## 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.

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| Page 2 | Mark Scheme | Syllabus | Paper |
| :---: | :---: | :---: | :---: |
|  | GCE A/AS LEVEL - May/June 2008 | 9701 | 04 |

1 (a) (i) A is $\mathrm{Cl}_{2} /$ chlorine
$B$ is NaCl or HCl or $\mathrm{Cl}^{-}$[or words], etc.
C is salt bridge or $\mathrm{KC} / \mathrm{KNO}_{3}$, etc.
D is platinum/Pt
E is $\mathrm{Fe}^{2+}+\mathrm{Fe}^{3+}$ or mixture of $\mathrm{Fe}(\mathrm{II})+\mathrm{Fe}(\mathrm{III})$ salts
mention of standard conditions ( $\left[\mathrm{Cl}^{-}\right]$of $1 \mathrm{~mol} \mathrm{dm}^{-3}$ or $\mathrm{Cl}_{2}$ at 1 atmos or $\mathrm{T}=25^{\circ} \mathrm{C} / 298 \mathrm{~K}$ )
(ii) $\mathrm{E}^{\ominus}=\mathrm{E}_{\mathrm{R}}{ }_{\mathrm{R}}-\mathrm{E}_{\mathrm{L}}^{\ominus}=0.77-1.36=(-) \mathbf{0 . 5 9}(\mathrm{V})$ (ignore sign)
(since R.H. electrode is negative) electrons flow (from right) to left or to the chlorine electrode or anticlockwise or from (beaker) $\mathbf{E}$ to (beaker) B
(b) (i) $\Delta \mathrm{H}=3 \times(-167.2)+(-48.5)-(-399.5)$

$$
\begin{equation*}
=-150.6 \text { or } 151\left(\mathrm{~kJ} \mathrm{~mol}^{-1}\right) \tag{1}
\end{equation*}
$$

(correct ans [2])
(ii) $2 \mathrm{Fe}^{3+}+\mathrm{Cu} \longrightarrow 2 \mathrm{Fe}^{2+}+\mathrm{Cu}^{2+}$
(or molecular: $2 \mathrm{FeCl}_{3}+\mathrm{Cu} \longrightarrow 2 \mathrm{FeCl}_{2}+\mathrm{CuCl}_{2}$ )
$\mathrm{E}^{\ominus}=0.77-0.34=(+) \mathbf{0 . 4 3}(\mathrm{V})$
(no mark for -0.43 V )
[Total: 12 max 11]

2 (a) (i) $\Delta H=4 \times 278-244-2 \times 496$
$=-124\left(\mathrm{~kJ} \mathrm{~mol}^{-1}\right)$
(correct ans [2])
(ii) shape is bent/V-shaped/non-linear (or diagram)
due to (one) lone pair and/or (1) odd/unpaired electron (or shown on diag)
(assume electrons are on chlorine unless explicitly stated otherwise, in which case award no mark)
(iii) $3 \mathrm{KClO}_{3}+\mathrm{H}_{2} \mathrm{SO}_{4} \longrightarrow \mathrm{~K}_{2} \mathrm{SO}_{4}+\mathrm{KClO}_{4}+\mathrm{H}_{2} \mathrm{O}+2 \mathrm{ClO}_{2}$
(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
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)

