## MARK SCHEME for the May/June 2013 series

## 9701 CHEMISTRY

9701/41
Paper 4 (A2 Structured Questions), maximum raw mark 100

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

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1 (a) The potential of an electrode compared to that of a standard hydrogen electrode (SHE) or the EMF of a cell composed of the test electrode and the SHE
all measurement concentrations of $1 \mathrm{~mol} \mathrm{dm}^{-3}$ and $298 \mathrm{~K} / 1$ atm pressure
(b)

$\mathrm{H}_{2}$ and good delivery system [1] $\mathrm{Fe}^{2+} / \mathrm{Fe}^{3+}$ solution labelled [1] platinum electrodes (both) [1] salt bridge and voltmeter [1] $\mathrm{H}^{+}$or HCl or $\mathrm{H}_{2} \mathrm{SO}_{4}$ [1] (acid is not sufficient)
(c) (i) $E^{\ominus}=0.77-0.54=0.23(\mathrm{~V})$
(ii) Since $E^{\ominus}$ is positive/ $E^{\ominus}>0$

So more products / the equilibrium will be over to the right / forward reaction is favoured ecf from (c)(i)
(iii) $K_{\mathrm{c}}=\left[\mathrm{Fe}^{2+}\right]^{2}\left[\mathrm{I}_{2}\right] /\left[\mathrm{Fe}^{3+}\right]^{2}\left[\mathrm{I}^{-}\right]^{2}$
units are $\mathbf{~ m o l}^{-1} \mathrm{dm}^{\mathbf{3}}$ ecf on expression
(iv) $\left(\left[\mathrm{Fe}^{2+}\right]\right.$ must always be twice $\left[\mathrm{I}_{2}\right]$, so) $\left[\mathrm{Fe}^{2+}\right]=0.02\left(\mathrm{~mol} \mathrm{dm}^{-3}\right)$
( $\left[\mathrm{I}^{-}\right]$must always be equal to $\left[\mathrm{Fe}^{3+}\right]$, so) $\left[\mathrm{I}^{-}\right]=2 \times 10^{-4}\left(\mathrm{~mol} \mathrm{dm}^{-3}\right)$
(v) $K_{\mathrm{c}}=\left\{(0.02)^{2} \times 0.01\right\} /\left\{\left(2 \times 10^{-4}\right)^{2} \times\left(2 \times 10^{-4}\right)^{2}\right\}$ correct expression
(allow ecf from incorrect expression in (c)(iii))
(allow ecf from (c)(iv))
$=\left(4 \times 10^{-6}\right) /\left(1.6 \times 10^{-1.5}\right)=2.5 \times 10^{9}\left(\mathrm{~mol}^{-1} \mathrm{dm}^{3}\right)$

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2 (a) (i)

plotting of points ( -1 for any error - plotted to within $1 / 2$ square) [1] a good best fit curve [1]
(ii) construction lines for two half-lives and $t_{1 / 2} \approx 63 \mathrm{~m}$ or $32 \mathrm{~m}( \pm 3 \mathrm{~min}) / \mathrm{t}_{1 / 2}$ is constant or construction lines for two tangents and mention of two values / concentration doubled, rate doubled
(iii) either ratio of (initial) rates (slopes) or ratio of $\mathrm{t}_{1 / 2}=2.0$
so reaction is first order w.r.t. [HCl]
(iv) rate $=\mathrm{k}\left[\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{CH}_{2} \mathrm{CH}_{3}\right][\mathrm{HCl}]$ conditional on (a)(iii) and ecf from (a)(iii)
(initial) rate $=0.2 / 95$ or $0.2 / 47$

$$
\begin{equation*}
\approx 2.1 \times 10^{-3} \text { or } 4.3 \times 10^{-3}\left(\mathrm{~mol} \mathrm{dm}^{-3} \mathrm{~min}^{-1}\right) \tag{1}
\end{equation*}
$$

$\mathrm{k}=2.1 \times 10^{-3} /(0.2 \times 0.1)$ or $4.3 \times 10^{-3} /(0.2 \times 0.2)$
$\approx 0.11\left(\mathrm{~mol}^{-1} \mathrm{dm}^{3} \mathrm{~min}^{-1}\right)$
(b) (i) because $\mathrm{H}_{2} \mathrm{O}$ is the solvent or its concentration cannot change
(ii) because HCl is a catalyst

