## MARK SCHEME for the October/November 2013 series

## 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 should be read in conjunction with the question paper and the Principal Examiner Report for Teachers.

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1 (a)

dative bond to an oxygen using two N electrons
8 electrons around N in 1 double +2 single bonds
a total of 24 electrons, including one, and only one "口"
(the extra electron, " $\mathrm{\square}$ ", can be in a bond or a lone pair)
(b) (i) $2 \mathrm{Mg}\left(\mathrm{NO}_{3}\right)_{2} \longrightarrow 2 \mathrm{MgO}+4 \mathrm{NO}_{2}+\mathrm{O}_{2}$
(ii) (down the group)
nitrates become more stable or are more difficult to decompose or need a higher temperature to decompose
because there is less polarisation of the anion/nitrate ion/N-O bonds
as radius of $\mathrm{M}^{2+}$ /metal ion increases or charge density of the cation decreases
(c) $\mathrm{Cu}+4 \mathrm{H}^{+}+2 \mathrm{NO}_{3}^{-} \longrightarrow \mathrm{Cu}^{2+}+2 \mathrm{NO}_{2}+2 \mathrm{H}_{2} \mathrm{O}$

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2 (a) any two from: molecules have negligible volume
negligible intermolecular forces or particles are not attracted to each other or to the walls of the container random motion no loss of kinetic energy during collisions or elastic collisions (NOT elastic molecules)
(b) (i) low temperature and high pressure
(ii) (at low T ) forces between particles are more important,
(at high P) volume of molecules are significant
(c) (i) endothermic; because the equilibrium moves to the right on heating or with increasing temperature or because bonds are broken during the reaction
(ii) e.g. halogenation or Friedel-Crafts alkylation/acylation

reactants [1] products [1]
other possibilities: $\mathrm{C}_{2}, \mathrm{I}_{2}, \mathrm{R}-\mathrm{Cl}, \mathrm{RCOCl}$ etc.
[Total: 7]

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3 (a) (i) $\mathrm{CH}_{3} \mathrm{Br}(\mathrm{g}) \longrightarrow \mathrm{CH}_{3}(\mathrm{~g})+\mathrm{Br}(\mathrm{g})$
(ii) $1 / 3 \mathrm{AlCl}_{3}(\mathrm{~g}) \longrightarrow 1 / 3 \mathrm{Al}(\mathrm{g})+\mathrm{Cl}(\mathrm{g})$
or $\mathrm{AlCl}_{3}(\mathrm{~g}) \longrightarrow \mathrm{AlCl}_{2}(\mathrm{~g})+\mathrm{Cl}(\mathrm{g})$
$\left(\mathrm{AlCl}_{3}(\mathrm{~g}) \longrightarrow \mathrm{Al}(\mathrm{g})+3 \mathrm{Cl}(\mathrm{g})\right.$ for (1) mark)
(b) (i) bond energies decrease from $\mathrm{Cl}_{2}$ to $\mathrm{I}_{2}$
due to increasing bond length or increase in number of electron shells
which causes less effective orbital overlap or less attraction for the shared pair
(ii) either because fluorine is electronegative, (hence each F wants to keep its electrons to itself)
or because the bond length is so short there is repulsion between the lone pairs (on F)
or repulsion between the nuclei (of F)
(c) (i) for chlorine:
$\begin{aligned} \Delta H=\mathrm{E}(\mathrm{H}-\mathrm{H})+\mathrm{E}(\mathrm{Cl}-\mathrm{Cl})-2 \mathrm{E}(\mathrm{H}-\mathrm{Cl})= & 436+242-(2 \times 431) \\ & =-184 \mathrm{~kJ} \mathrm{~mol}^{-1}\end{aligned}$
for iodine:

$$
\begin{align*}
\Delta H=\mathrm{E}(\mathrm{H}-\mathrm{H})+\mathrm{E}(\mathrm{I}-\mathrm{I})-2 \mathrm{E}(\mathrm{H}-\mathrm{I}) & =436+151-(2 \times 299) \\
& =-11 \mathrm{~kJ} \mathrm{~mol}^{-1}
\end{align*}
$$

(ii) Hydrides become less thermally stable down the group from Cl to I as the $\mathrm{H}-\mathrm{X}$ bond energy decreases (more than does the $\mathrm{X}-\mathrm{X}$ bond energy)
(d) (i)

$$
\begin{array}{rll} 
& \mathrm{Na} & \mathrm{O} \\
& 15.2 / 23 & 31.8 / 16 \\
\Rightarrow & 0.661 & 1.99 \\
\div 0.661 \Rightarrow & 1.0 & 3.0
\end{array}
$$

