UNIVERSITY OF CAMBRIDGE INTERNATIONAL EXAMINATIONS

GCE Advanced Subsidiary Level and GCE Advanced Level

MARK SCHEME for the May/June 2008 question paper

9701 CHEMISTRY

9701/04 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.

All Examiners are instructed that alternative correct answers and unexpected approaches in candidates' scripts must be given marks that fairly reflect the relevant knowledge and skills demonstrated.

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

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International Examinations

1 (a) (i) **A** is Cl_2/chlorine [1]

B is NaCl *or* HCl *or* Cl^- [or words], etc. [1]

C is salt bridge or KCl/KNO_3, etc. [1]

D is platinum/Pt [1]

E is Fe^{2+} + Fe^{3+} or mixture of Fe(II) + Fe(III) salts [1]

mention of standard conditions ([Cl^-] of 1 mol dm^{-3} *or* Cl_2 at 1 atmos
or T = 25°C/298 K) [1]

(ii) $E^\ominus = E^\ominus_R - E^\ominus_L = 0.77 - 1.36 = (-)\mathbf{0.59}$ (V) (ignore sign) [1]

(since R.H. electrode is negative) electrons flow (from right) **to left** *or* to the chlorine electrode *or* anticlockwise *or* from (beaker) **E** to (beaker) **B** [1] **[8]**

(b) (i) $\Delta H = 3 \times(-167.2) + (-48.5) - (-399.5)$ [1]
$= \mathbf{-150.6}$ *or* **151** (kJ mol^{-1}) [1]
(correct ans [2])

(ii) $2Fe^{3+} + Cu \longrightarrow 2Fe^{2+} + Cu^{2+}$ [1]
(*or* molecular: 2FeCl_3 + Cu $\longrightarrow$ 2FeCl_2 + CuCl_2)

$E^\ominus = 0.77 - 0.34 = (+)$ **0.43** (V) [1]
(no mark for –0.43V) **[4]**

[Total: 12 max 11]

2 (a) (i) $\Delta H = 4 \times 278 - 244 - 2 \times 496$ [1]
$= \mathbf{-124}$ (kJ mol^{-1}) [1]
(correct ans [2])

(ii) shape is bent/V-shaped/non-linear (*or* diagram) [1]
due to (one) lone pair *and/or* (1) odd/unpaired electron (*or* shown on diag) [1]
(assume electrons are on chlorine unless explicitly stated otherwise, in which case award no mark)

(iii) $3KClO_3 + H_2SO_4 \longrightarrow K_2SO_4 + KClO_4 + H_2O + 2ClO_2$ [1] **[5]**

(b) (i) coal-fired power stations; fuel in cars; car exhausts/gas emissions; other named use of a fossil fuel; contact process; cement manufacture; brick manufacture; roasting of sulphide ores; burning tyres (any 2) [1]
(NOT volcanoes etc; NOT burning of natural gas)
(no marks for only 1 correct source)

(ii) causes **acid rain** [1]
which lower pH of lakes; leaches aluminium from soils; kills fish/plants/rainforests; dissolves/corrodes/damages buildings (any 1) [1]
(NOT asthma etc – since this is not environmental) **[3]**

(c) (i) CO_2: simple + molecular/covalent *or* weak intermolecular forces
SiO_2: giant/macro + molecular/covalent
SnO_2: ionic/electrovalent (ignore "giant") (all 3 correct) [2]
(2 correct = [1], 1 correct = [0])

(ii) SnO_2 is stable, PbO_2 is not *or* SnO_2 is the more stable [1]
$PbO_2 \longrightarrow PbO + ½\ O_2$ [1]

(iii) $H_2O + CO_2 \rightleftharpoons H^+ + HCO_3^-$ [1]
$K_c = [H^+][HCO_3^-]/[H_2O][CO_2]$ *or* $= [H^+][HCO_3^-]/[CO_2]$ ecf [1]

