## MARK SCHEME for the May/June 2014 series

## 9701 CHEMISTRY

9701/42
Paper 4 (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) (i)

(ii) (colour due to absorbance of visible light)
due to electron promoted (from lower) to upper orbital/energy level
in $\mathrm{Zn}^{2+}$ there's no space in higher orbital for the electron to go or completely filled d-orbitals/shell
(b) (i) yellow is due to $\left[\mathrm{CuCl}_{4}\right]^{2-}$
reaction is ligand displacement/exchange
(ii) (solution goes blue) due to $\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$
blue ppt. or (s)
of $\mathrm{Cu}(\mathrm{OH})_{2}$ or $\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{4}(\mathrm{OH})_{2}\right]$ etc.
purple or deep / dark blue solution or (aq)
due to $\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\right]^{2+}$ or $\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]^{2+}$
(c) (i) $2 \mathrm{KI}+\mathrm{K}_{2} \mathrm{~S}_{2} \mathrm{O}_{8} \longrightarrow 2 \mathrm{~K}_{2} \mathrm{SO}_{4}+\mathrm{I}_{2}$ or
ionic: $2 \mathrm{I}^{-}+\mathrm{S}_{2} \mathrm{O}_{8}{ }^{2-} \longrightarrow 2 \mathrm{SO}_{4}{ }^{2-}+\mathrm{I}_{2}$
(ii) $\mathrm{Fe}^{2+}$ is a homogeneous catalyst
(iii) equations: $2 \mathrm{Fe}^{2+}+\mathrm{S}_{2} \mathrm{O}_{8}{ }^{2-} \longrightarrow 2 \mathrm{Fe}^{3+}+2 \mathrm{SO}_{4}{ }^{2-}$ $2 \mathrm{Fe}^{3+}+2 \mathrm{I}^{-} \longrightarrow 2 \mathrm{Fe}^{2+}+\mathrm{I}_{2}$
or verbal equivalent, e.g. reactants are both negative ions, so repel each other or $\mathrm{Fe}^{2+}$ can be oxidised by $\mathrm{S}_{2} \mathrm{O}_{8}{ }^{2-}$ and $\mathrm{Fe}^{3+}$ can be reduced by I-

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2 (a) A : voltmeter or V or potentiometer
B: platinum or Pt
C: $1 \mathrm{moldm}^{-3}$ and $\mathrm{H}^{+}$or $\mathrm{HCl}\left(\right.$ or $\left.0.5 \mathrm{M} \mathrm{H}_{2} \mathrm{SO}_{4}\right)$
D: lead (metal) or Pb
(b) (i) $\mathrm{a} \checkmark$ in the box next to $-\mathbf{0 . 1 7} \mathrm{V}$ a comment that the $\left[\mathrm{Pb}^{2+}\right]$ has decreased plus a description of the outcome, e.g. as $\left[\mathrm{Pb}^{2+}\right]$ decreases (from 1 moldm ), $\mathrm{Pb}^{2+}(\mathrm{aq})+2 \mathrm{e}^{-} \rightleftharpoons \mathrm{Pb}(\mathrm{s})$ goes over to the left hand side, or as $\left[\mathrm{Pb}^{2+}\right]$ decreases, $\mathrm{Pb}^{2+}$ is less likely to be reduced
(ii) $\quad\left(K_{\text {sp }}=\right)\left[\mathrm{Pb}^{2+}\right]\left[\mathrm{Cl}^{-}\right]^{2}$
(iii) if $\left[\mathrm{PbCl}_{2}\right]=3.5 \times 10^{-2},\left[\mathrm{~Pb}^{2+}\right]=3.5 \times 10^{-2}$ and $\left[\mathrm{Cl}^{-}\right]=7.0 \times 10^{-2}$
so $K_{\text {sp }}=\left(3.5 \times 10^{-2}\right) \times\left(7.0 \times 10^{-2}\right)^{2}=1.715(1.7) \times 10^{-4} \mathrm{~mol}^{3} \mathrm{dm}^{-9}(\geqslant 2 \mathrm{sf})$
(c) (i) the $\left(\mathrm{M}^{2+} / \mathrm{M}\right) E^{\ominus}$ for the two elements are very similar or are -0.13 and -0.14 V
$E^{\ominus}\left(\mathrm{Sn}^{4+} / \mathrm{Sn}^{2+}\right)=0.15 \mathrm{~V}$ and $E^{\circ}\left(\mathrm{Pb}^{4+} / \mathrm{Pb}^{2+}\right)=1.69 \mathrm{~V}$
so $\mathrm{Sn}^{2+}$ is quite easily oxidised (to $\mathrm{Sn}^{4+}$ ) or is a stronger reductant or $\mathrm{Pb}^{2+}$ is not easily oxidised (to $\mathrm{Pb}^{4+}$ ) or $\mathrm{Pb}^{4+}$ is a stronger oxidant or $\mathrm{Pb}^{4+}$ is easily reduced
(ii) e.g. $\mathrm{PbCl}_{2}+\mathrm{Zn} \longrightarrow \mathrm{Pb}+\mathrm{ZnCl}_{2}$ (or ionic) (other acceptable reductants: $\mathrm{Fe}, \mathrm{Mg}, \mathrm{Ca}$ but not Na or K)
$\mathrm{Sn}^{2+}+\mathrm{Br}_{2} \longrightarrow \mathrm{Sn}^{4+}+2 \mathrm{Br}^{-}$
(other acceptable oxidants: $\mathrm{VO}^{2+}, \mathrm{Cr}_{2} \mathrm{O}_{7}^{2-}, \mathrm{Ag}^{+}, \mathrm{Cl}_{2}, \mathrm{Br}_{2}, \mathrm{~F}_{2}, \mathrm{Fe}^{3+}, \mathrm{MnO}_{4}^{-}$)
(d) (i) $\mathrm{Pb}^{2+}(\mathrm{g})+2 \mathrm{Cl}^{-}(\mathrm{g}) \longrightarrow \mathrm{PbCl}_{2}(\mathrm{~s})$
(ii) $\Delta H_{\mathrm{f}}=\Delta H_{\text {at }}+\mathrm{E}(\mathrm{Cl}-\mathrm{Cl})+1^{\text {st }} \mathrm{IE}+2^{\text {nd }} \mathrm{IE}+2 \times \mathrm{E}_{\mathrm{A}}(\mathrm{Cl})+\mathrm{LE}$
$-359=195+242+716+1450-2 \times 349+L E$
LE $=2 \times 349-359-195-242-716-1450$
$\mathrm{LE}=\mathbf{- 2 2 6 4}\left(\mathrm{kJ} \mathrm{mol}^{-1}\right)$
(iii) $\mathrm{LE}\left(\mathrm{PbCl}_{2}\right)>\mathrm{LE}\left(\mathrm{PbBr}_{2}\right)$ or more exothermic or stronger lattice
because $\mathrm{Cl}^{-}$/chloride anion has smaller radius/size than $\mathrm{Br}^{-} /$bromide