| Syllabus | Paper |
| :---: | :---: |
| 9701 | 04 |

(c) (i) $\mathrm{CO}_{2}$ : simple + molecular/covalent or weak intermolecular forces
$\mathrm{SiO}_{2}$ : giant/macro + molecular/covalent
$\mathrm{SnO}_{2}$ : ionic/electrovalent (ignore "giant")
(all 3 correct) [2]
( 2 correct $=[1], 1$ correct $=[0]$ )
(ii) $\mathrm{SnO}_{2}$ is stable, $\mathrm{PbO}_{2}$ is not or $\mathrm{SnO}_{2}$ is the more stable
$\mathrm{PbO}_{2} \longrightarrow \mathrm{PbO}+1 / 2 \mathrm{O}_{2}$
(iii) $\mathrm{H}_{2} \mathrm{O}+\mathrm{CO}_{2}(\rightleftharpoons) \mathrm{H}^{+}+\mathrm{HCO}_{3}^{-}$
$K_{\mathrm{c}}=\left[\mathrm{H}^{+}\right]\left[\mathrm{HCO}_{3}^{-}\right] /\left[\mathrm{H}_{2} \mathrm{O}\right]\left[\mathrm{CO}_{2}\right]$ or $=\left[\mathrm{H}^{+}\right]\left[\mathrm{HCO}_{3}^{-}\right] /\left[\mathrm{CO}_{2}\right]$
(iv) $\mathrm{HCO}_{3}^{-}+\mathrm{H}^{+} \longrightarrow \mathrm{H}_{2} \mathrm{CO}_{3}$ or $\mathrm{H}_{2} \mathrm{O}+\mathrm{CO}_{2}$ (or equation with $\mathrm{H}_{3} \mathrm{O}^{+}$) [1]
$\mathrm{HCO}_{3}^{-}+\mathrm{OH}^{-} \longrightarrow \mathrm{CO}_{3}^{2-}+\mathrm{H}_{2} \mathrm{O}\left(\mathrm{NB}\right.$ NOT $\mathrm{H}_{2} \mathrm{CO}_{3}+\mathrm{OH}^{-} \rightarrow$ )
(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)

3 (a) tetrahedral diagram (either dashed+wedge, or similar representation)
angles (all) $109^{\circ}-110^{\circ}$
(award [0] for part (a) if an angle of $90^{\circ}$ or $180^{\circ}$ is mentioned)
(b) volatility decreases or boiling points increase
(allow b.pt. $\mathrm{CCl}_{4}>\mathrm{SiCl}_{4}$ but b.pt. increases thereafter)
due to greater van der Waals'/intermolecular forces or due to more electrons
(mention of "ions" negates this mark)
(c) (i) $\mathrm{Pb}^{4+} / \mathrm{Pb}^{2+}: E^{\ominus}=+1.69 \mathrm{~V}, \mathrm{Sn}^{4+} / \mathrm{Sn}^{2+}: E^{\ominus}=+0.15 \mathrm{~V}$,
[both] [1]
a valid comment about relative redox power or stability, e.g.:
(hence) $\mathrm{Sn}^{2+}$ easily oxidised or $\mathrm{Sn}^{4+}$ is more stable than $\mathrm{Sn}^{2+}$ or
$\mathrm{Pb}^{4+}$ is easily reduced or $\mathrm{Pb}^{2+}$ is more stable than $\mathrm{Pb}^{4+}$ or
+2 oxidation state more stable down the group
(ii) $\begin{aligned} & \mathrm{Sn}^{2+}+\mathrm{I}_{2} \longrightarrow \mathrm{Sn}^{4+}+2 \mathrm{I}^{-} \\ & \\ & \\ & \\ & \\ & \\ & \text {(N.B. no marks in (ii) for } E^{4+} \text { values) }\end{aligned}$
(d) (i) for Si: $\Delta \mathrm{H}=244-2(359)=-474\left(\mathrm{~kJ} \mathrm{~mol}^{-1}\right)$
for $\mathrm{Sn}: \Delta \mathrm{H}=244-2(315)=-386\left(\mathrm{~kJ} \mathrm{~mol}^{-1}\right)$
(allow [1] out of [2] salvage mark for 474 \& 386; 962 \& 874; or $-962 \&-874$ )
(ii) Yes: the +4 state becomes decreasingly stable - the $\Delta H$ is less exothermic
(mark is for relating $\Delta H$ s to stability: allow ecf from $\mathbf{d}(\mathbf{i})$ and also from $\mathbf{c}(\mathbf{i})$ )

| Page 4 | Mark Scheme | Syllabus | Paper |
| :---: | :---: | :---: | :---: |
|  | GCE A/AS LEVEL - May/June 2008 | 9701 | 04 |