(iv) $HCO_3^- + H^+ \longrightarrow H_2CO_3$ *or* $H_2O + CO_2$ (or equation with H_3O^+) [1]
$HCO_3^- + OH^- \longrightarrow CO_3^{2-} + H_2O$ (NB **NOT** $H_2CO_3 + OH^- \rightarrow$) [1]

(words can substitute for one of the equations but not both. If two correct word descriptions are given, in the absence of at least one correct equation, award [1] mark only) **[8]**

[Total: 16 max 15]

3 (a) tetrahedral diagram (either dashed+wedge, or similar representation) [1]
angles (all) 109° – 110° [1]
(award [0] for part **(a)** if an angle of 90° or 180° is mentioned) **[2]**

(b) volatility decreases *or* boiling points increase
(allow b.pt. CCl_4 > $SiCl_4$ but b.pt. increases thereafter) [1]
due to greater van der Waals'/intermolecular forces *or* due to more electrons [1]
(mention of "ions" negates this mark) **[2]**

(c) (i) Pb^{4+}/Pb^{2+}: $E^\ominus = +1.69V$, Sn^{4+}/Sn^{2+}: $E^\ominus = +0.15V$, [both] [1]
a valid comment about relative redox power *or* stability, e.g.:
(hence) Sn^{2+} easily oxidised *or* Sn^{4+} is more stable than Sn^{2+} *or*
Pb^{4+} is easily reduced *or* Pb^{2+} is more stable than Pb^{4+} *or*
+2 oxidation state more stable down the group [1]

(ii) $Sn^{2+} + I_2 \longrightarrow Sn^{4+} + 2I^-$ [1]
$Pb^{4+} + SO_2 + 2H_2O \longrightarrow 4H^+ + SO_4^{2-} + Pb^{2+}$ [1]
(N.B. no marks in **(ii)** for $E^\ominus$ values) **[4]**

(d) (i) for Si: $\Delta H = 244 – 2(359) =$ **–474** (kJ mol^{-1}) [1]
for Sn: $\Delta H = 244 – 2(315) =$ **–386** (kJ mol^{-1}) [1]
(allow [1] out of [2] salvage mark for 474 & 386; 962 & 874; *or* –962 & –874)

(ii) Yes: the +4 state becomes decreasingly stable – the ΔH is less exothermic [1]
(mark is for relating ΔHs to stability: allow ecf from **d(i)** and also from **c(i)**) **[3]**

[Total: 11]

4 **(a)** ester [1] **[1]**

(b) reaction I: acid/H^+/HC*l*/H_2SO_4 <u>or</u> alkali/OH^-/NaOH (followed by H^+) [1]
heat/reflux and aqueous (allow H_3O^+ to equal H^+ + aq, also assume "conc" *or* "dil" means aq (but NOT H_2SO_4) also allow aqueous ethanol) [1]
(for heat: allow T ≥ 80°C; **not** "warm")

reaction II: methanol/CH_3OH [1]
heat with **conc.** H_2SO_4/H_3PO_4 *or* HC*l*(**g**) [**NOT** conc HC*l*] [1] **[4]**

(c) **(i)** $BrCH_2$-CHBr-CH_2Br [1]

(ii) HO_2C-CO-CO_2H [1] **[2]**

(d) 890g of triglyceride produces 3 × 298 = 894g of biodiesel [1]
∴ 500kg produces 500 × 894/890 = **502**kg biodiesel ecf [1]
(correct ans [2])
(1004/1005kg *or* 167kg is worth [1]: 333kg is worth [0]) **[2]**

(e) **(i)** $C_{17}H_{35}CO_2CH_3 + 27.5\ O_2 \longrightarrow 19CO_2 + 19H_2O$ [1]
(*or* $C_{19}H_{38}O_2$)

(ii) 10 × 44 × 19/298 = **28.(05)/28.1**kg ecf from equ [2]
(–1 for each error)
some ecf values: n = 18 ⇒ 26.6kg
n = 17 ⇒ 25.1kg (allow [2] for each)
n = 16 ⇒ 23.6kg **[3]**