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3 (a) (i) density $=$ mass per unit volume
(ii) mass per atom or $A_{r}$ is larger (for Fe )

Or
Fe 55.8 and Ca 40.1
Fe radii/volume of atom/ion is smaller
or
$\mathrm{R}_{\mathrm{Fe}}=0.116 \mathrm{~nm}$ whereas $\mathrm{R}_{\mathrm{Ca}}=0.197 \mathrm{~nm}$
(b)

| reaction | acid- <br> base | ligand <br> exchange | precipitation | redox |
| :--- | :---: | :---: | :---: | :---: |
| $\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}+4 \mathrm{NH}_{3} \rightarrow\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\right]^{2+}+6 \mathrm{H}_{2} \mathrm{O}$ |  | $\checkmark$ |  |  |
| $\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}+4 \mathrm{HCl} \rightarrow\left[\mathrm{CuCl}_{4}\right]^{2-}+4 \mathrm{H}^{+}+6 \mathrm{H}_{2} \mathrm{O}$ |  | $\checkmark$ |  |  |
| $2 \mathrm{FeCl}_{2}+\mathrm{Cl}_{2} \rightarrow 2 \mathrm{FeCl} l_{3}$ |  |  |  | $\checkmark$ |
| $\left[\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}+2 \mathrm{OH}^{-} \rightarrow \mathrm{Fe}(\mathrm{OH})_{2}+6 \mathrm{H}_{2} \mathrm{O}$ | $\checkmark$ |  | $\checkmark$ |  |
| $2 \mathrm{Fe}(\mathrm{OH})_{2}+1 / 2 \mathrm{O}_{2}+\mathrm{H}_{2} \mathrm{O} \rightarrow 2 \mathrm{Fe}(\mathrm{OH})_{3}$ |  |  |  | $\checkmark$ |
| $\mathrm{CrO}+2 \mathrm{HCl} \rightarrow \mathrm{CrO}_{2} \mathrm{Cl}_{2}+\mathrm{H}_{2} \mathrm{O}$ | $\checkmark$ | $\checkmark$ |  |  |
| $\mathrm{Cr}\left(\mathrm{H}_{2} \mathrm{O}\right)_{3}(\mathrm{OH})_{3}+\mathrm{OH}^{-} \rightarrow\left[\mathrm{Cr}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}(\mathrm{OH})_{4}\right]^{-}+$ | $\checkmark$ | $\checkmark$ |  |  |
| $\mathrm{H}_{2} \mathrm{O}$ |  |  |  |  |
| $\left[\mathrm{Cr}(\mathrm{OH})_{4}\right]^{-}+1 \frac{1}{2} \mathrm{H}_{2} \mathrm{O}_{2}+\mathrm{OH}^{-} \rightarrow \mathrm{CrO}_{4}{ }^{2-}+4 \mathrm{H}_{2} \mathrm{O}$ |  | $\checkmark$ |  | $\checkmark$ |

(Where more than one tick appears on a line in the table above - these are alternatives - but allow the mark if both are given).
(c) $\mathrm{n}\left(\mathrm{H}_{2}\right)=8 / 24=0.33 \mathrm{~mol}$
from equation, this is produced from 0.22 mol of $\mathrm{Al} \operatorname{ecf}(\times 2 / 3)$
$A_{r}(\mathrm{Al})=27$ thus mass of $\mathrm{Al}=27 \times 0.22=5.9-6 \mathrm{~g}$ hence $5.9-6.0 \%$ ecf $(\times 27)$
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4 (a) (due to the) strong $\mathrm{N} \equiv \mathrm{N}$ bond
(b) (i) Any balanced equation forming a stable nitrogen oxide e.g. $\mathrm{N}_{2}+\mathrm{O}_{2} \longrightarrow 2 \mathrm{NO}$

$$
\begin{align*}
& \text { or } \\
& \mathrm{N}_{2}+2 \mathrm{O}_{2} \longrightarrow 2 \mathrm{NO}_{2} \tag{1}
\end{align*}
$$

(ii) in lightning
in an engine/combustion of fuels (or a specific example)
(iii) ( $\mathrm{NO}_{x}$ produces) acid rain or forms (photochemical) smog
(c) (base is a) proton acceptor
basicities: ethylamine $>\mathrm{NH}_{3}>$ phenylamine
ethylamine (more basic) due to electron donating ethyl group
phenylamine (less basic) due to lone pair being delocalised into the ring
(d) (i) step 1: nucleophilic substitution
step 2: hydrolysis
(ii) step 1: KCN (in ethanol) and reflux
step 2: $\mathrm{H}_{3} \mathrm{O}^{+}$/ aqueous acid and reflux
(iii) T is