(ii) $3 \mathrm{Br}_{2}+6 \mathrm{NaOH} \longrightarrow \mathrm{NaBrO}_{3}+5 \mathrm{NaBr}+3 \mathrm{H}_{2} \mathrm{O}$ or $3 \mathrm{Br}_{2}+6 \mathrm{OH}^{-} \longrightarrow \mathrm{BrO}_{3}^{-}+5 \mathrm{Br}^{-}+3 \mathrm{H}_{2} \mathrm{O}$
[Total: 15]

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4 (a) (i) Carbon (graphite) has delocalised electrons whereas silicon's electrons are localised.
(ii) Tin has metallic structure or delocalised/mobile electrons whereas germanium has localised electrons or giant covalent structure
(b) (i) $2 \mathrm{PbO}_{2} \longrightarrow 2 \mathrm{PbO}+\mathrm{O}_{2}$
(ii) $\mathrm{PbO}_{2}+4 \mathrm{HCl} \longrightarrow \mathrm{PbCl}_{2}+\mathrm{Cl}_{2}+2 \mathrm{H}_{2} \mathrm{O}$
(iii) $\mathrm{SnO}+2 \mathrm{NaOH} \longrightarrow \mathrm{Na}_{2} \mathrm{SnO}_{2}+\mathrm{H}_{2} \mathrm{O}$
(iv) $\mathrm{GeCl}_{4}+2 \mathrm{H}_{2} \mathrm{O} \longrightarrow \mathrm{GeO}_{2}+4 \mathrm{HCl}$
[Total: 6]

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5 (a) (i) $\mathrm{Br}_{2}(\mathrm{aq}$
electrophilic substitution

(ii) no special conditions electrophilic addition

product [1]
(iii) light/UV or heat
(free) radical substitution

balanced equation in (i) (i.e. $3 \mathrm{Br}_{2}$ and 3 HBr )
product [1]
balanced equation in (iii) (i.e. $\mathrm{Br}_{2}$ and HBr )
(b) (i)

C

D
$\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}$
E

3 correct structures (can be in any order) $3 \times$ [1]
(ii) results of tests:

$$
\begin{array}{ll}
\text { with 2,4-DNPH: } & \text { C and D } \\
\text { with } \mathrm{I}_{2}+\mathrm{OH}^{-}: & \text {D only } \\
\text { with } \mathrm{NaOH}: & \mathbf{D} \text { and } \mathbf{E}
\end{array}
$$

(N.B. letters may be different - must refer to the candidate's formulae)

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6 (a) A (Bronsted-Lowry) acid is a proton donor.
(b) (i)

carboxylic acid
at least one $\mathrm{H}_{2} \mathrm{O}$ molecule in the right orientation: attached to $-\mathrm{CO}_{2} \mathrm{H}$ attached to $-\mathrm{NH}_{2}$
lone pair (on oxygen in $\mathrm{H}_{2} \mathrm{O}$ or $-\mathrm{CO}_{2} \mathrm{H}$ or on nitrogen) shown at least once on a H -bond
$\delta+$ and $\delta$ - shown at least once (at each end of the same H -bond)
(ii)

(c) allow either $\mathrm{S}_{\mathrm{N}} 1$ or $\mathrm{S}_{\mathrm{N}} 2$

any three of $\delta+$ and $\delta$ - shown in $\mathrm{C}-\mathrm{Cl}$
curly arrow from lone pair on $\mathrm{NH}_{3}$ to $(\delta+)$ carbon
curly arrow from $\mathrm{C}-\mathrm{Cl}$ bond to Cl
5 -coordinate transition state or carbocation intermediate if $S_{N} 1$, with correct charge
(d) lysine @ pH 1: $\quad{ }^{+} \mathrm{NH}_{3}\left(\mathrm{CH}_{2}\right)_{4} \mathrm{CH}\left(\mathrm{NH}_{3}{ }^{+}\right) \mathrm{CO}_{2} \mathrm{H}$
aspartic acid @ pH 12: $\quad{ }^{-} \mathrm{O}_{2} \mathrm{CCH}_{2} \mathrm{CH}\left(\mathrm{NH}_{2}\right) \mathrm{CO}_{2}{ }^{-}$

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(e) (i) 6 (six)
(ii) either $\mathrm{H}_{2} \mathrm{NCH}\left(\mathrm{CH}_{3}\right) \mathrm{CO}-\mathrm{NHCH}\left(\mathrm{CH}_{2} \mathrm{OH}\right) \mathrm{CO}_{2} \mathrm{H}$
or $\mathrm{H}_{2} \mathrm{NCH}\left(\mathrm{CH}_{2} \mathrm{OH}\right) \mathrm{CO}-\mathrm{NHCH}\left(\mathrm{CH}_{3}\right) \mathrm{CO}_{2} \mathrm{H}$
(f) (i) Compounds have the same structural formula but ....
different (spatial) arrangement/position or orientation of atoms in space
(ii) J
(iii)


