

UNIVERSITY OF CAMBRIDGE INTERNATIONAL EXAMINATIONS
GCE Advanced Level

**MARK SCHEME for the October/November 2011 question paper
for the guidance of teachers**

9701 CHEMISTRY

9701/43

Paper 4 (A2 Structured Questions), maximum raw mark 100

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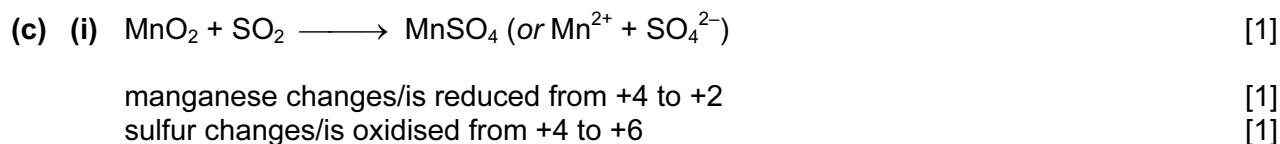


Page 2	Mark Scheme: Teachers' version	Syllabus	Paper
	GCE A LEVEL – October/November 2011	9701	43

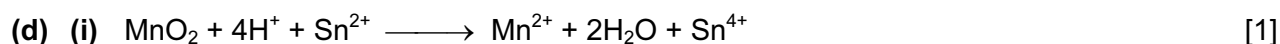


- (b) (i) Any two from
- H^+ is on the oxidant/L.H. side of each of the $\frac{1}{2}$ -equations, *or* H^+ is a reactant
 - (increasing $[\text{H}^+]$) will make E^\ominus more positive
 - (increasing $[\text{H}^+]$) will drive the reaction over to the R.H./reductant side *or* forward direction
- [1] + [1]

- (ii) KMnO_4 : Purple/violet to colourless (allow very pale pink) [1]
 $\text{K}_2\text{Cr}_2\text{O}_7$ Orange to green [1]
[4]



- (ii) **No effect**, because H^+ does not appear in the overall equation *or* its effect on the $\text{MnO}_2/\text{Mn}^{2+}$ change is cancelled out by its effect on the $\text{SO}_2/\text{SO}_4^{2-}$ change [1]
[4]



- (ii) $n(\text{MnO}_4^-) = 0.02 \times 18.1/1000 = 3.62 \times 10^{-4} \text{ mol}$ [1]
 $n(\text{Sn}^{2+}) = 3.62 \times 10^{-4} \times 5/2 = 9.05 \times 10^{-4} \text{ mol}$ [1]
 $n(\text{Sn}^{2+})$ that reacted with $\text{MnO}_2 = (20 - 9.05) \times 10^{-4} = 1.095 \times 10^{-3} \text{ mol}$ [1]
reaction is 1:1, so this is also $n(\text{MnO}_2)$
mass of $\text{MnO}_2 = 1.095 \times 10^{-3} \times (54.9+16+16) = 0.0952 \text{ g}$ [1]
 \Rightarrow **95% – 96%**; 2 or more s.f. [1]
[6]

[Total: 16]

Page 3	Mark Scheme: Teachers' version	Syllabus	Paper
	GCE A LEVEL – October/November 2011	9701	43

