## MARK SCHEME for the October/November 2012 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) $\mathrm{MgCl}_{2}$ : forms a (colourless) solution or dissolves.
$\mathrm{AlCl}_{3}: \quad$ produces a white ppt or steamy fumes

$$
\begin{align*}
& 2 \mathrm{AlCl}_{3}\left(\text { or } \mathrm{Al}_{2} \mathrm{Cl}_{6}\right)+3 \mathrm{H}_{2} \mathrm{O} \longrightarrow \mathrm{Al}_{2} \mathrm{O}_{3}+6 \mathrm{HCl}  \tag{1}\\
& \left.\left(\text { or } \mathrm{AlCl} l_{3}+3 \mathrm{H}_{2} \mathrm{O} \longrightarrow \mathrm{OH}\right)_{3}+3 \mathrm{HCl}\right)
\end{align*}
$$

or forms a (colourless) solution or dissolves

$$
\begin{equation*}
\mathrm{AlCl}_{3}+6 \mathrm{H}_{2} \mathrm{O} \longrightarrow\left[\mathrm{Al}\left(\mathrm{H}_{2} \mathrm{O}\right)_{5}(\mathrm{OH})\right]^{2+}+\mathrm{H}^{+}+3 \mathrm{Cl}^{-} \tag{1}
\end{equation*}
$$

$\mathrm{SiCl}_{4}$ : produces a white ppt or steamy fumes
$\mathrm{SiCl}_{4}+2 \mathrm{H}_{2} \mathrm{O} \longrightarrow \mathrm{SiO}_{2}+4 \mathrm{HCl}$
(or balanced equation giving $\mathrm{H}_{2} \mathrm{SiO}_{3}$ or $\mathrm{Si}(\mathrm{OH})_{4}$ )
[Total: 5]
(b) (i) $\mathrm{n}(\mathrm{NaCl})=1.10 / 58.5=1.88 \times 10^{-2} \mathrm{~mol}$
$\mathrm{n}(\mathrm{KCl})=0.90 / 74.6=1.21 \times 10^{-2} \mathrm{~mol}$
total $n(C T)=3.08$ or 3.09 or $3.1 \times 10^{-2} \mathrm{~mol}$ [2 or more sig. figs.] allow ecf
(ii) $\mathrm{Ag}^{+}(\mathrm{aq})+\mathrm{Cl}(\mathrm{aq}) \longrightarrow \mathrm{AgCl}(\mathrm{s})$
(iii) moles sampled for the titration $=3.09 \times 10^{-2} \times 10 / 1000=3.09 \times 10^{-4} \mathrm{~mol}$ ecf this equals $n\left(\mathrm{Ag}^{+}\right)$, so vol of $\mathrm{AgNO}_{3}=3.09 \times 10^{-4} \times 1000 / 0.02=15.5 \mathbf{~ c m}^{\mathbf{3}}$ ecf
[Total: 5]
(c) (i) bonds broken are C-H and I-I $=410+151=561 \mathrm{~kJ} \mathrm{~mol}^{-1}$ (all bonds $=5731 \mathrm{~kJ} \mathrm{~mol}^{-}$ bonds formed are $\mathrm{C}-\mathrm{I}$ and $\mathrm{H}-\mathrm{I}=240+299=539 \mathrm{~kJ} \mathrm{~mol}^{-1}$ (all bonds $=5709 \mathrm{~kJ} \mathrm{~mol}^{-1}$ ) $\Delta H=+22 \mathrm{~kJ} \mathrm{~mol}^{-1}$
(ii) $\mathbf{4} \mathrm{HI}+\mathbf{2} \mathrm{HNO}_{3} \longrightarrow \mathbf{2} \mathrm{I}_{2}+\mathrm{N}_{2} \mathrm{O}_{3}+\mathbf{3} \mathrm{H}_{2} \mathrm{O}$ (or double)

N : (is reduced from) 5 to 3
I : (is oxidised from) -1 to $\mathbf{0}$

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2 (a) catalyst: any two from the following three bullets for [1] mark:

- speeds up/increases (NOT alters or changes) the rate of a reaction
- lowers energy barrier/ $E_{\text {act }}$ or offers a lower energy pathway
- is not used up or remains unchanged or does not alter its mass/concentration or does not appear in stoichiometric equation or is regenerated
homogeneous: (catalyst and reactants) in the same phase/state
(b) (i) e.g. car exhausts/engines or aeroplanes or lightning or burning fuels or power stations
nitrogen reacts with oxygen or $\mathrm{N}_{2}+\mathrm{O}_{2}$
(ii) $\mathrm{NO}_{2}+\mathrm{SO}_{2} \longrightarrow \mathrm{NO}+\mathrm{SO}_{3}$
$\mathrm{NO}+1 / \mathrm{O}_{2} \longrightarrow \mathrm{NO}_{2}$
$\mathrm{SO}_{3}+\mathrm{H}_{2} \mathrm{O} \longrightarrow \mathrm{H}_{2} \mathrm{SO}_{4}$
$4 \mathrm{NO}_{2}+2 \mathrm{H}_{2} \mathrm{O}+\mathrm{O}_{2} \rightarrow 4 \mathrm{HNO}_{3}$ or $3 \mathrm{NO}_{2}+\mathrm{H}_{2} \mathrm{O} \rightarrow 2 \mathrm{HNO}_{3}+\mathrm{NO}$ (any 3 equations) $3 \times[1]$
[Total: 5]
(c)

$\Delta H$ shown as negative
both $E_{\mathrm{a}}$ labelled and correct - i.e. for the forward reaction
$E_{a}($ cat $)<E_{a}$ (uncat)

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3 (a) $\left(1 s^{2} 2 s^{2} 2 p^{6}\right) 3 s^{2} 3 p^{6} 3 d^{9}$
[Total: 1]
(b) (i) electron / orbitals near ligands are at a higher energy due to repulsion from ligand lone pairs
(ii) when an electron moves to higher orbital / energy level or is promoted it absorbs a photon or light (mention of light being emitted negates this mark)
(iii) (different ligands produce) different (sizes of) energy gap or $\Delta \mathrm{E}$
(c)

solutions at $1 \mathrm{~mol} \mathrm{dm}^{-3}(1 \mathrm{M})$ and $298(\mathrm{~K}) / 25^{\circ} \mathrm{C}$
salt bridge and voltmeter
platinum/carbon/graphite electrode
(this mark is negated by inclusion of $\mathrm{H}_{2}$ around the electrode)
copper electrode
$\mathrm{Fe}^{3+} / \mathrm{Fe}^{2+}$ mixture and $\mathrm{Cu}^{2+}$ or $\mathrm{CuSO}_{4}$ etc
[Total: 5]
(d) Parts (i) - (iii) have to correspond to each other.
either or
(i)

| ligand <br> exchange/substitution/displacement/replacement | precipitation/acid-base/deprotonation |
| :--- | :--- |
| $\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}+4 \mathrm{NH}_{3} \rightarrow\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\left(\mathrm{NH}_{3}\right)_{4}\right]^{2+}+4 \mathrm{H}_{2} \mathrm{O}$ <br> or $\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}+4 \mathrm{NH}_{3} \rightarrow\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\right]^{2+}+6 \mathrm{H}_{2} \mathrm{O}$ <br> or $\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}+\mathrm{nNH}_{3} \rightarrow\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6-n}\left(\mathrm{NH}_{3}\right)_{n}\right]^{2+}+$ <br> $\mathrm{nH} \mathrm{H}_{2} \mathrm{O}$ | $\mathrm{Cu}^{2+}+2 \mathrm{NH}_{3}+2 \mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{Cu}(\mathrm{OH})_{2}+2 \mathrm{NH}_{4}^{+}$ <br> or $\mathrm{Cu}^{2+}+2 \mathrm{NH}_{4} \mathrm{OH} \rightarrow \mathrm{Cu}(\mathrm{OH})_{2}+2 \mathrm{NH}_{4}^{+}$ <br> or $\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}+2 \mathrm{NH}_{3} \rightarrow\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{4}(\mathrm{OH})_{2}\right]$ <br> $+2 \mathrm{NH}_{4}^{+}$ |
| turns purple or deep/dark/royal blue | forms a pale blue ppt |

[1] + [1] + [1]

