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

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 must be read in conjunction with the question papers and the report on the examination.

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UNIVERSITY of CAMBRIDGE
International Examinations

1 **(a)** Cr^{3+}: $1s^22s^22p^6$ $\mathbf{3s^2\ 3p^6\ 3d^3}$ [1]
Mn^{2+}: $1s^22s^22p^6$ $\mathbf{3s^2\ 3p^6\ 3d^5}$ [1]
[2]

(b) **(i)** Any two from

- H^+ is on the oxidant/L.H. side of each of the ½-equations, *or* H^+ is a reactant
- (increasing $[H^+]$) will make $E^\ominus$ more positive
- (increasing $[H^+]$) 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]
$K_2Cr_2O_7$ Orange to green [1]
[4]

(c) **(i)** $MnO_2 + SO_2 \longrightarrow MnSO_4$ (*or* $Mn^{2+} + SO_4^{2-}$) [1]

manganese changes/is reduced from +4 to +2 [1]
sulfur changes/is oxidised from +4 to +6 [1]

(ii) **No effect**, because H^+ does not appear in the overall equation *or* its effect on the MnO_2/Mn^{2+} change is cancelled out by its effect on the SO_2/SO_4^{2-} change [1]
[4]

(d) **(i)** $MnO_2 + 4H^+ + Sn^{2+} \longrightarrow Mn^{2+} + 2H_2O + Sn^{4+}$ [1]

(ii) $n(MnO_4^-) = 0.02 \times 18.1/1000 = 3.62 \times 10^{-4}$ mol [1]
$n(Sn^{2+}) = 3.62 \times 10^{-4} \times 5/2 = 9.05 \times 10^{-4}$ mol [1]
$n(Sn^{2+})$ that reacted with $MnO_2 = (20 - 9.05) \times 10^{-4} = 1.095 \times 10^{-3}$ mol [1]
reaction is 1:1, so this is also $n(MnO_2)$
mass of $MnO_2 = 1.095 \times 10^{-3} \times (54.9+16+16) = 0.0952$ g [1]
$\Rightarrow$ **95% – 96%;** 2 or more s.f. [1]
[6]

[Total: 16]

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. $Cr(CO)_6$ is 1 **and** order w.r.t. PR_3 is zero [1]
because **(a)** $Cr(CO)_6$ 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[$Cr(CO)_6$] [1]

k = (**0.9 – 1.1) × $\mathbf{10^{-3}}$** (s^{-1}) (one or more s.f.) [1]

either $rate_0 = 0.01/1020 = 9.8 \times 10^{-6}$ mol sec^{-1} when [$Cr(CO)_6$] = 0.01 mol dm^{-3}
so $k = 9.8 \times 10^{-6}/0.01 = \mathbf{9.8 \times 10^{-4}}$
or $t_{1/2} \approx 700$ sec
$k = 0.693/700 = \mathbf{9.9 \times 10^{-4}}$

(iv) (units of k are) **$\mathbf{sec^{-1}}$** [1]

(v) N.B. the chosen mechanism must be consistent with the rate equation in **(iii)**. Thus:
either if rate = k[$Cr(CO)_6$]
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 $Cr(CO)_6$ is involved in slow step *or* [PR_3] does not affect the rate [1]

or

if rate = k[$Cr(CO)_6$][PR_3], then
mechanism **A** or **C** or **D** is consistent [1]
because both reactants are involved in slow step [1]
[9]

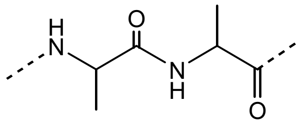
[Total: 11]

3 **(a)** **(i)** **E** is $CH_3CH(NH_2)CN$ [1]

(ii) $C_6H_5CH_2CHO$ [1]
[2]

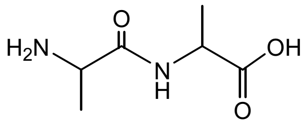
(b) **(i)** a polymer/polypeptide of amino acids, (joined by peptide bonds)
(allow '**chain** of amino acids' but not 'sequence': the idea of 'many' has to be conveyed)
[1]

(ii)



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

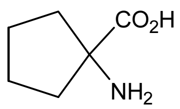
Allow peptide bond shown in full (C=O) in a dipeptide ala-ala for 1 mark



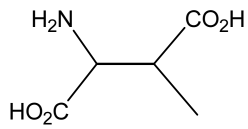
[3]

