CAMBRIDGE INTERNATIONAL EXAMINATIONS

GCE Advanced Level

MARK SCHEME for the October/November 2012 series

9701 CHEMISTRY

9701/43 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) $MgCl_2$: forms a (colourless) solution **or** dissolves. [1]

$AlCl_3$: produces a white ppt **or** steamy fumes [1]

$2AlCl_3$ (**or** Al_2Cl_6) + $3H_2O \longrightarrow Al_2O_3 + 6HCl$ [1]
(**or** $AlCl_3 + 3H_2O \longrightarrow Al(OH)_3 + 3HCl$)

or forms a (colourless) solution **or** dissolves [1]

$AlCl_3 + 6H_2O \longrightarrow [Al(H_2O)_5(OH)]^{2+} + H^+ + 3Cl^-$ [1]

$SiCl_4$: produces a white ppt **or** steamy fumes [1]

$SiCl_4 + 2H_2O \longrightarrow SiO_2 + 4HCl$ [1]
(or balanced equation giving H_2SiO_3 **or** $Si(OH)_4$)

[Total: 5]

(b) (i) $n(NaCl) = 1.10/58.5 = 1.88 \times 10^{-2}$ mol [1]
$n(KCl) = 0.90/74.6 = 1.21 \times 10^{-2}$ mol [1]

total $n(Cl^-) = 3.08$ or 3.09 or 3.1×10^{-2} mol [2 or more sig. figs.] allow ecf

(ii) $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$ [1]

(iii) moles sampled for the titration = $3.09 \times 10^{-2} \times 10/1000 = 3.09 \times 10^{-4}$ mol ecf [1]

this equals $n(Ag^+)$, so vol of $AgNO_3 = 3.09 \times 10^{-4} \times 1000/0.02 =$ **15.5 cm^3** ecf [1]

[Total: 5]

(c) (i) bonds broken are C–H and I–I = 410 + 151 = 561 kJ mol^{-1} (all bonds = 5731 kJ mol^{-1})

bonds formed are C–I and H–I = 240 + 299 = 539 kJ mol^{-1} (all bonds = 5709 kJ mol^{-1})
ΔH = **+22** kJ mol^{-1} [2]

(ii) **4** HI + **2** $HNO_3 \longrightarrow$ **2** $I_2 + N_2O_3 +$ **3** H_2O (**or** double) [1]

N: (is reduced from) **5 to 3**
I: (is oxidised from) **–1 to 0** [1]

[Total: 4]

[TOTAL: 14]

2 **(a)** catalyst: any two from the following three bullets for [1] mark:

- speeds up/increases (NOT alters or changes) the rate of a reaction
- lowers energy barrier/E_{act} **or** offers a lower energy pathway
- is not used up **or** remains unchanged **or** does not alter its mass/concentration **or** does not appear in stoichiometric equation **or** is regenerated [1]

homogeneous: (catalyst and reactants) in the same phase/state [1]

[Total: 2]

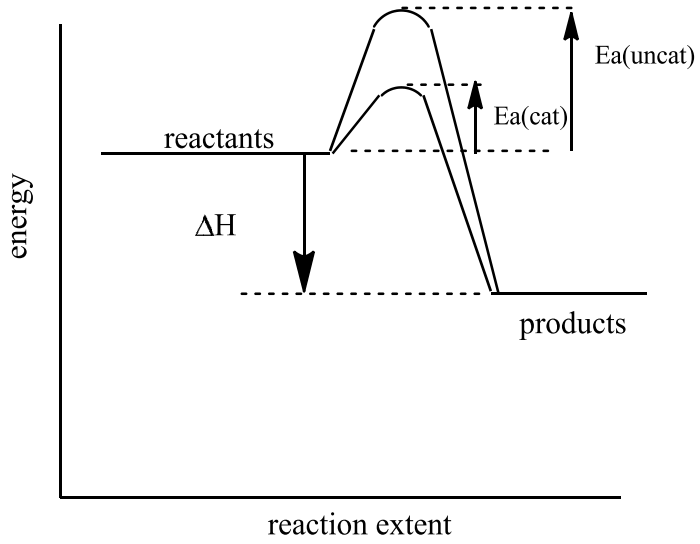
(b) **(i)** e.g. car exhausts/engines **or** aeroplanes **or** lightning **or** <u>burning</u> fuels **or** power stations [1]

nitrogen reacts with oxygen **or** $N_2 + O_2$ [1]

(ii) $NO_2 + SO_2 \longrightarrow NO + SO_3$
$NO + ½\ O_2 \longrightarrow NO_2$
$SO_3 + H_2O \longrightarrow H_2SO_4$
$4NO_2 + 2H_2O + O_2 \rightarrow 4HNO_3$ **or** $3NO_2 + H_2O \rightarrow 2HNO_3 + NO$ (any 3 equations) 3 × [1]