4
(a) ester
(b) reaction I: acid $/ \mathrm{H}^{+} / \mathrm{HC} / / \mathrm{H}_{2} \mathrm{SO}_{4}$ or alkali/ $\mathrm{OH}^{-} / \mathrm{NaOH}$ (followed by $\mathrm{H}^{+}$)
heat/reflux and aqueous (allow $\mathrm{H}_{3} \mathrm{O}^{+}$to equal $\mathrm{H}^{+}+$aq, also assume "conc" or "dil" means aq (but NOT $\mathrm{H}_{2} \mathrm{SO}_{4}$ ) also allow aqueous ethanol)
(for heat: allow $\mathrm{T} \geq 80^{\circ} \mathrm{C}$; not "warm")
reaction II: methanol/ $/ \mathrm{CH}_{3} \mathrm{OH}$
heat with conc. $\mathrm{H}_{2} \mathrm{SO}_{4} / \mathrm{H}_{3} \mathrm{PO}_{4}$ or $\mathrm{HCl}(\mathrm{g})$ [NOT conc HCl ]
(c) (i) $\mathrm{BrCH}_{2}-\mathrm{CHBr}-\mathrm{CH}_{2} \mathrm{Br}$
(ii) $\mathrm{HO}_{2} \mathrm{C}-\mathrm{CO}-\mathrm{CO}_{2} \mathrm{H}$
(d) 890 g of triglyceride produces $3 \times 298=894 \mathrm{~g}$ of biodiesel
$\therefore 500 \mathrm{~kg}$ produces $500 \times 894 / 890=502 \mathrm{~kg}$ biodiesel
(correct ans [2])
(1004/1005kg or 167 kg is worth [1]: 333kg is worth [0])
(e) (i) $\mathrm{C}_{17} \mathrm{H}_{35} \mathrm{CO}_{2} \mathrm{CH}_{3}+27.5 \mathrm{O}_{2} \longrightarrow 19 \mathrm{CO}_{2}+19 \mathrm{H}_{2} \mathrm{O}$
(or $\mathrm{C}_{19} \mathrm{H}_{38} \mathrm{O}_{2}$ )
(ii) $10 \times 44 \times 19 / 298=\mathbf{2 8 . ( 0 5 )} / \mathbf{2 8 . 1} \mathbf{k g}$ ecf from equ [2]
( -1 for each error)
some ecf values: $\mathrm{n}=18 \Rightarrow 26.6 \mathrm{~kg}$
$\mathrm{n}=17 \Rightarrow 25.1 \mathrm{~kg}$ (allow [2] for each)
$\mathrm{n}=16 \Rightarrow 23.6 \mathrm{~kg}$
(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 $\mathrm{CO}_{2}$ cycle (e.g. no net increase in $\mathrm{CO}_{2}$, 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

| Page 5 Mark Scheme | Syllabus | Paper |  |
| :---: | :---: | :---: | :---: |
|  | GCE A/AS LEVEL - May/June 2008 | 9701 | 04 |

5 (a) reaction I electrophilic addition
reaction II electrophilic substitution
(salvage: award [1] out of [2] for "addition" + "substitution", even if nucleophilic)
(b) reaction I: intermediate

second step, attack of $\mathrm{Br}^{-}$on bromocation.


reaction II: intermediate

(or with $\oplus$ in 2-position)
or

(make sure $\oplus$ is not at $\mathrm{sp}^{3} \mathrm{C}$-atom)
second step, loss of $\mathrm{H}^{+}$from bromocation.

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

| Page 6 | Mark Scheme | Syllabus | Paper |
| :---: | :---: | :---: | :---: |
|  | GCE A/AS LEVEL - May/June 2008 | 9701 | 04 |

6

A

C

D

B

E
[deduct [1] mark if ring circle omitted more than once]
[allow ecf for $\mathbf{E}$ from structure of $\mathbf{D}$ ]
[allow ecf for $\mathbf{B}$ from structure of $\mathbf{A}$ ]
[allow $-\mathrm{CO}_{2}^{-}$for E ]
[Total: 5]

7

| polymer | addition/condensation? | formulae of monomers |
| :---: | :---: | :---: |
| 1 | condensation | $\mathrm{HO}_{2} \mathrm{C}-\mathrm{CO}_{2} \mathrm{H}$ or $\mathrm{ClCO}-\mathrm{COCl}$ $\mathrm{NH}_{2}-\mathrm{CH}_{2}-\mathrm{CH}_{2}-\mathrm{NH}_{2}$ |
| 2 | condensation | $\begin{aligned} & \mathrm{HO}-\mathrm{CH}_{2}-\mathrm{CH}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)-\mathrm{CO}_{2} \mathrm{H} \\ & \mathrm{HO}-\mathrm{CH}_{2}-\mathrm{CH}\left(\mathrm{CH}_{3}\right)-\mathrm{CO}_{2} \mathrm{H} \end{aligned}$ |
| 3 | addition | $\begin{gathered} \mathrm{CH}_{2}=\mathrm{CH}-\mathrm{CH}_{3} \\ \mathrm{CH}_{2}=\mathrm{CH}-\mathrm{CONH} \\ \mathrm{CH}_{2}=\mathrm{CH}-\mathrm{C}_{6} \mathrm{H}_{5} \end{gathered}$ |
| $\Uparrow$ $\Uparrow$ <br> $[2]$ $[6]$ <br> $(2$ correct: $[1])$ $(6$ correct: $[5])$ <br>  etc |  |  |

