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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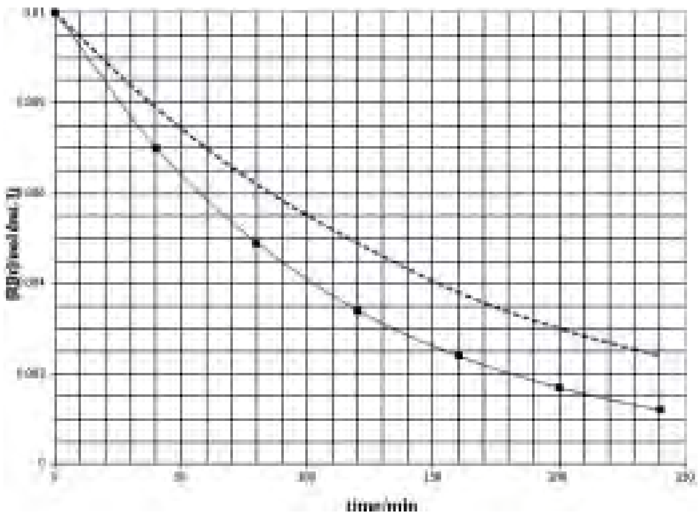
CAMBRIDGE
International Examinations

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) $t_{½}$ = 118 min or 79 min (± 5 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 $t_{½}$
or
ratio of times for [RBr] to fall to the same level: all should be = 1.5 [1]

therefore reaction is first order w.r.t. $[OH^-]$ [1]

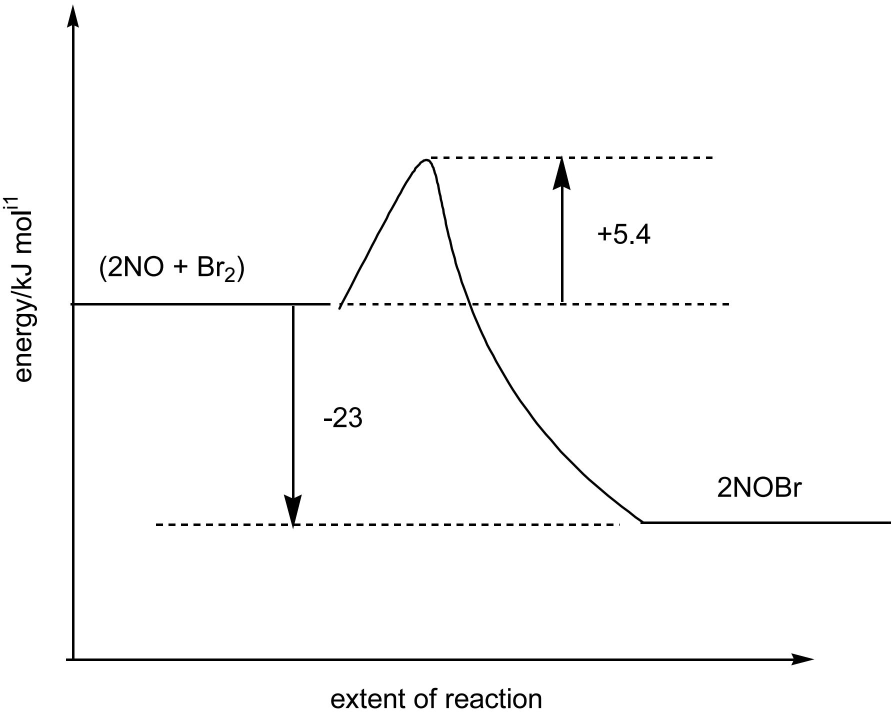
(iv) rate = k[RBr]$[OH^-]$ [1]

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

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

[8 max 7]

