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.

Mark schemes should be read in conjunction with the question paper and the Principal Examiner Report for Teachers.

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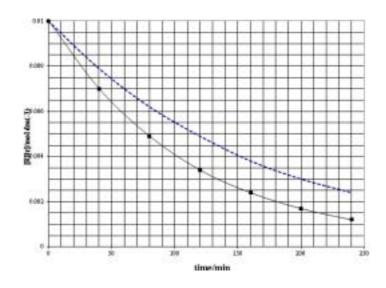
Cambridge is publishing the mark schemes for the May/June 2013 series for most IGCSE, GCE Advanced Level and Advanced Subsidiary Level components and some Ordinary Level components.



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





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

good line of best fit [1]

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

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_{1/2}

or

[1]

[1]

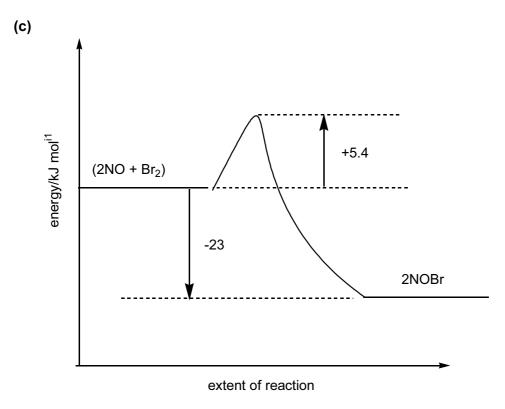
(iv) rate =
$$k[RBr][OH^-]$$
 [1]

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)

 ΔH labelled correctly (arrow down, or double headed, or just a line) $E_{\rm a}$ labelled correctly (arrow up, or double headed, or just a line)

all four points [2]

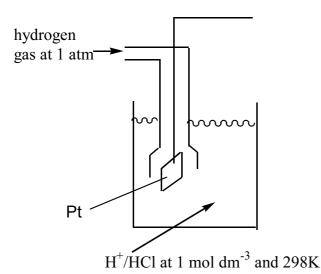
three or two points [1]

[2]

[Total: 11]

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2 (a) (i)



H₂(g) going in (i.e. not being produced) [1]

platinum electrode in contact with solution, with H₂ bubbling over it [1]

H⁺ or HCl or H₂SO₄ [1]

solution at 1 mol dm⁻³(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 cm³ vol of salt = 85 cm³ [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]

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

or hydrolysis of amides: RCONH₂ (+
$$H_3O^+$$
) \longrightarrow RCO₂H + NH₄⁺ hydrolysis of nitriles: RCN (+ H_3O^+ + H_2O) \longrightarrow RCO₂H + NH₄⁺ nitration of benzene (or any arene): C₆H₆ + HNO₃ \longrightarrow C₆H₅NO₂ (+ H₂O) dehydration of alcohols, e.g. : CH₃CH(OH)CH₃ \longrightarrow CH₃CH=CH₂ + H₂O (or the reverse)

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

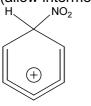
[Total: 17]

[3]

3 (a) (i)
$$HNO_3 + H_2SO_4$$
 [1] conc (both acids) and $30^{\circ}C < T < 60^{\circ}C$ or warm [1]

(ii) dilute HNO_3 or HNO_3 (aq) and room temp. (allow $T \le 30^{\circ}C$) [1]

(b) (allow intermediate from methylbenzene)



[1] [1]

(c)
$$Sn/tin (or SnCl_2, Fe) + HCl (NOT H_2SO_4 or H^+, Zn, or LiAlH_4.)$$
 [1]

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(d) (i)

[1] + [1]

[1]

(ii) NaNO₂ + HCl or H₂SO₄ or H⁺ or HNO₂

[1]

T ≤ 10°C [4 max 3]

[1] (e) (i) amide

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

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

[1]

[3]

[Total: 11]

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

successive ionisation energies rise steadily (no big jumps)

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

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

[1]

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

 $[3 \times 1]$

[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 4×1]

[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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5 (a) (i)

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

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

(iii) 3 moles of H_2 [1]

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

on heating: 4 moles of NaOH [1]

(b) (i) hydrolysis [1]

(ii) alkene or C=C [1]

(iii) with Na₂CO₃(aq): carboxylic <u>acid</u> [1]

with $Br_2(aq)$: phenol [1]

(iv)

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

G (ring subst. allow 2 or 3 Br in ring) [1] (addition to C=C: allow one of the aliphatic Br to be OH, but not both) [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 $0.1 \text{ g} = 1/1800 (5.56 \times 10^{-4}) \text{ mol}$ [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]

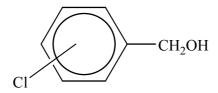
[Total: 10]

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7. **(a) (i)**
$$\frac{43.3}{3.35} = \frac{100}{1.1 \text{ x n}}$$

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

- (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 –CH₂– 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 CH₃ 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 δ 4.5-6.0 (alkene) region no splitting of cyclopropane peak (any two points)

[2]

[၁]

[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 ₂ OH) ₄	[1]
	(iv)	water	[1] [5]
	• • •	ater is bonded to the polymer by) hydrogen bonding drogen bonds are weak <i>or</i> easily broken	[1] [1] [2]
	(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] [3]