(2 correct: [1])
( $\mathrm{C}=\mathrm{C}$ bonds not needed, but penalise $-[1]$ if $\mathrm{C}-\mathrm{C}$ drawn instead of $\mathrm{C}=\mathrm{C}$ )
(if more than 7 formulae drawn, then penalise -[1] for each formula in excess of 7 )

| Page 7 | Mark Scheme | Syllabus | Paper |
| :---: | :---: | :---: | :---: |
|  | GCE A/AS LEVEL - May/June 2008 | 9701 | 04 |

8
(a) primary: covalent (ignore amide, peptide etc)
diagram showing peptide bond: (-CHR-)CONH(-CHR-)
secondary: hydrogen bonds (NOT "..between side chains")
diagram showing $\mathrm{N}-\mathrm{H} \cdots \mathrm{O}=\mathrm{C}$
tertiary: two of the following:

- hydrogen bonds (diag. must show H -bonds other than those in $\alpha$-helix or $\beta$-pleated sheet - e.g. ser-ser)
- electrostatic/ionic attraction,
- van der Waals'/hydrophobic forces/bonds,
- (covalent) disulphide (links/bridges)
suitable diagram of one of the above
(for disulphide: $\mathrm{S}-\mathrm{S}$ not $\mathrm{S}=\mathrm{S}$ or $\mathrm{SH}-\mathrm{SH}$ )
(b) met-ala-gly-ala-gly-arg-val-lys
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.
(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)
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)

| Page 8 | Mark Scheme | Syllabus | Paper |
| :---: | :---: | :---: | :---: |
|  | GCE A/AS LEVEL - May/June 2008 | 9701 | 04 |

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)
(salvage: if just "mass \& charge" is mentioned, with no reference to species or molecule, award [1])
(b) (i) $\mathrm{CH}_{3} \mathrm{COCH}_{3}$ would show
a single peak/no splitting since all the Hs are in the same chemical environment or a peak at $\delta=2.1$ due to $\mathrm{CH}_{3} \mathrm{CO}$ group
$\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHO}$ would show 3 (sets of) peaks since there are 3 different proton environments
or there would be a peak at $\delta=9.5-10.0$ due to the -CHO group
or a peak at $\delta=0.9$ due to $\mathrm{CH}_{3}$
or a peak at $\delta 1.3$ due to $\mathrm{CH}_{2}$
(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:

- $\mathrm{CH}_{3} \mathrm{COCH}_{3}$ would form fewer fragments (must be stated in words)
- $\mathrm{CH}_{3} \mathrm{COCH}_{3}$ would form a fragment of $\mathrm{CH}_{3} \mathrm{CO}^{+}$or at $(\mathrm{m} / \mathrm{e}) 43$
- $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHO}$ would form a fragment of $\mathrm{CH}_{3} \mathrm{CH}_{2}{ }^{+}$or $\mathrm{CHO}^{+}$at (m/e) 29
- $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHO}$ would form a fragment of $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CO}^{+}$or at (m/e) 57
[charges on fragments not required for mark]
any 3 points [3]
(c) (i) peaks at $(\mathrm{m} / \mathrm{e}) 79$ and 81 or at $(\mathrm{m} / \mathrm{e}) 94$ and 96
(ii) in chlorine the $M$ and $M+2$ peaks are the ratio $3: 1$ whereas in bromine they are approx. 1:1

| Page 9 | Mark Scheme | Syllabus | Paper |
| :---: | :---: | :---: | :---: |
|  | GCE A/AS LEVEL - May/June 2008 | 9701 | 04 |

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
(b) (i) spheres with a diameter of the order of nanometres/in the nanometre range/between 10 \& 500 nm
(ii) it is (highly) acidic or low pH or contains HCl (NOT contains enzymes)
(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)
(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 $\mathrm{CO}_{2} \mathrm{H}$ groups, and an amide linkage between the aminoacid and another $\mathrm{CO}_{2} \mathrm{H}$ 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]