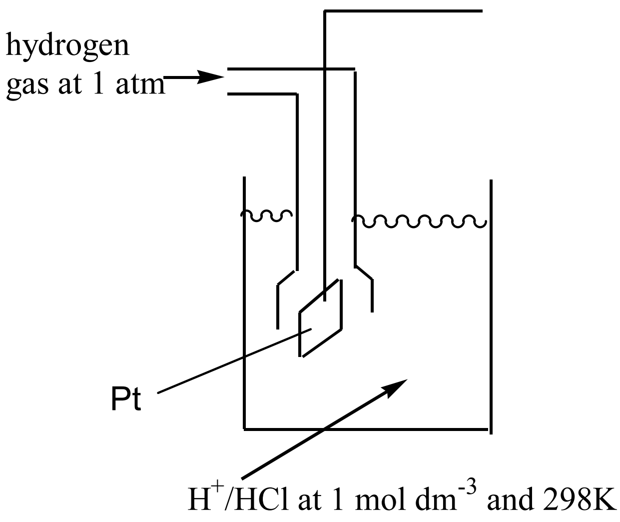
(c)



four marking points: one activation "hump"
2NOBr (not just NOBr)
ΔH 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]

2 (a) (i)



H_2(g) going in (i.e. not being produced) [1]
platinum electrode in contact with solution, with H_2 bubbling over it [1]
H^+ *or* HC*l* *or* H_2SO_4 [1]
solution at 1 mol dm^{-3}(*or* 0.5 M if H_2SO_4) **and** T=298 K, p=1 atm [1]

(ii) $E^\ominus$ = 1.33 – (-0.41) = 1.74 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]
[8]

(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) *or* $[H^+] = 10^{-5.5} = 3.16 \times 10^{-6}$ [1]

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

$\therefore$ [B] / [A] = $10^{0.753}$ = 5.66
or = $1.79 \times 10^{-5} / 3.16 \times 10^{-6}$ = 5.66
(*or* [A] / [B] = <u>0.177</u>) [1]
(correct ratio = [3] marks)

since B + A = 100, $\therefore$ (100–A) / A = 5.66 $\Rightarrow$ <u>vol of acid = 15 cm^3</u>
<u>vol of salt = 85 cm^3</u> [1]
[4]

(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: $RCONH_2$ (+ H_3O^+) $\longrightarrow$ $RCO_2H + NH_4^+$

hydrolysis of nitriles: RCN (+ $H_3O^+ + H_2O$) $\longrightarrow$ $RCO_2H + NH_4^+$

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]

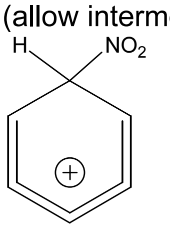
[Total: 17]

3 **(a)** **(i)** $HNO_3 + H_2SO_4$ [1]
conc (both acids) **and** 30°C < T < 60°C *or* warm [1]

(ii) dilute HNO_3 *or* HNO_3(aq)
and room temp. (allow T ≤ 30°C) [1]

[3]

(b) (allow intermediate from methylbenzene)



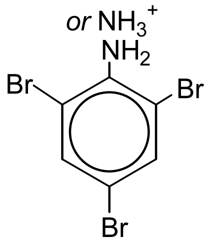
[1]

[1]

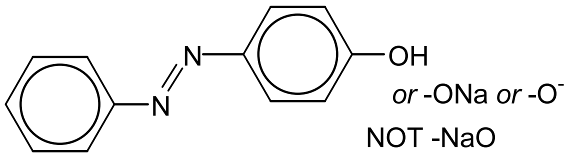
(c) Sn/tin (*or* $SnCl_2$, Fe) + HCl (NOT H_2SO_4 *or* H^+, Zn, *or* $LiAlH_4$.) [1]

[1]

(d) **(i)**



A



B

[1] + [1]

(ii) $NaNO_2$ + HC*l* *or* H_2SO_4 *or* H^+ *or* HNO_2 [1]

T ≤ 10°C [1]

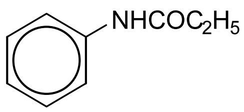
[4 max 3]

(e) **(i)** amide [1]