[Total: 5]

(c)



ΔH shown as negative [1]
both E_a labelled and correct – i.e. for the forward reaction [1]
E_a(cat) < E_a(uncat) [1]

[Total: 3]

[TOTAL: 10]

3 **(a)** $(1s^2 2s^2 2p^6)3s^2 3p^6 3d^9$ [1]

[Total: 1]

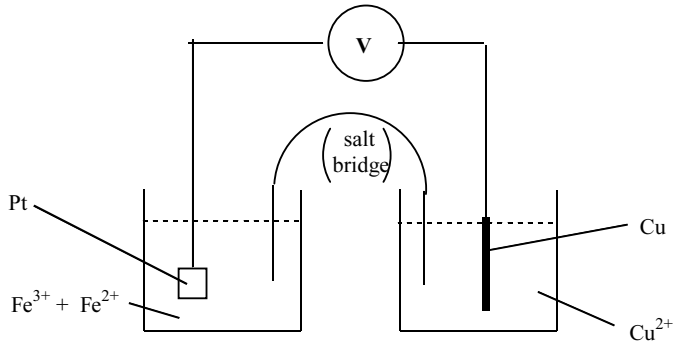
(b) **(i)** electron / orbitals near ligands are at a higher energy [1]
due to repulsion from ligand lone pairs [1]

(ii) when an electron moves to higher orbital / energy level **or** is promoted [1]
it absorbs a photon **or** light (mention of light being *emitted* negates this mark) [1]

(iii) (different ligands produce) different (sizes of) energy gap **or** ΔE [1]

[Total: 5]

(c)



solutions at 1 mol dm^{-3} (1 M) and 298(K)/25°C [1]
salt bridge and voltmeter [1]
platinum/carbon/graphite electrode [1]
(this mark is negated by inclusion of H_2 around the electrode)
copper electrode [1]
Fe^{3+}/Fe^{2+} mixture **and** Cu^{2+} **or** $CuSO_4$ etc [1]

[Total: 5]

(d) *Parts* **(i)** – **(iii)** *have to correspond to each other.*

	either	*or*
(i)	ligand exchange/substitution/displacement/replacement	precipitation/acid-base/deprotonation
(ii)	$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightarrow [Cu(H_2O)_2(NH_3)_4]^{2+} + 4H_2O$ *or* $[Cu(H_2O)_6]^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+} + 6H_2O$ *or* $[Cu(H_2O)_6]^{2+} + nNH_3 \rightarrow [Cu(H_2O)_{6-n}(NH_3)_n]^{2+} + nH_2O$	$Cu^{2+} + 2NH_3 + 2H_2O \rightarrow Cu(OH)_2 + 2NH_4^+$ *or* $Cu^{2+} + 2NH_4OH \rightarrow Cu(OH)_2 + 2NH_4^+$ *or* $[Cu(H_2O)_6]^{2+} + 2NH_3 \rightarrow [Cu(H_2O)_4(OH)_2] + 2NH_4^+$
(iii)	turns purple **or** deep/dark/royal blue	forms a pale blue ppt

[1] + [1] + [1]

(iv) $E^{\ominus}$ will decrease/ be less positive/more negative...
...because $[Cu^{2+}]$ decreases **or** $Cu^{2+} + 2e^- \rightleftharpoons Cu$ shifts to the LHS **or**
$E^{\ominus}[Cu(NH_3)_4]^{2+} = -0.05V$ **or** $[Cu(NH_3)_4]^{2+}$ is more stable. [1]

[Total: 4]

(e) (i) aldehyde [1]

(ii) red ppt./solid [1]

(iii) $2Cu^{2+} + CH_3CHO + 5OH^- \rightarrow Cu_2O + CH_3CO_2^- + 3H_2O$ [1]

[Total: 3]

(f) pH $= pK_a + \log [salt]/[acid] = -\log(9.3 \times 10^{-4}) + \log (0.8/0.5)$
$= 3.032 + 0.204 =$ **3.23/3.24** (3 or more sig. figs.) [2]

[Total: 2]

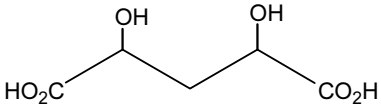
[TOTAL: 20]

4 (a) (i) ketone/carbonyl [NOT aldehyde] [1]

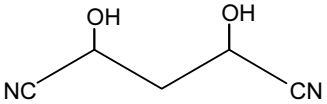
(ii) carboxylic acid (<u>name</u> of group needed. NOT 'carboxyl') [1]

[Total: 2]

