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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

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Page 2	Mark Scheme	Syllabus	Paper
	GCE A LEVEL – October/November 2012	9701	43

1 (a) MgCl₂: forms a (colourless) solution **or** dissolves.

A
$$lCl_3$$
: produces a white ppt **or** steamy fumes [1]

$$2A lC l_3 (or A l_2 C l_6) + 3H_2O \longrightarrow A l_2O_3 + 6HC l$$

$$(or A lC l_3 + 3H_2O \longrightarrow A l(OH)_3 + 3HC l)$$
[1]

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

SiC14: produces a white ppt or steamy fumes

$$\operatorname{SiC} l_4 + 2\operatorname{H}_2\operatorname{O} \longrightarrow \operatorname{SiO}_2 + 4\operatorname{HC} l \tag{1}$$

(or balanced equation giving H_2SiO_3 or $Si(OH)_4$)

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

[1]

[1]

[Total: 5]

(c) (i) bonds broken are C–H and I–I =
$$410 + 151 = 561 \,\text{kJ mol}^{-1}$$
 (all bonds = $5731 \,\text{kJ mol}^{-1}$) bonds formed are C–I and H–I = $240 + 299 = 539 \,\text{kJ mol}^{-1}$ (all bonds = $5709 \,\text{kJ mol}^{-1}$) $\Delta H = +22 \,\text{kJ mol}^{-1}$ [2]

(ii) 4 HI + 2 HNO₃
$$\longrightarrow$$
 2 I₂ + N₂O₃ + 3 H₂O (or double) [1]

N: (is reduced from) 5 to 3

[Total: 4]

[TOTAL: 14]

Page 3	Mark Scheme	Syllabus	Paper
	GCE A LEVEL – October/November 2012	9701	43

- **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

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

[Total: 2]

[1]

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

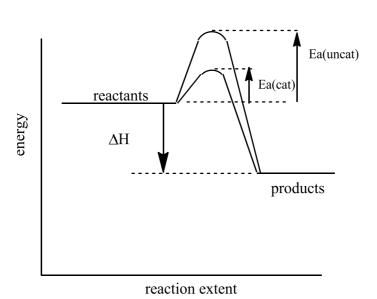
nitrogen reacts with oxygen **or** $N_2 + O_2$ [1]

(ii)
$$NO_2 + SO_2 \longrightarrow NO + SO_3$$

 $NO + \frac{1}{2}O_2 \longrightarrow NO_2$
 $SO_3 + H_2O \longrightarrow H_2SO_4$
 $4NO_2 + 2H_2O + O_2 \rightarrow 4HNO_3$ or $3NO_2 + H_2O \rightarrow 2HNO_3 + NO$ (any 3 equations) $3 \times [1]$

[Total: 5]

(c)



$$\Delta H$$
 shown as negative both E_a labelled and correct – i.e. for the forward reaction $E_a(cat) < E_a(uncat)$

[1] [1]

[1]

[Total: 3]

[TOTAL: 10]

Page 4	Mark Scheme	Syllabus	Paper
	GCE A LEVEL – October/November 2012	9701	43

3 (a) $(1s^22s^22p^6)3s^23p^63d^9$

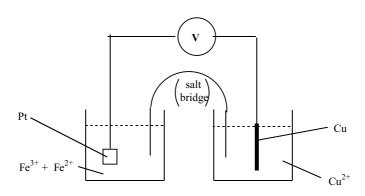
[Total: 1]

[1]