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

%N = (14 x 100)/149 = 9.4% [1]

(iii)



[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]

(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* ΔE *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]
[3]

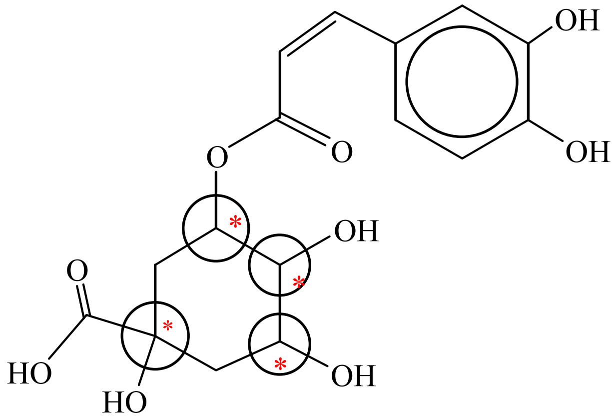
(d) (pale) blue solution [1]

gives a (pale) blue ppt. [1]

which re-dissolves, *or* forms a solution, which is dark/deep blue *or* purple [1]
[3]

[Total: 14]

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]

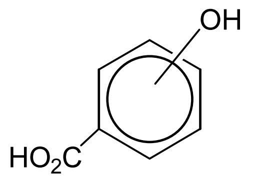
on heating: 4 moles of NaOH [1]
[6]

(b) (i) hydrolysis [1]

(ii) alkene *or* C=C [1]

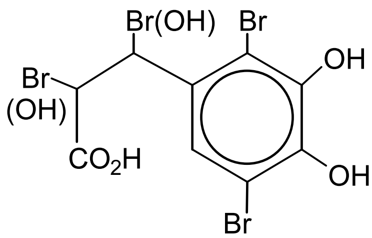
(iii) with Na_2CO_3(aq): carboxylic <u>acid</u> [1]
with Br_2(aq): phenol [1]

(iv)



F

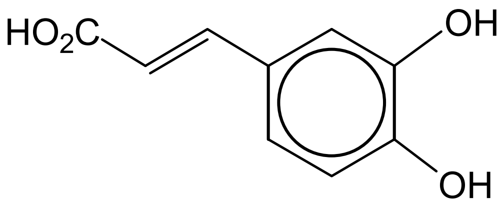
(OH can be at the 3, 4, or 5 positions, but not the 2 or 6 positions) [1]



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]

(vi)



skeletal or structural [1]
[9 max 8]

(c) M_r(**E**) = 180, so 0.1 g = 1/1800 (5.56 x 10^{-4}) mol [1]

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

volume of 0.1M NaOH = 1000/(600 x 0.1) = 16.7 cm^3 [1]
[3]

[Total: 17]

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]

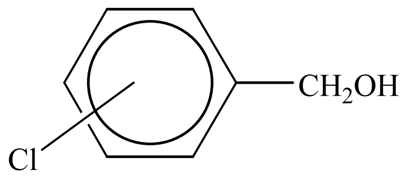
7. **(a)** **(i)** $\frac{43.3}{3.35} = \frac{100}{1.1 \times n}$

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

(ii) The M and M+2 peaks are in the ratio 3 : 1 hence the halogen is chlorine/C*l* [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 $–CH_2–$ 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)

[6]

[9 max 7]

(b) **(i)** we expect propene to have a CH_3 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]

[3]

[Total: 10]

8 **(a)** **(i)** $CH_2 = CH–CO_2H$ *or* $CH_2 = CH–CO_2R$ *or* $CH_2 = CH–COCl$ [2]

(ii) addition (polymerisation) [1]

(iii) $C(CH_2OH)_4$ [1]

(iv) water [1]
[5]

(b) (water is bonded to the polymer by) hydrogen bonding [1]
hydrogen bonds are weak *or* easily broken [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. [1]
because the chains are more strongly / tightly held [1]
[3]

[Total: 10]