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3 (a) (i) B and D
(ii) D
(b) heat with dilute $\mathrm{H}^{+}(\mathrm{aq})$ or $\mathrm{H}_{2} \mathrm{SO}_{4}(\mathrm{aq})$
(c) (i) $K_{\mathrm{a}}$ larger than that for ethanol because
the ethanoate ion $/ \mathrm{CH}_{3} \mathrm{CO}_{2}^{-}$is stabilised by charge delocalisation or
the $\mathrm{O}-\mathrm{H}$ bond is weakened due to its proximity to $\mathrm{C}=\mathrm{O}$ /carbonyl group or the second electronegative/oxygen atom
$K_{\mathrm{a}}$ smaller than that for chloroethanoic acid because
electron-withdrawing/electronegative chlorine (atom) makes the anion more stable or $\mathrm{O}-\mathrm{H}$ bond weaker or H more easily lost
(ii) $\left[\mathrm{H}^{+}\right]=\sqrt{ }\left(\left[\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}\right] \times K_{\mathrm{a}}\right)=\sqrt{ }\left(0.1 \times 1.75 \times 10^{-5}\right)=\mathbf{1 . 3 2 ( 3 )} \times \mathbf{1 0}^{-\mathbf{3}}\left(\mathrm{moldm}^{-3}\right)$
$\mathrm{pH}=-\log _{10}\left[\mathrm{H}^{+}\right]=2.88(2.9)$
(d) (i) $\mathrm{n}(\mathrm{NaOH})$ at start $=0.1 \times 20 / 1000=2.0 \times 10^{-3} \mathrm{~mol}$ $\mathrm{n}(\mathrm{NaOH})$ at finish $=1.0 \times 10^{-\mathbf{3}} \mathrm{mol}$
(ii) this is in $30 \mathrm{~cm}^{3}$ of solution,
so $[\mathrm{NaOH}]$ at finish $=1.0 \times 10^{-3} / 0.030=3.3(3) \times 10^{-2} \mathrm{moldm}^{-3}(\geqslant 2$ s.f. $)$ ecf from (i)
(iii) $\left[\mathrm{H}^{+}\right]=K_{\mathrm{w}} /\left[\mathrm{OH}^{-}\right]=1 \times 10^{-14} / 3.33 \times 10^{-2}=3.0 \times 10^{-13} \mathrm{moldm}^{-3}$
$\mathrm{pH}=-\log _{10}\left[\mathrm{H}^{+}\right]=12.5(2)$
or $\mathrm{pOH}=-\log _{10}\left(3.33 \times 10^{-2}\right)=1.48$
$\mathrm{pH}=\mathrm{pK}_{\mathrm{w}}-\mathrm{pOH}=14-1.48=\mathbf{1 2 . 5 ( 2 )}$
(iv) $\mathrm{pH} /$ vol curve: start at pH 2.88 (2.9) ecf
vertical (over at least 2 pH units) portion at $\mathrm{V}=10 \mathrm{~cm}^{3}$
levels off at $\mathrm{pH} 12.5 \pm 0.3$ ecf
(v) indicator is thymolphthalein