- (b) (i) electron / orbitals near ligands are at a higher energy 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 ∆E [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)	$\begin{split} & [\text{Cu}(\text{H}_2\text{O})_6]^{2^+} + 4\text{NH}_3 \rightarrow [\text{Cu}(\text{H}_2\text{O})_2(\text{NH}_3)_4]^{2^+} + 4\text{H}_2\text{O} \\ & \textit{or} \ [\text{Cu}(\text{H}_2\text{O})_6]^{2^+} + 4\text{NH}_3 \rightarrow [\text{Cu}(\text{NH}_3)_4]^{2^+} + 6\text{H}_2\text{O} \\ & \textit{or} \ [\text{Cu}(\text{H}_2\text{O})_6]^{2^+} + \text{nNH}_3 \rightarrow [\text{Cu}(\text{H}_2\text{O})_{6-n}(\text{NH}_3)_n]^{2^+} + \\ & \text{nH}_2\text{O} \end{split}$	$Cu^{2+} + 2NH_3 + 2H_2O \rightarrow Cu(OH)_2 + 2NH_4^+$ 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]

Page 5	Mark Scheme	Syllabus	Paper
	GCE A LEVEL – October/November 2012	9701	43

(iv) E° will decrease/ be less positive/more negative...

...because $[Cu^{2+}]$ decreases or $Cu^{2+} + 2e^- \Rightarrow Cu$ shifts to the LHS or $E^{e}[Cu(NH_3)_4]^{2+} = -0.05V$ 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 = p K_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))

(ii) heat/reflux/boil/hot/T>60°C in H_3O^+ or aqueous/dilute $H^+/HC1/H_2SO_4$ (NOT HNO₃) [1]

[Total: 4]

Page 6	Mark Scheme	Syllabus	Paper
	GCE A LEVEL – October/November 2012	9701	43

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

[1]

$$HO_2C$$
 CO_2H A

[1]

[Total: 3]

[1]

(ii) phenol and alkene/C=C/C-C double bond

[1]

[Total: 2]

allow
H₃CO
CHO
CHO
OH

complete formula

[2]

[Total: 2]

[TOTAL: 13]

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

[1]

[1]

 $\begin{array}{l} \text{e.g. } C_2H_5NH_2 + CH_3Br \longrightarrow C_2H_5NHCH_3 + HBr \\ \textbf{or} \ C_2H_5NH_2 + CH_3COCl \longrightarrow CH_3CONHC_2H_5 + HC\mathit{l} \end{array}$

[1]

Page 7	Mark Scheme	Syllabus	Paper
	GCE A LEVEL – October/November 2012	9701	43

(iii) the lone pair (on N) in phenylamine overlaps with ring **or** is delocalised 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) NaNO₂ + HC
$$1$$
/H⁺ or HNO₂ (HNO₃ or NO₃⁻ negates this mark) [1]
-10 °C < T \leq 10 °C or 'less than 10 °C' [1]

(ii) alizarin yellow R:

$$O_2N$$
 O_2N
 O_2N

[1] + [1]

methyl orange:

$$(CH_3)_2N$$

and

$$H_2N$$
 SO_3Na

(NH₂ 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

[Total: 7]

[1]

[TOTAL: 13]

Page 8	Mark Scheme	Syllabus	Paper
	GCE A LEVEL – October/November 2012	9701	43

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

[Total: 1]

(b) (i) structure –
$$\alpha$$
-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
F41 - F41	F4 7 . F47

[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]

(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]

Page 9	Mark Scheme	Syllabus	Paper
	GCE A LEVEL – October/November 2012	9701	43

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 CH₃ **or** 3 adjacent H triplet/3 peaks (at δ 1.1) shows an adjacent CH₂ **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 CH₂ next to C=O [1]

[Total: 5]

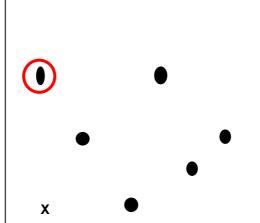
(b) (i)

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]

Page 10	Mark Scheme	Syllabus	Paper
	GCE A LEVEL – October/November 2012	9701	43

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 ${\bf B}$ – van der Waals'/London (dispersion) forces/induced-instantaneous/induced dipoles

NOT just 'dipole' [1]

[Total: 2]

[TOTAL: 7]