- 2 (a) (i) A molecule/ion/species with a lone pair (of electrons) or electron pair donor...
.... that bonds to a metal ion/transition element.... [1]
- (ii) ...by means of a dative/coordinate (covalent) bond [1]
[2]
- (b) (i) straight line from (0, 0.01) to point at (350, 0.0028) with all points on the line [1]
- (ii) order w.r.t. $\text{Cr}(\text{CO})_6$ is 1 **and** order w.r.t. PR_3 is zero [1]
because (a) $\text{Cr}(\text{CO})_6$ graph has a constant half-life (which is 700 s)
or construction lines on graph showing this) [1]
because (b) PR_3 graph is a straight line (of constant slope) or line shows a constant rate
of reaction or no change in rate or shows a linear decrease [1]
- (iii) rate = $k[\text{Cr}(\text{CO})_6]$ [1]
 $k = (0.9 - 1.1) \times 10^{-3} \text{ (s}^{-1}\text{)}$ (one or more s.f.) [1]
either $\text{rate}_0 = 0.01/1020 = 9.8 \times 10^{-6} \text{ mol sec}^{-1}$ when $[\text{Cr}(\text{CO})_6] = 0.01 \text{ mol dm}^{-3}$
so $k = 9.8 \times 10^{-6}/0.01 = 9.8 \times 10^{-4}$
or $t_{1/2} \approx 700 \text{ sec}$
 $k = 0.693/700 = 9.9 \times 10^{-4}$
- (iv) (units of k are) sec^{-1} [1]
- (v) N.B. the chosen mechanism must be consistent with the rate equation in (iii). Thus:
either if rate = $k[\text{Cr}(\text{CO})_6]$
mechanism **B** is consistent [1]
because it's the only mechanism that does NOT involve PR_3 in its slow/rate-determining
step or only $\text{Cr}(\text{CO})_6$ is involved in slow step or $[\text{PR}_3]$ does not affect the rate [1]
- or
if rate = $k[\text{Cr}(\text{CO})_6][\text{PR}_3]$, then
mechanism **A** or **C** or **D** is consistent [1]
because both reactants are involved in slow step [1]
[9]

[Total: 11]

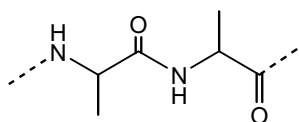
Page 4	Mark Scheme: Teachers' version	Syllabus	Paper
	GCE A LEVEL – October/November 2011	9701	43

3 (a) (i) E is $\text{CH}_3\text{CH}(\text{NH}_2)\text{CN}$ [1]

(ii) $\text{C}_6\text{H}_5\text{CH}_2\text{CHO}$ [1]
[2]

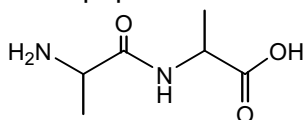
(b) (i) a polymer/polypeptide of amino acids, (joined by peptide bonds)
(allow 'chain' of amino acids' but not 'sequence': the idea of 'many' has to be conveyed) [1]

(ii)



peptide bond shown in full (C=O) in an ala-ala fragment in a chain
two repeat units [1]
[1]

Allow peptide bond shown in full (C=O) in a dipeptide ala-ala for 1 mark

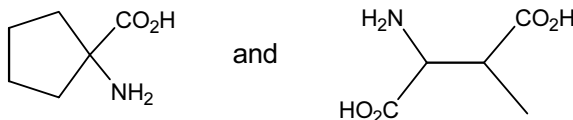


[3]

(c) (i) HCl or H_2SO_4 or NaOH or H^+ or OH^- reagents [1]
+ heat and $\text{H}_2\text{O}/\text{aq}$ (allow H_3O^+).

If T is quoted, $80\text{ }^\circ\text{C} < T < 120\text{ }^\circ\text{C}$. NOT warm. conditions [1]

(ii)



(if a structural formula, it must have all H atoms) allow protonated or deprotonated versions [1] + [1]

[max 3]

(d) (i) $\text{NH}_3^+ - \text{CH}(\text{CH}_3) - \text{CO}_2^-$ [1]

(ii)

compound	zwitterion

[3]

[4]

(e) (i) A buffer is a solution whose pH stays **fairly** constant *or* which maintains **roughly** the same pH *or* which resists/minimises changes in pH [1]
when **small/moderate** amounts of acid/ H^+ *or* alkali/ OH^- are added [1]

(ii) $\text{NH}_2\text{CH}(\text{CH}_3)\text{CO}_2\text{H} + \text{H}(\text{Cl}) \longrightarrow \text{}^+\text{NH}_3\text{CH}(\text{CH}_3)\text{CO}_2\text{H} + \text{Cl}^-$ [1]

(iii) blood contain HCO_3^- (*or* in an equation) [1]
which absorbs H^+ *or* equn $\text{H}^+ + \text{HCO}_3^- \longrightarrow \text{H}_2\text{CO}_3 (\text{H}_2\text{O} + \text{CO}_2)$ [1]
or absorbs OH^- *or* equn $\text{OH}^- + \text{HCO}_3^- \longrightarrow \text{CO}_3^{2-} + \text{H}_2\text{O}$ [1]