(f) any one of the following.
- (saving) diminishing resources
- economic argument (NOT just "cheaper") – e.g. oil will become increasingly more expensive as it runs out
- ref to CO_2 cycle (e.g. no net increase in CO_2, i.e. "carbon neutral") *or* less global warming (due to a smaller carbon "footprint")
- renewable/sustainable
- the effect of biofuel cultivation on world food prices

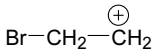
[1] **[1]**

[Total: 13]

5 (a) reaction I electrophilic addition [1]

reaction II electrophilic substitution [1]
(salvage: award [1] out of [2] for "addition" + "substitution", even if nucleophilic) **[2]**

(b) reaction I: intermediate [1]



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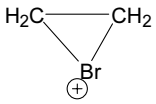
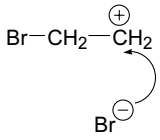


second step, attack of Br^- on bromocation. [1]



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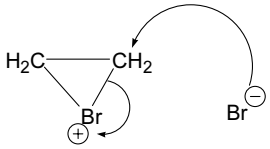
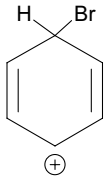


reaction II: intermediate [1]



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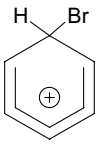
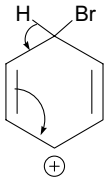


(*or* with ⊕ in 2-position) (make sure ⊕ is not at sp^3 C-atom)

second step, loss of H^+ from bromocation. [1]



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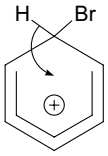
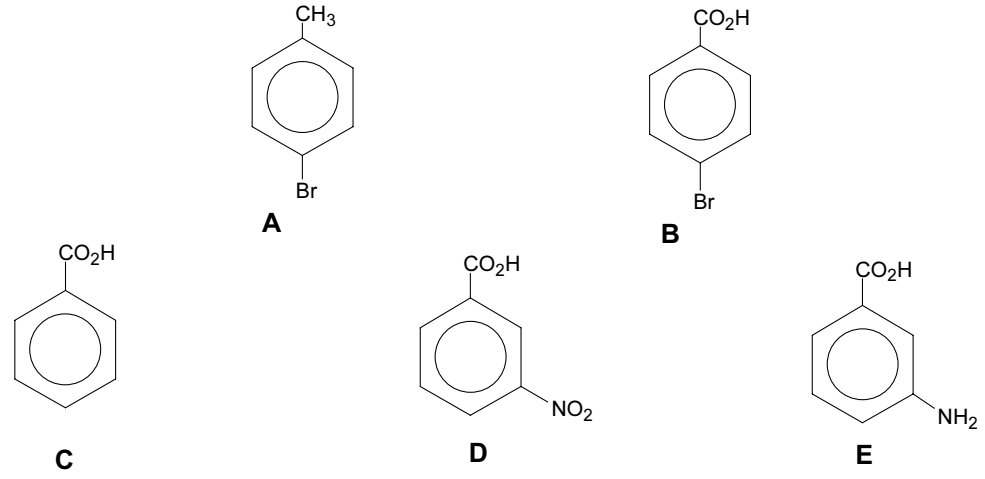


[4]

(c) **Delocalised** ring of electrons (in benzene) is **stable**, (so is re-formed in second step in benzene.)
or electrons in the ethene π bond are localised/more available for reaction with electrophiles
[1] **[1]**

[Total: 7]

6



5 x [1]

[deduct [1] mark if ring circle omitted more than once]
[allow ecf for **E** from structure of **D**]
[allow ecf for **B** from structure of **A**]
[allow $-CO_2^-$ for **E**] **[5]**

[Total: 5]

