 or 3 Br in ring)

[1]

[1]

(ii)  $C_{16}H_{18}O_9$ [1]

3 moles of H<sub>2</sub> (iii) [1]

(iv) in cold: 3 moles of NaOH [1]

on heating: 4 moles of NaOH [1] [6]

(b) (i) hydrolysis [1]

(ii) alkene or C=C [1]

(iii) with Na<sub>2</sub>CO<sub>3</sub>(aq): carboxylic acid [1]

with Br<sub>2</sub>(aq): phenol [1]

(iv)

(OH can be at the 3, 4, or 5 positions, but not the 2 or 6

(addition to C=C: allow one of the aliphatic Br to be OH, but not both) positions) [1]

(v) geometrical or cis-trans or E-Z [1]

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skeletal or structural [1]

[9 max 8]

(c) 
$$M_r(\mathbf{E}) = 180$$
, so 0.1 g = 1/1800 (5.56 x 10<sup>-4</sup>) mol [1]

3 mol NaOH react with 1 mol of **E**, so 
$$n(NaOH) = 3/1800 = 1/600 \text{ mol} = 1.67 \times 10^{-3} \text{ mol}$$
 [1]

volume of 0.1M NaOH = 
$$1000/(600 \times 0.1) = 16.7 \text{ cm}^3$$
 [1]

[Total: 17]

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### 6 (a)

substance	protein synthesis	formation of DNA
cysteine	✓	
cytosine		✓
glutamine	✓	
guanine		✓

[3]

[3]

(b) (i) Hydrogen bonding

[1]

Between bases or between A,T, C and G (all four needed)

[1]

(ii) Bonds are (relatively) weak or easily broken

[1]

This enables strands to separate or DNA to unzip/unwind/unravel.

[1] **[4]** 

- (c) changes / mutations in DNA
  - by the addition / insertion /deletion / substitution / replacement of a base
  - adds / deletes / replaces an amino acid or changes the amino acid sequence
  - this causes a loss of function or changes the shape / tertiary structure of the protein

any three points [3]

[3]

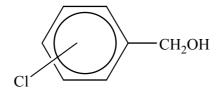
[Total: 10]

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7. **(a) (i)** 
$$43.3 = 100$$
  $3.35 = 1.1 \times n$ 

n = 
$$\frac{100 \times 3.35}{43.3 \times 1.1}$$
 = 7.03 = 7 (calculation must be shown) [1]

- (ii) The M and M+2 peaks are in the ratio 3 : 1 hence the halogen is chlorine/C1 [1]
- (iii) L contains 7 hydrogen atoms *or* there are 3 types/environments of proton/H [1]
- (iv) The multiplet with 4 hydrogens or peaks at δ 7.3 suggests a benzene ring The singlet with 2 hydrogens or peak at δ 4.7 suggests a –CH<sub>2</sub>– group The singlet with 1 hydrogen or peak at δ 2.3 suggests an –OH group or reaction with Na suggests an OH group OH must be an alcohol, not a phenol (due to its δ value) Since L also contains 7 carbon atoms and chlorine, this accounts for 126 of the 142 mass, the remaining atom must be oxygen Thus L is



(allow the 2-, 3- or 4- isomer)

[9 max 7]

(b) (i) we expect propene to have a CH<sub>3</sub> peak *or* a peak at m/e 15 *or* cyclopropane would have fewer peaks

[1]

(ii) cyclopropane would have 1 peak (ignore splitting) propene would have 2 (or 3, or 4) peaks (ignore splitting) or propene would have peaks in the  $\delta$  4.5-6.0 (alkene) region no splitting of cyclopropane peak (any two points)

[2]

[3]

[Total: 10]

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8	(a) (i)	$CH_2 = CH - CO_2H$ or $CH_2 = CH - CO_2R$ or $CH_2 = CH - COC1$	[2]
	(ii)	addition (polymerisation)	[1]
	(iii)	C(CH <sub>2</sub> OH) <sub>4</sub>	[1]
	(iv)	water	[1] <b>[5]</b>
		ater is bonded to the polymer by) hydrogen bonding drogen bonds are weak <i>or</i> easily broken	[1] [1] <b>[2]</b>
	(c) (i)	cross-linking causes no reduction in the number of –OH groups or cross-linking molecules also have –OH groups	[1]
	(ii)	property e.g. becomes harder / more rigid / less flexible / stronger / higher melting point. because the chains are more strongly / tightly held	[1] [1] <b>[3]</b>

[Total: 10]