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(iv) $E^{9}$ will decrease/ be less positive/more negative...
...because $\left[\mathrm{Cu}^{2+}\right]$ decreases or $\mathrm{Cu}^{2+}+2 \mathrm{e}^{-} \rightleftharpoons \mathrm{Cu}$ shifts to the LHS or $E^{\ominus}\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\right]^{2+}=-0.05 \mathrm{~V}$ or $\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\right]^{2+}$ is more stable.
[Total: 4]
(e) (i) aldehyde
(ii) red ppt./solid
(iii) $2 \mathrm{Cu}^{2+}+\mathrm{CH}_{3} \mathrm{CHO}+5 \mathrm{OH}^{-} \rightarrow \mathrm{Cu}_{2} \mathrm{O}+\mathrm{CH}_{3} \mathrm{CO}_{2}^{-}+3 \mathrm{H}_{2} \mathrm{O}$
[Total: 3]
(f) $\mathrm{pH}=\mathrm{p} K_{\mathrm{a}}+\log [$ salt $] /[$ acid $]=-\log \left(9.3 \times 10^{-4}\right)+\log (0.8 / 0.5)$

$$
\begin{equation*}
=3.032+0.204=3.23 / 3.24 \text { ( } 3 \text { or more sig. figs.) } \tag{2}
\end{equation*}
$$

[Total: 2]
[TOTAL: 20]

4 (a) (i) ketone/carbonyl [NOT aldehyde]
(ii) carboxylic acid (name of group needed. NOT 'carboxyl')
[Total: 2]
(b) (i) (allow structural, displayed or skeletal formulae in (b), (c) and (e))

B

C

D

$$
\begin{equation*}
[1]+[1]+[1] \tag{1}
\end{equation*}
$$

(ii) heat/reflux/boil/hot/T $>60^{\circ} \mathrm{C}$ in $\mathrm{H}_{3} \mathrm{O}^{+}$or aqueous/dilute $\mathrm{H}^{+} / \mathrm{HCl} / \mathrm{H}_{2} \mathrm{SO}_{4}\left(\mathrm{NOT} \mathrm{HNO}_{3}\right)$
[Total: 4]

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(c) (i) reduction/redox (allow nucleophilic addition or hydrogenation, as appropriate from (ii)) [1]
(ii) $\mathrm{NaBH}_{4}$ or $\mathrm{LiAlH}_{4}$ or $\mathrm{H}_{2}+\mathrm{Ni} / \mathrm{Pt}$ or $\mathrm{Na}+$ ethanol
(iii)


A
(d) (i) alkene/C=C/C-C double bond
(ii) phenol and alkene/ $\mathrm{C}=\mathrm{C} / \mathrm{C}-\mathrm{C}$ double bond
(e)

curcumin
allow

complete formula

5 (a) (i) contains a lone pair on N (that can react with $\mathrm{H}^{+}$)
(ii) e.g. $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{NH}_{2}+\mathrm{H}(\mathrm{Cl}) \longrightarrow \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{NH}_{3}{ }^{+}(\mathrm{C} t)$
or $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{NH}_{2}+\mathrm{H}_{3} \mathrm{O}^{+} \longrightarrow \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{NH}_{3}{ }^{+}+\mathrm{H}_{2} \mathrm{O}$
or $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{NH}_{2}+\mathrm{H}_{2} \mathrm{O} \longrightarrow \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{NH}_{3}{ }^{+}+\mathrm{OH}^{-}$etc
e.g. $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{NH}_{2}+\mathrm{CH}_{3} \mathrm{Br} \longrightarrow \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{NHCH}_{3}+\mathrm{HBr}$
or $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{NH}_{2}+\mathrm{CH}_{3} \mathrm{COCl} \longrightarrow \mathrm{CH}_{3} \mathrm{CONHC}_{2} \mathrm{H}_{5}+\mathrm{HCl}$

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(iii) the lone pair (on N ) in phenylamine overlaps with ring or is delocalised
electron density of N is reduced or N becomes more positive or lone pair is less available
(iv)

(b) (i) $\mathrm{NaNO}_{2}+\mathrm{HCl} / \mathrm{H}^{+}$or $\mathrm{HNO}_{2}\left(\mathrm{HNO}_{3}\right.$ or $\mathrm{NO}_{3}^{-}$negates this mark)
$-10^{\circ} \mathrm{C}<\mathrm{T} \leqslant 10^{\circ} \mathrm{C}$ or less than $10^{\circ} \mathrm{C}{ }^{\prime}$
(ii) alizarin yellow R :

methyl orange:

and

$\left(\mathrm{NH}_{2}\right.$ alternatives as above)
(iii) makes the molecule (more) hydrophilic/soluble in water (due to H -bonding or ionic solvation)
or increases its melting point