$\mathbf{W}$ is


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5 (a)

|  |  |  |  |
| :---: | :---: | :---: | :---: |
| Na | $\mathrm{H}_{2} \mathrm{O}$ | $\mathbf{H}_{2}$ | $\mathbf{H}_{2}$ |
| $\mathrm{KOH}(\mathrm{aq})$ | $\mathbf{X}$ | $\mathbf{x}$ | $\mathbf{x}$ |
| $\mathrm{Na}_{2} \mathrm{CO}_{3}(\mathrm{aq})$ | $\mathbf{X}$ | $\mathbf{x}$ | $\mathbf{C O}_{2}$ |

(b) (i) $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{C}-\mathrm{Cl}$ (any unambiguous structure or name)
(ii) reduction or hydrogenation
(iii) either $\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}$ and heat with (conc) $\mathrm{H}_{2} \mathrm{SO}_{4}$
or
$\mathrm{CH}_{3} \mathrm{COCl}$
(iv) reflux
dilute HCl

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(c) (i)

| reagent and conditions | product with $\mathbf{A}$ | product with $\mathbf{B}$ |
| :---: | :---: | :---: |
| Br 2 (aq) |  |  |
| heat with HBr |  |  |$\quad$ no reaction

(ii) either: $\mathrm{Cr}_{2} \mathrm{O}_{7}^{2-} / \mathbf{H}^{+}$: no observation with $\mathbf{A}$ and goes from orange to green with $\mathbf{B}$. or. $\mathrm{Br}_{2}(\mathrm{aq})$ : white ppt. with $\mathbf{A}$ and no observation/ppt with $\mathbf{B}$
[Total: 17]

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6 (a)

| substance | protein synthesis | formation of DNA |
| :--- | :---: | :---: |
| adenine |  | $\checkmark$ |
| alanine | $\checkmark$ |  |
| aspartate | $\checkmark$ |  |
| phosphate |  | $\checkmark$ |

(b) protein : hydrogen bonds
between -NH and $\mathrm{C}=\mathrm{O}$ groups on different (peptide) groups
DNA: hydrogen bonds
between bases / A \& T / C \& G on different chains
(c) primary: covalent bonds between (successive) amino acids tertiary :

| hydrogen bonds | between $-\mathrm{COOH} /-\mathrm{OH}$ and $-\mathrm{NH}_{2}$ (in side chains) |
| :---: | :---: |
| ionic bonds | between $-\mathrm{NH}_{3}{ }^{+}$and $-\mathrm{CO}_{2}{ }^{-}$(in side chains) |
| disulfide bonds | between cysteine molecules / residues / -SH groups <br> (in side chains) |
| van der Waals/VDW <br> forces | between alkyl groups / non-polar residues (in side |
| chains) |  |

any two rows

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7 (a) Any four from:

- extract DNA
- use restriction enzymes (to break DNA into fragments)
- use polymerase chain reaction (to increase concentration of fragments)
- place samples on (agarose) gel
- carry out electrophoresis
- label fragments (transferred to a membrane) with radioactive isotope
(b)

| item for testing | suitable for DNA fingerprinting |
| :--- | :---: |
| human hair | $\checkmark$ |
| piece of a flint tool | $x$ |
| piece of Iron Age pot | $x$ |
| piece of Roman leather | $\checkmark$ |

(c) insecticides: gas-liquid or thin-layer chromatography
dyes : paper or thin-layer chromatography
drugs: gas-liquid
or
thin-layer chromatography
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$8 \quad$ (a) (i)

(ii) Addition
(iii) Hydrogen bonding
(b) (i) more / increase water absorbing properties (allow attracts water more) more polar(ity)/more hydrophilic / has ionic side-chains (as well as hydrophilic ones)
(ii) It should be biodegradable/decompose
(c) idea of ion exchange / replacement of $\mathrm{Na}^{+}$for $\mathrm{Cd}^{2+} / \mathrm{Pb}^{2+}$
(the metal ions) will be attracted to the carboxylate ions
(d) (i) condensation
(ii) $\mathrm{OH} /$ alcohol groups
so highly soluble / able to form hydrogen bonds