(iv) $[\text{CH}_3\text{CO}_2\text{Na}] = 0.05$ $[\text{CH}_3\text{CO}_2\text{H}] = 0.075$ [1]
 $\text{pH} = 4.76 + \log (0.05/0.075) = \mathbf{4.58}$ *or* $\mathbf{4.6}$ [1]

[7]

[Total: 19]

Page 6	Mark Scheme: Teachers' version	Syllabus	Paper
	GCE A LEVEL – October/November 2011	9701	43



- (b) (down the group) nitrates become **more stable** or require a higher temperature to decompose [1]
as size/radius of (cat)ion increases or charge density of ion decreases [1]
so polarisation/distortion of **anion/nitrate** decreases [1]
[3]



- (ii) radius of Li ion/ Li^+ is less than that of Na ion/ Na^+ (or polarising power of M^+ is greater) [1]

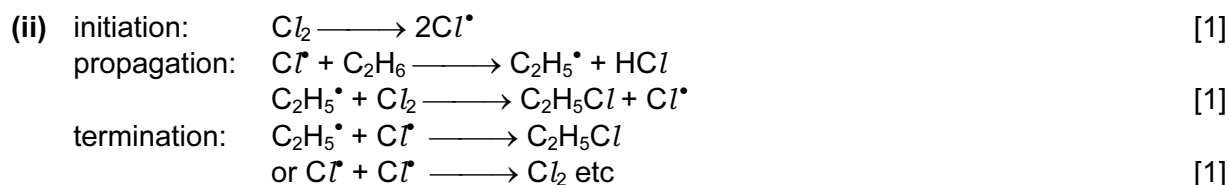
- (iii) Brown/orange fumes/gas would be evolved or glowing splint relights [1]
Since the nitrate is likely to be thermally unstable or decomposes (just like the carbonate) or the balanced equation: $2\text{LiNO}_3 \longrightarrow \text{Li}_2\text{O} + 2\text{NO}_2 + \frac{1}{2}\text{O}_2$ [1]
[4]

[Total: 8]

Page 7	Mark Scheme: Teachers' version	Syllabus	Paper
	GCE A LEVEL – October/November 2011	9701	43

- 5 (a) Alkanes are non-polar *or* have no dipole *or* C–H bonds are strong *or* C and H have similar electronegativities [1]
[1]

- (b) (i) (free) radical substitution *or* substitution by homolytic fission [1]



all 3 names [1]

(iii)

structural formula of by-product	formed by
CH₂Cl–CH₂Cl (or isomer)	further substitution
CH₃CH₂CH₂CH₃	(termination of 2 ×) C₂H₅[•]
CH₃CH₂CH₂CH₂Cl (or isomer)	substitution of C₄H₁₀ by-product

[3]

accept in the “formed by” column the formulae of radicals that will produce the compound in the “by-product” column, or the reagents, e.g. $C_4H_9^\bullet + Cl_2$ *or* $C_4H_9^\bullet + Cl^\bullet$ *or* $C_4H_{10} + Cl_2$ (giving $CH_3CH_2CH_2CH_2Cl$).

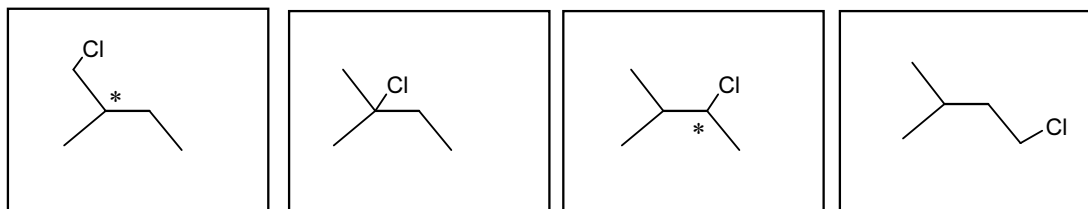
do not allow anything more *Cl*-substituted than **dichlorobutane**.

N.B. C_2H_5Cl is the **major** product, not a **by-product**, so do not allow C_2H_5Cl .