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## Section B

7 (a) (i) Metals such as $\mathrm{Hg}, \mathrm{Ag}, \mathrm{Cd}, \mathrm{Pb}, \mathrm{Cu}$ (identified - NOT just "heavy metals") (allow names, atomic symbols or ions, names or formulae of salts - e.g. $\left.\mathrm{Pb}\left(\mathrm{NO}_{3}\right)_{2}\right)$ or penicillin or organophosphorus insecticide etc.
(ii) The ion/inhibitor binds to a part of the enzyme molecule away from the active site or to an allosteric site
This changes the shape of the active site or denatures the enzyme
OR
the inhibitor forms a covalent/permanent bond with the active site blocking entry of the substrate
(iii)

(b) (i) (DNA) $\longrightarrow$ mRNA $\longrightarrow$ ribosome $\longrightarrow$ tRNA $\longrightarrow$ (Protein)
(ii) stop codon/it is used to stop the growth of a protein chain (allow: used at the start of protein synthesis)
(c) (i) Adenosine diphosphate (ADP) or AMP and (inorganic) phosphate/ $/ \mathrm{P}_{i} / \mathrm{PO}_{4}{ }^{3-} / \mathrm{H}_{3} \mathrm{PO}_{4}$
(ii) Any two of -
muscle contraction
transport of ions/molecules or active transport or exocytosis or $\mathrm{Na} / \mathrm{K}$ pump synthesis of new compounds/proteins etc.
movement of electric charge in nerve cells
bioluminescence
non-shivering thermogenesis
DNA synthesis/reproduction
[Total: 10]

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8 (a) NMR and radiowaves (or VHF/UHF or $40-800 \mathrm{MHz}$ )
(b) NMR: protons have (nuclear) spin
or (spinning) proton produces magnetic moment/field or two spin states
or protons can align with or against an applied magnetic field
there is insufficient electron density/cloud around H atoms for X -ray crystallography
(c) Sulfur, because it has the highest electron density
(d) (i) $\frac{4.5}{1.5}=\frac{100}{1.1} \times \mathrm{n}$
$\mathrm{n}=\frac{100 \times 0.15}{4.5 \times 1.1}=3.03=3$
(calculation must be shown) [1]
(ii) the -OH peak (broad singlet) at $\delta 4.6$
(iii) 3 (three)
(iv) $\mathbf{Q}$ has peak at $11.7 \delta$.
which is due to $-\mathrm{CO}_{2} \mathrm{H}$
(This can only be formed by oxidising a primary alcohol.)
or $\mathbf{P}$ has 4 peaks in its NMR spectrum, not 3
in a secondary alcohol with 3 carbons, two (methyl) groups will be in the same chemical environment (or wtte)
or analysis of the splitting pattern in $\mathbf{P}$ : the peaks at $\delta 0.9$ and 3.6 are triplets,
so each must be adjacent to a $-\mathrm{CH}_{2}-$ group. (hence $-\mathrm{CH}_{2}-\mathrm{CH}_{2}-\mathrm{CH}_{3}$ )
(v) $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CO}_{2} \mathrm{H}$ (structure needed, not name)

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9 (a) (i) diamond and graphite
(ii) any three from
diamond
transparent/colourless
non-conductor
hard/non slippery
more dense than graphite
higher
(b) Because each carbon is only bonded to 3 others or is unsaturated/doubly-bonded/ $\mathrm{sp}^{2}$ or has 3 bonding locations (NOT forms only 3 bonds)
$\mathrm{C}_{60} \mathrm{H}_{60}$
(c) (i) Number of atoms carbon present $=0.001 \times 6.02 \times 10^{23} / 12=5.02 \times 10^{19}$
(ii) Number of hexagons present $=5.02 \times 10^{19} / 2=2.51 \times 10^{19}$

Area of sheet $=690 \times 2.51 \times 10^{19}=1.73 \times \mathbf{1 0}^{\mathbf{2 2}} \mathrm{nm}^{2}$
(iii) Graphene: Yes, since it has free/delocalised/mobile electrons

Buckminsterfullerene: No, (although there is delocalisation within each sphere) it consists of separate/simple/discrete molecules/spheres/particles, (so no delocalisation from one sphere to the next) or electrons are trapped within each molecule/sphere