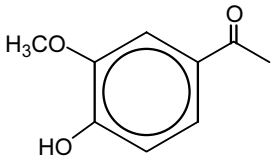
(b) (i) *(allow structural, displayed or skeletal formulae in* **(b)**, **(c)** *and* **(e)***)*



B



C



D

[1] + [1] + [1]

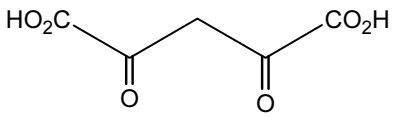
(ii) heat/reflux/boil/hot/T>60°C in H_3O^+ **or** aqueous/dilute $H^+/HCl/H_2SO_4$ (**NOT** HNO_3) [1]

[Total: 4]

(c) (i) reduction/redox (allow nucleophilic addition **or** hydrogenation, as appropriate from **(ii)**) [1]

(ii) $NaBH_4$ **or** $LiAlH_4$ **or** H_2 + Ni/Pt **or** Na + ethanol [1]

(iii)



A

[1]

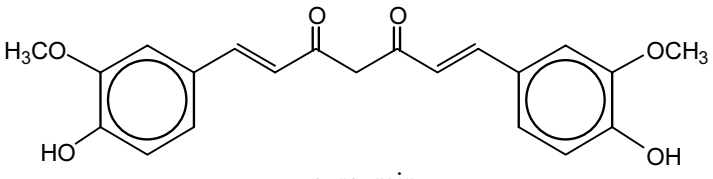
[Total: 3]

(d) (i) alkene/C=C/C-C double bond [1]

(ii) phenol **and** alkene/C=C/C-C double bond [1]

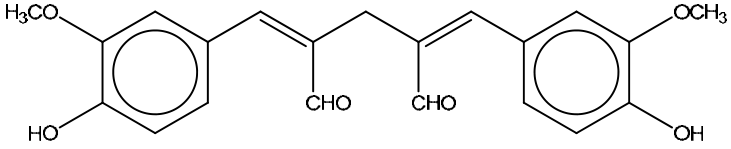
[Total: 2]

(e)



curcumin

allow



complete formula [2]

[Total: 2]

[TOTAL: 13]

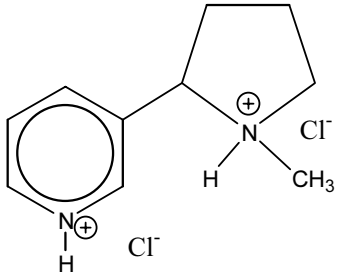
5 (a) (i) contains a lone pair on N (that can react with H^+) [1]

(ii) e.g. $C_2H_5NH_2 + H(Cl) \longrightarrow C_2H_5NH_3^+ (Cl^-)$ [1]
or $C_2H_5NH_2 + H_3O^+ \longrightarrow C_2H_5NH_3^+ + H_2O$
or $C_2H_5NH_2 + H_2O \longrightarrow C_2H_5NH_3^+ + OH^-$ etc

e.g. $C_2H_5NH_2 + CH_3Br \longrightarrow C_2H_5NHCH_3 + HBr$
or $C_2H_5NH_2 + CH_3COCl \longrightarrow CH_3CONHC_2H_5 + HCl$ [1]

(iii) the lone pair (on N) in phenylamine overlaps with ring **or** is delocalised [1]
electron density of N is reduced **or** N becomes more positive **or** lone pair is less available [1]

(iv)

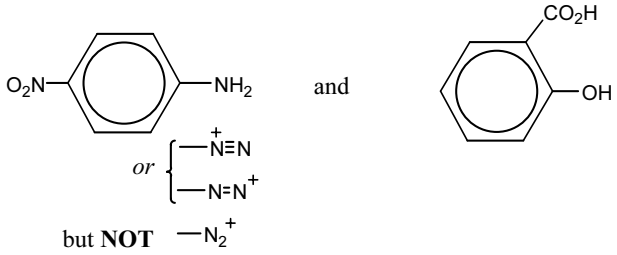


[1] + [1]

[7 max 6]

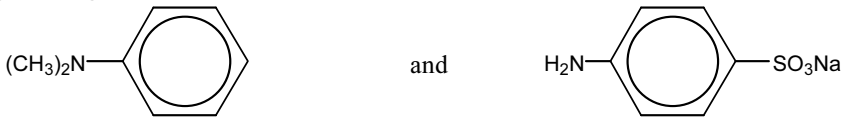
(b) (i) $NaNO_2$ + HC*l*/H^+ **or** HNO_2 (HNO_3 or NO_3^- negates this mark) [1]
$-10\,^oC < T \leqslant 10\,^oC$ *or* 'less than 10 °C' [1]

(ii) alizarin yellow R:



[1] + [1]

methyl orange:



(NH_2 alternatives as above)