7

polymer	addition/condensation?	formulae of monomers
1	condensation	$HO_2C\text{-}CO_2H$ *or* $ClCO\text{-}COCl$ $NH_2\text{-}CH_2\text{-}CH_2\text{-}NH_2$
2	condensation	$HO\text{-}CH_2\text{-}CH(C_2H_5)\text{-}CO_2H$ $HO\text{-}CH_2\text{-}CH(CH_3)\text{-}CO_2H$
3	addition	$CH_2{=}CH\text{-}CH_3$ $CH_2{=}CH\text{-}CONH_2$ $CH_2{=}CH\text{-}C_6H_5$

⇑ [2] (2 correct: [1])

⇑ [6] (6 correct: [5]) etc

(2 correct: [1])
(C=C bonds not needed, but penalise –[1] if C-C drawn instead of C=C)
(if more than 7 formulae drawn, then penalise –[1] for each formula in excess of 7) **[8]**

[Total: 8]

8 (a) primary: covalent (ignore amide, peptide etc) [1]
diagram showing peptide bond: (-CHR-)CONH(-CHR-) [1]

secondary: hydrogen bonds (NOT "..between side chains") [1]
diagram showing N-H···O = C [1]

tertiary: two of the following:
- hydrogen bonds (diag. must show H-bonds *other* than those in *α*-helix *or* *β*-pleated sheet – e.g. ser-ser)
- electrostatic/ionic attraction,
- van der Waals'/hydrophobic forces/bonds,
- (covalent) disulphide (links/bridges) [1] + [1]

suitable diagram of **one** of the above [1]
(for disulphide: S-S **not** S=S or SH-SH) **[7]**

(b) met-ala-gly-ala-gly-arg-val-lys [2]
any **possible** sequence with more than 8 residues, that "uses" all 6 tripeptides (overlapping or not), and that starts with *met* and ends with *lys* is worth [1] mark
any sequence that does **not** start with *met* or end with *lys* gets zero. **[2]**

(c) CARE – this is not about DNA!
candidates should describe **TWO** potential effects on tertiary or quaternary structures caused by amino acid sidechains...
these include: disruption of H-bonding
disruption of disulphide bridges
disruption of electrostatic/ionic attraction
disruption of van der Waals' forces
(only allow effects on the secondary structure if proline is specifically mentioned)
2 x [1]

then award [1] mark each for **two** of the following bullet points:
- a description of the amino acids involved in the above, (*or* a labelled diagram)
  (award [1] mark for each example)
  a description of an *effect* of interchanging amino acids, such as the..
- unfolding of tertiary structure/different folding/different shape (NOT denatured)
- inactivity of an enzyme *or* changing the active site
- causing of a protein to become less soluble/coagulate (e.g. sickle cells)

2 x [1]
[4]

[Total: 13 max 12]

9 (a) (i)+(ii) any two of:
molecular mass/size/M_r/shape
(overall electrical) charge (on the species)
voltage/size/P.D. (of applied electric field) [1] + [1]
(salvage: if just "mass & charge" is mentioned, with no reference to species or molecule, award [1])

[2]

(b) (i) CH_3COCH_3 would show
a single peak/no splitting since all the Hs are in the same chemical environment
or a peak at δ = 2.1 due to CH_3CO group [1]

CH_3CH_2CHO would show 3 (sets of) peaks since there are 3 different proton environments
or there would be a peak at δ = 9.5 – 10.0 due to the –CHO group
or a peak at δ = 0.9 due to CH_3
or a peak at δ1.3 due to CH_2 [1]

(reasons needed for the marks. Salvage: if reasons are not given, but candidate states that propanone will have one peak and propanal three, then award [1] mark)

(ii) different fragments:

- CH_3COCH_3 would form **fewer** fragments (must be stated in words)
- CH_3COCH_3 would form a fragment of CH_3CO^+ *or* at (m/e) 43
- CH_3CH_2CHO would form a fragment of $CH_3CH_2^+$ *or* CHO^+ at (m/e) 29
- CH_3CH_2CHO would form a fragment of $CH_3CH_2CO^+$ *or* at (m/e) 57

[charges on fragments not required for mark]

any 3 points [3]