(c) **(i)** HCl *or* H_2SO_4 *or* NaOH *or* H^+ *or* OH^- reagents [1]
+ heat and H_2O/aq (allow H_3O^+).
If T is quoted, 80 °C < T < 120 °C. NOT warm. conditions [1]

(ii)



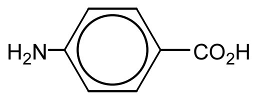
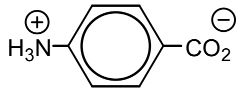
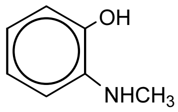
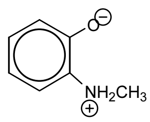
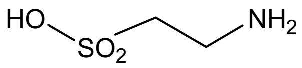
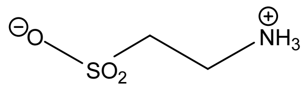
and



(if a structural formula, it must have all H atoms) allow protonated or deprotonated versions [1] + [1]
[max 3]

(d) (i) $NH_3^+–CH(CH_3)–CO_2^-$ [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) $NH_2CH(CH_3)CO_2H + H(Cl) \longrightarrow {}^+NH_3CH(CH_3)CO_2H\ (+\ Cl^-)$ [1]

(iii) blood contain $\mathbf{HCO_3^-}$ (*or* in an equation) [1]
which absorbs H^+ *or* equn $H^+ + HCO_3^- \longrightarrow H_2CO_3\ (H_2O + CO_2)$
or absorbs OH^- *or* equn $OH^- + HCO_3^- \longrightarrow CO_3^{2-} + H_2O$ [1]

(iv) $[CH_3CO_2Na] = 0.05\ [CH_3CO_2H] = 0.075$ [1]
pH = 4.76 + log (0.05/0.075) = **4.58** *or* **4.6** [1]

[7]

[Total: 19]

4 **(a)** $Ca(NO_3)_2 \longrightarrow CaO + 2NO_2 + ½\, O_2$ [1]

[1]

(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]

(c) **(i)** $Li_2CO_3 \longrightarrow Li_2O + CO_2$ [1]

(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: $2LiNO_3 \longrightarrow Li_2O + 2NO_2 + ½O_2$ [1]

[4]

[Total: 8]

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]

(ii) initiation: $Cl_2 \longrightarrow 2Cl^{\bullet}$ [1]

propagation: $Cl^{\bullet} + C_2H_6 \longrightarrow C_2H_5^{\bullet} + HCl$

$C_2H_5^{\bullet} + Cl_2 \longrightarrow C_2H_5Cl + Cl^{\bullet}$ [1]

termination: $C_2H_5^{\bullet} + Cl^{\bullet} \longrightarrow C_2H_5Cl$

or $Cl^{\bullet} + Cl^{\bullet} \longrightarrow Cl_2$ etc [1]

all 3 names [1]

(iii)

structural formula of by-product	formed by
$CH_2Cl–CH_2Cl$ (or isomer)	**further substitution**
$CH_3CH_2CH_2CH_3$	**(termination of 2 ×) $C_2H_5^{\bullet}$**
$CH_3CH_2CH_2CH_2Cl$ (or isomer)	**substitution of C_4H_{10} 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 **di**chlorobutane.

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

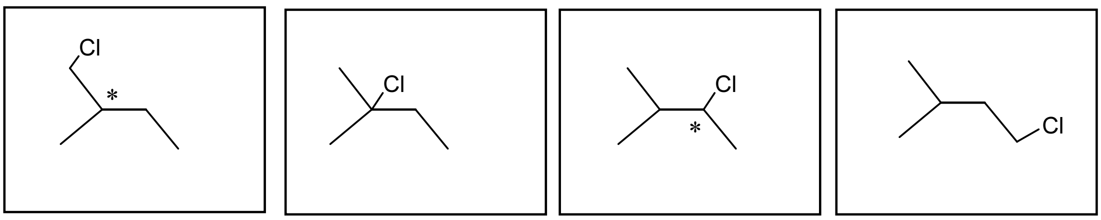
(iv) J/K = **2.3 : 1** *or* 7:3 *or* 21:9 [2]

(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]

6 **(a)** **(i)** **K**, because it is the (only) one to contain nitrogen *or* it's an amino acid *or* because it contains CO_2H *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. Hg^{2+}, Ag^{+}. Pb^{2+} 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]

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]

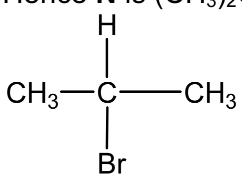
(ii) Bromine [1]

(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]

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]