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4. (a) (i) addition

## AND

(ii) substitution
(b) $\mathrm{Br}_{2}+\mathrm{AlBr}_{3} \longrightarrow \mathrm{Br}^{+}+\mathrm{AlBr}_{4}^{-}$(or can use $\mathrm{AlCl}_{3}$ or $\mathrm{FeCl}_{3}$ or $\mathrm{FeBr}_{3}$ etc.)
(c) (i) The two intermediate cations:

(ii) The ring (of $\pi$ electrons) in benzene is a stable configuration or is unchanged after the reaction.
(d) E is benzoic acid
reaction 1: heat with $\mathrm{KMnO}_{4}\left(+\mathrm{OH}^{-}\right.$or $\left.\mathrm{H}^{+}\right)$
reaction 2: heat with $\mathrm{Cl}_{2}+\mathrm{AlCl}_{3}$ or $\mathrm{FeCl}_{3}$
(e) G is

reaction 3: $\mathrm{SOCl}_{2}$ or $\mathrm{PCl}_{5}$
reaction 4: $\mathrm{LiAlH}_{4}$

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5. (a) (i) Na reacts with -OH or hydroxyl/alcohol groups
(ii) Fehling's solution reacts with - CHO or aldehyde groups
(b) alkene or $\mathrm{C}=\mathrm{C}$ or carbon double bond or phenol or phenylamine
(c)
$\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}(\mathrm{OH}) \mathrm{CHO}$
$\mathrm{CH}_{3} \mathrm{CH}(\mathrm{OH}) \mathrm{CH}_{2} \mathrm{CHO}$
$\mathrm{HOCH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CHO}$



[1] $+[1]+[1]$
(d) (i) the $\mathrm{CH}_{3} \mathrm{CH}(\mathrm{OH})$ group or the $\mathrm{CH}_{3} \mathrm{CO}$ group or methyl secondary alcohol or methyl ketone
(ii) $\mathrm{CH}_{3} \mathrm{CH}(\mathrm{OH}) \mathrm{CH}_{2} \mathrm{CHO}$
(e) (i) optical isomerism
(ii)



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## Section B

6. (a) (i)


Peptide bond correct
Rest of structure correct (skeletal, displayed or structural formula, or a mix)
(ii) Condensation or nucleophilic substitution or addition-elimination
(iii) Water/ $\mathrm{H}_{2} \mathrm{O}$
(b)

| DNA | RNA |
| :--- | :--- |
| Contains deoxyribose | Contains ribose |
| Contains thymine/T | Contains uracil/U |
| Double strand/chain/helix <br> or two strands | Single strand/chain |

(c) (i) (met) - leu - thr - pro - glu
(ii) Mutations or addition/insertion/deletion/substitution/replacement (of a base)
(iii) Changing A (or the 14th base) into U

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7 (a) (i) (Electrophoresis): the size/shape $/ M_{r}$ of the amino acid or its charge
(ii) (Paper chromatography): the partition of the amino acid between, or the relative solubility of the compound in, the 2 phases or solvent/water and stationary phase/filter paper.
(b) Use ninhydrin as a locating agent
(c) $\quad$ The $R_{f}$ value or retardation/retention factor or the distance travelled by the acid compared to that travelled by a standard sample of the amino acid
(d) $\quad \mathbf{R}$ - glutamic acid; $\mathbf{S}$ - glycine; $\mathbf{T}$ - lysine
(e)

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8. (a) (i) Any addition polymer (e.g. polyethene, polypropene, polystyrene, PVC, PTFE, PVA, Teflon)
(ii) Any condensation polymer (e.g. polyamide, polyester, nylon, Terylene, PET, PLA, Kevlar, Nomex)
(b) Hydrolysis or nucleophilic substitution

Ester and amide / peptide or $-\mathrm{CO}_{2}-$ and - $\mathrm{CONH}-$
(c)



Correct ester linkage
$\mathrm{CH}_{3}$ side chain on only one monomer unit
(d) Plant materials do not generally contain unsaturated hydrocarbons/alkenes/ $\mathrm{C}=\mathrm{C}$
(e) (i) Y van der Waals' forces
$\mathbf{Z}$ hydrogen bonding
(ii) Z, because it can form hydrogen bonds with water or it contains polar CO and NH groups