- (iv) J/K = **2.3 : 1** *or* 7:3 *or* 21:9 [2]
 (reason: straightforward relative rate suggests 21:1, but there are 9 primary to 1 tertiary, so divide this ratio by 9. $21/9 = 2.33$)
 allow [1] mark if J/K ratio is given as 21:1;

[10]

(c)



4 isomers 4 × [1]

2 chiral atoms identified correctly, even in incorrect structures

[1] + [1]
[max 5]

[Total: 16]

Page 8	Mark Scheme: Teachers' version	Syllabus	Paper
	GCE A LEVEL – October/November 2011	9701	43

- 6 (a) (i) **K**, because it is the (only) one to contain nitrogen *or* it's an amino acid *or* because it contains CO₂H *or* NH groups [1]
- (ii) molecule: **J**, polymer: RNA (**not** DNA) [1]
or molecule: **L**, polymer: starch, cellulose, glycogen *or* polysaccharide (**not** carbohydrate) [2]
- (b) (i) Covalent bonding [1]
- (ii) Hydrogen bonding [1]
- (iii) Ionic/electrovalent bonding *or* disulphide/–S–S– bonding *or* van der Waals' forces [1]
[3]
- (c) (i) Enzymes [1]
- (ii) • change in pH
• increase in T (NOT decrease; T > 40 °C *or* “too high” are OK)
• addition of heavy metal ions *or* specific, e.g. Hg²⁺, Ag⁺, Pb²⁺ etc.
any two bullet points [1] + [1]
- change in pH disrupts ionic bonds
or metal ions disrupt ionic bonds
or metal ions disrupt –S–S– bonds
or heating disrupts hydrogen bonds
any one [1]
- This changes: the 3D structure *or* shape of the enzyme *or* the active site [1]
[max 4]
- [Total: 9]**

Page 9	Mark Scheme: Teachers' version	Syllabus	Paper
	GCE A LEVEL – October/November 2011	9701	43

7 (a)

structural information	analytical technique
three-dimensional arrangement of atoms and bonds in a molecule	X-ray crystallography/diffraction
chemical environment of protons in a molecule	NMR (spectroscopy) only
identity of amino acids present in a polypeptide	Electrophoresis / chromatography / mass spectrometry

[1] + [1] + [1]
[3]

(b) (i) **paper chromatography;**

The components **partition** between the solvent/moving phase and the water/liquid stationary phase *or* separation relies on different solubilities (of components) in the moving solvent and the stationary water phase. [1]

(ii) **thin-layer chromatography.**

Separation depends on the differential **adsorption** of the components onto the solid particles/phase *or* Al_2O_3 *or* SiO_2 . [1]

[2]

(c) (i) No. of carbon atoms present = $\frac{0.2 \times 100}{5.9 \times 1.1} = 3.08$ hence 3 carbons [1]

(ii) Bromine [1]

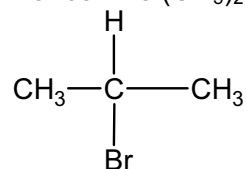
(iii) **One** bromine is present as there is only an M+2 peak / no M+4 peak *or* the M and M+2 peaks are of similar height [1]

(iv) *NMR spectrum shows a single hydrogen split by many adjacent protons and 6 protons in an identical chemical environment. This suggests...*

two $-CH_3$ groups and a lone proton attached to the central carbon atom [1]

Empirical formula of **N** is C_3H_7Br [1]

Hence **N** is $(CH_3)_2CHBr$ *or*



[1]

[6]

[Total: 11]

Page 10	Mark Scheme: Teachers' version	Syllabus	Paper
	GCE A LEVEL – October/November 2011	9701	43

- 8 (a) (i) Soluble form would be most effective [1]
- (ii) **Q**, since the 'mini-pills'/granules/powder have a larger surface area
or **P**, because it has no protective casing [1]
- (iii) The gel coat stops it being broken down while passing through the upper part of the digestive system/stomach
or the gel coat is stable to stomach acid. [1]
[3]
- (b) The drug is taken quickly/directly to the target
or more accurate dosing can be achieved [1]
- When the drug is taken by mouth it has to pass through the stomach/intestine wall to get into the bloodstream. or some is digested/lost to the system [1]
[2]
- (c) (i) condensation (polymerisation) [1]
- (ii) hydrogen bonds or van der Waals' [1]
- (iii) It would change the overall shape of the (drug) molecule
The 'fit' into the active site would be less effective [1] + [1]
- (iv) Hydrolysis [1]
[5]
- [Total: 10]**