[1] + [1]

(iii) makes the molecule (more) hydrophilic/soluble in water (due to H-bonding or ionic solvation)
or increases its melting point [1]

[Total: 7]

[TOTAL: 13]

6 **(a)** It has no chiral centre/asymmetric carbon/optical isomers **or** is not optically active [1]

[Total: 1]

(b) **(i)** structure – α-helix *or* β-(pleated) sheet [1]

hydrogen (bonding) (for either) [1]

(ii) *any two pairs from the following:*

bonding	***possible amino acid***
van der Waals'	ala, gly, leu, ile, val, pro, phe, try, met
ionic	asp, arg, glu, his, lys
disulfide bond	cysteine
hydrogen bond	asn, asp, arg, gln, glu, his, lys, ser, thr, try, tyr

[1] + [1] [1] + [1]

(candidates can identify amino acids by name, three-letter abbreviation, formula of sidechain or formula of whole amino acid)

[Total: 6]

(c) (globular proteins/enzymes need) polar/H-bonding/ionic (side chains) so as to....
....enhance their solubility **or** as part of their active site **or** to help their catalytic activity [1]

[Total: 1]

(d) **(i)** A – T [1]
C – G [1]

(ii) (start **or** met) – **gly – ser – leu – ala – ser** – (stop)
If an amino acid is shown before gly, then it must be met.
correct sequence of the 5 **in bold** [2]

(iii) leu would be replaced by val [1]

[Total: 5]

[TOTAL: 13]

7 (a) (i) No. of carbon atoms present in **J** is $\frac{100 \times 1.3}{1.1 \times 23.5}$ = 5 carbons (must show working) [1]

(NMR spectrum shows) **10 H** (atoms present) (no reasoning need be shown) [1]

(ii) Oxygen **or** O_2 **or** O [1]

(iii) **J** is $(CH_3CH_2)_2C=O$ [1]

any one from:
quartet/4 peaks (at δ 2.5) shows an adjacent CH_3 **or** 3 adjacent H
triplet/3 peaks (at δ 1.1) shows an adjacent CH_2 **or** 2 adjacent H
two (chemical/hydrogen) environments
pair of peaks in ratio 6 :4 are (two) ethyl groups **or** the triplet + quartet shows an ethyl group
δ 2.5 implies there's a CH_2 next to C=O [1]

[Total: 5]

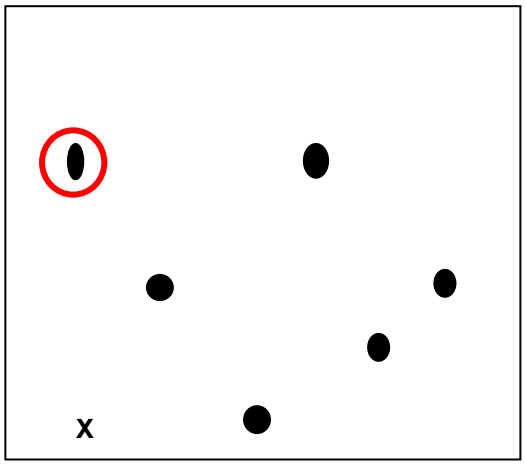
(b) (i)

technique	*physical method*
paper chromatography	**partition**
thin-layer chromatography	**adsorption**
gas-liquid chromatography	**partition**

[2]

(ii) 4 [1]

(iii)



correct spot circled [1]

(iv) 3 [1]

[Total: 5]

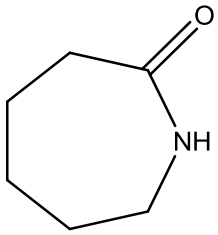
[TOTAL: 10]

8 (a) A monomers: $H_2N–(CH_2)_6–NH_2$ and $HO_2C–(CH_2)_4–CO_2H$ **or** $ClCO(CH_2)_4COCl$ [1]

Condensation **or** nucleophilic substitution **or** addition-elimination [1]

B monomer: $H_2C=CHCH_3$ [1]

Addition (NOT additional) [1]

C monomer: $H_2N–(CH_2)_5–CO_2H$ **or** $H_2N–(CH_2)_5–COCl$ **or** 

[1]

Condensation [1]

[max 5]

(b) (i) Need a statement from both columns for [1] mark.

(a)	(b)
more compact packing in **A** chains closer in **A** chains further apart in **B**	stronger (inter-chain) forces in **A** hydrogen bonding in **A** weaker (inter-chain) **or** van der Waals' forces in **B** **B** contains side-chain/branched chains

[1]

(ii) Polymer **B** – van der Waals'/London (dispersion) forces/induced-instantaneous/induced dipoles
NOT just 'dipole' [1]

[Total: 2]

[TOTAL: 7]