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6 (a) It has no chiral centre/asymmetric carbon/optical isomers or is not optically active
[Total: 1]
(b) (i) structure - $\alpha$-helix or $\beta$-(pleated) sheet
hydrogen (bonding) (for either)
(ii) any two pairs from the following:

| bonding | possible amino acid |
| :--- | :--- |
| van der Waals' | ala, gly, leu, ile, val, pro, phe, try, met |
| ionic | asp, arg, glu, his, lys |
| disulfide bond | cysteine |
| hydrogen bond | asn, asp, arg, gln, glu, his, lys, ser, thr, try, tyr |
| $[1]+[1]$ |  |

(candidates can identify amino acids by name, three-letter abbreviation, formula of sidechain or formula of whole amino acid)
[Total: 6]
(c) (globular proteins/enzymes need) polar/H-bonding/ionic (side chains) so as to.... ....enhance their solubility or as part of their active site or to help their catalytic activity
[Total: 1]
(d) (i) $\mathrm{A}-\mathrm{T}$
$C-G$
(ii) (start or met) - gly - ser - leu - ala - ser - (stop)

If an amino acid is shown before gly, then it must be met. correct sequence of the 5 in bold
(iii) leu would be replaced by val

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7 (a) (i) No. of carbon atoms present in J is $100 \times 1.3=5$ carbons (must show working)
$1.1 \times 23.5$
(NMR spectrum shows) $\mathbf{1 0} \mathbf{H}$ (atoms present) (no reasoning need be shown)
(ii) Oxygen or $\mathrm{O}_{2}$ or O
(iii) J is $\left(\mathrm{CH}_{3} \mathrm{CH}_{2}\right)_{2} \mathrm{C}=\mathrm{O}$
any one from:
quartet/4 peaks (at $\delta 2.5$ ) shows an adjacent $\mathrm{CH}_{3}$ or 3 adjacent H
triplet/3 peaks (at $\delta 1.1$ ) shows an adjacent $\mathrm{CH}_{2}$ or 2 adjacent H
two (chemical/hydrogen) environments
pair of peaks in ratio $6: 4$ are (two) ethyl groups or the triplet + quartet shows an ethyl group
$\delta 2.5$ implies there's a $\mathrm{CH}_{2}$ next to $\mathrm{C}=\mathrm{O}$
[Total: 5]
(b) (i)

| technique | physical method |
| :--- | :--- |
| paper chromatography | partition |
| thin-layer chromatography | adsorption |
| gas-liquid chromatography | partition |

(ii) 4
(iii)

correct spot circled
(iv) 3

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8 (a) A monomers: $\mathrm{H}_{2} \mathrm{~N}-\left(\mathrm{CH}_{2}\right)_{6}-\mathrm{NH}_{2}$ and $\mathrm{HO}_{2} \mathrm{C}-\left(\mathrm{CH}_{2}\right)_{4}-\mathrm{CO}_{2} \mathrm{H}$ or $\mathrm{ClCO}\left(\mathrm{CH}_{2}\right)_{4} \mathrm{COCl}$
Condensation or nucleophilic substitution or addition-elimination
B monomer: $\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCH}_{3}$
Addition (NOT additional)

C monomer: $\mathrm{H}_{2} \mathrm{~N}-\left(\mathrm{CH}_{2}\right)_{5}-\mathrm{CO}_{2} \mathrm{H}$ or $\mathrm{H}_{2} \mathrm{~N}-\left(\mathrm{CH}_{2}\right)_{5}-\mathrm{COCl}$ or


Condensation
(b) (i) Need a statement from both columns for [1] mark.

| (a) | (b) |
| :--- | :--- |
| more compact packing in $\mathbf{A}$ <br> chains closer in $\mathbf{A}$ <br> chains further apart in B | stronger (inter-chain) forces in $\mathbf{A}$ <br> hydrogen bonding in $\mathbf{A}$ <br> weaker (inter-chain) or van der Waals' forces in B <br> B contains side-chain/branched chains |

(ii) Polymer B - van der Waals'/London (dispersion) forces/induced-instantaneous/induced dipoles
NOT just 'dipole'
[Total: 2]
[TOTAL: 7]

