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

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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) × 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 $k = 9.8 \times 10^{-6}/0.01 =$ **9.8×10^{-4}**
or $t_{1/2} \approx 700$ sec
$k = 0.693/700 =$ **9.9×10^{-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 = $k[Cr(CO)_6]$
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]

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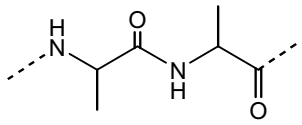
3 (a) (i) **E** is $CH_3CH(NH_2)CN$ [1]

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

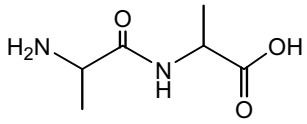
(b) (i) a polymer/polypeptide of amino acids, (joined by peptide bonds)
(allow '**chain** of amino acids' but not 'sequence': the idea of 'many' has to be conveyed)
[1]

(ii)



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

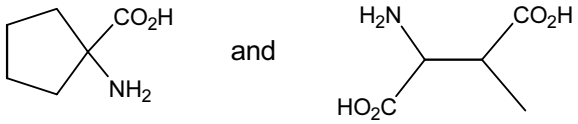
Allow peptide bond shown in full (C=O) in a dipeptide ala-ala for 1 mark



[3]

(c) (i) HC*l 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 ^oC < T < 120 ^oC. NOT warm. conditions [1]

(ii)



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

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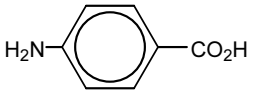
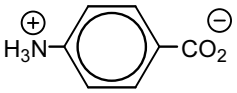
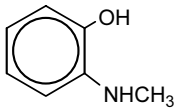
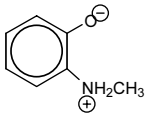
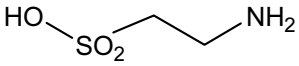
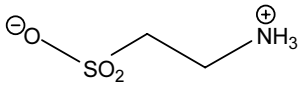
(d) (i) $NH_3^+–CH(CH_3)–CO_2^-$ [1]

(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 **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]

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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]

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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 C*l*–substituted than **di**chlorobutane.

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

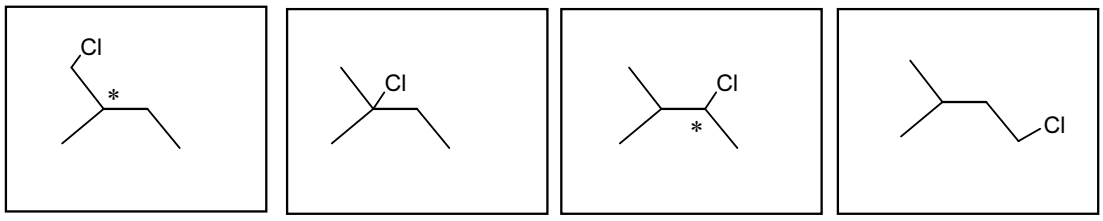
(iv) J/K = **2.3 : 1** *or* 7:3 *or* 21:9 [2]

(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]

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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]

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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]

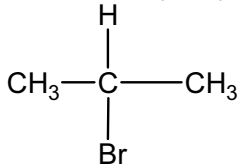
(ii) Bromine [1]

(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]

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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]

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