[5]

(c) (i) peaks at (m/e) 79 **and** 81 *or* at (m/e) 94 **and** 96 [1]

(ii) in chlorine the M and M+2 peaks are the ratio 3:1 [1]
whereas in bromine they are approx. 1:1 [1] **[3]**

[Total: 10 max 9]

10 (a) any **two** of the following:

- to speed delivery (of drug to target organ), i.e. faster response
- to avoid the drug being hydrolysed/reacted/decomposed (NOT digested) in the stomach
- to allow a smaller dose to be used *or* greater accuracy of dosage
- patient does not have to be conscious

2 × [1] **[2]**

(b) (i) spheres with a diameter of the order of nanometres/in the nanometre range/between 10 & 500 nm [1]

(ii) it is (highly) acidic *or* low pH *or* contains HC*l* (NOT contains enzymes) [1]

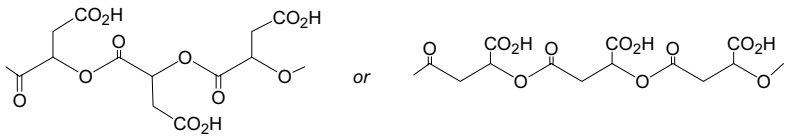
(iii) use hydrogels: of different (wall) thickness/strength (to release drug over time)
of different chemical composition (for different breakdown times)
incorporating pores/holes (in their walls) (any two) [1] + [1]

[4]

(c) for the **homopolymer, *either*** using the amino acid the minimum is:

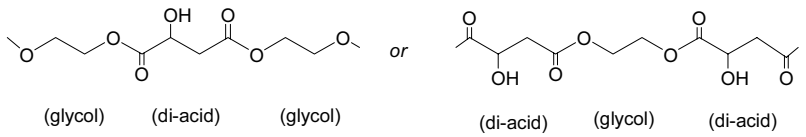
-CO-CHR-NH-CO-CHR-NH-CO-CHR-NH-

or using the hydroxyacid the minimum is:

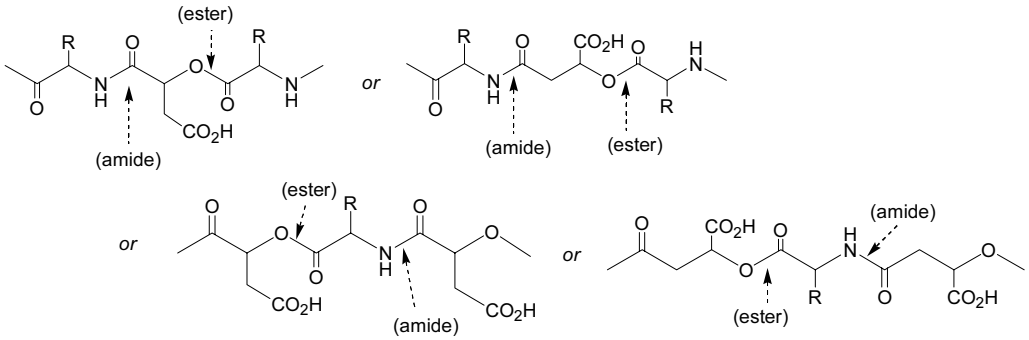


(–[1] for each error) [2]

for the **heteropolymer, *either*** using the glycol compound and the di-acid the minimum is:



or using the amino acid and the di-acid, the minimum is:



(A heteropolymer incorporating all three monomers can also be drawn. This should include an ester linkage between the glycol and one of the CO_2H groups, and an amide linkage between the aminoacid and another CO_2H group. Deduct [1] mark from the whole of section **(c)** if complete compounds are shown rather than sections of chains. Allow 4-monomer sections instead of 3. Allow [2] marks for a polymer section even if **one** end is incomplete (e.g. is lacking an oxygen atom), but if **both** ends are incomplete deduct [1]) (–[1] for each error) [2] **[4]**

[Total: 10 max 9]