## Electrolysis, Electrode Potentials \& Cells Mark Scheme 7

| Level | International A Level |
| :--- | :--- |
| Subject | Chemistry |
| Exam Board | CIE |
| Topic | Electrochemistry |
| Sub-Topic | Electrolysis, Electrode Potentials \& Cells |
| Paper Type | Theory |
| Booklet | Mark Scheme 7 |

Time Allowed:

Score:
Percentage:

66 minutes
/55
/100

Grade Boundaries:

| A* | A | B | C | D | E | U |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $>85 \%$ | $777.5 \%$ | $70 \%$ | $62.5 \%$ | $57.5 \%$ | $45 \%$ | $<45 \%$ |

1 (a) (i) a solution that resists/minimises a change in its pH or helps maintain its pH ....
(NOT any of: "maintains pH "; "keeps pH constant"; "no change in pH ") .....when small amounts of acid/ $\mathrm{H}^{+}$or base/ $\mathrm{OH}^{-}$are added (both acid and base are needed)
(ii) $\mathrm{HCO}_{3}{ }^{-}$reacts with $\mathrm{H}^{+}$ions as follows:

$$
\mathrm{HCO}^{-}+\mathrm{H}^{+} \longrightarrow \mathrm{H}_{2} \mathrm{CO}_{3}\left(\text { or } \mathrm{H}_{2} \mathrm{O}+\mathrm{CO}_{2}\right)
$$

and with $\mathrm{OH}^{-}$ions thus:

$$
\mathrm{HCO}_{3}^{-}+\mathrm{OH}^{-} \longrightarrow \mathrm{CO}_{3}^{2-}+\mathrm{H}_{2} \mathrm{O}
$$

(the equation arrows can be equilibrium arrows, as long as $\mathrm{HCO}_{3}^{-}$is on the left)
(iii) $\left(\mathrm{pK}_{\mathrm{a}}=-\log \left(\mathrm{K}_{\mathrm{a}}\right)=7.21\right)$
$\mathrm{pH}=\mathrm{pK}_{\mathrm{a}}+\log ([$ base $] /[$ acid $]=7.21+\log (0.5 / 0.3)$ $=7.43$ (7.4)
(b) (i) $\mathrm{K}_{\mathrm{sp}}=\left[\mathrm{Ag}^{+}\right]^{3}\left[\mathrm{PO}_{4}{ }^{3-}\right]$ and units: $\mathrm{mol}^{4} \mathrm{dm}^{-12}$
(ii) call $\left[\mathrm{PO}_{4}{ }^{3-}\right]=\mathrm{x}$, then $\left[\mathrm{Ag}^{+}\right]=3 \mathrm{x}$, and $\mathrm{K}_{\text {sp }}=27 \mathrm{x}^{4}$
$\mathrm{x}=\left(\mathrm{K}_{\mathrm{sp}} / 27\right)^{1 / 4}=\left(1.25 \times 10^{-20} / 27\right)^{1 / 4}=4.64 \times 10^{-6} \mathrm{~mol} \mathrm{dm}^{-3}$
$\left[\mathrm{Ag}^{+}\right]=3 \mathrm{x}=1.39 \times 10^{-5}\left(\mathrm{~mol} \mathrm{dm}^{-3}\right) \quad$ (allow $\left.1.4 \times 10^{-5}\right)$
(c) $\quad \mathrm{H}_{3} \mathrm{PO}_{3}+2 \mathrm{Fe}^{3+}+\mathrm{H}_{2} \mathrm{O} \quad \longrightarrow \mathrm{H}_{3} \mathrm{PO}_{4}+2 \mathrm{Fe}^{2+}+2 \mathrm{H}^{+}$
$E \Theta_{\text {cell }}=0.77-(-0.28)=(+) 1.05 \mathrm{~V}$

$$
\text { or } 3 \mathrm{H}_{3} \mathrm{PO}_{3}+3 \mathrm{H}_{2} \mathrm{O}+2 \mathrm{Fe}^{3+} \longrightarrow 3 \mathrm{H}_{3} \mathrm{PO}_{4}+6 \mathrm{H}^{+}+2 \mathrm{Fe}
$$

$E \theta_{\text {cell }}=-0.04-(-0.28)=(+) 0.24 \mathrm{~V}$

| $2 \quad$ (a (i) | $\mathrm{K}=\mathrm{C} t /$ chloride $/ \mathrm{F}^{-} /$fluoride <br> $\mathrm{H}_{2} \mathrm{SO}_{4}+2 \mathrm{NaCl} \rightarrow \mathrm{Na}_{2} \mathrm{SO}_{4}+2 \mathrm{HCl}$ (or equation with F or $\mathbf{K}$ for Cl ) $\mathbf{O R}$ $\mathrm{H}_{2} \mathrm{SO}_{4}+\mathrm{NaCl} \rightarrow \mathrm{NaHSO}_{4}+\mathrm{HCl}$ (or equation with F or $\mathbf{K}$ for Cl ) <br> ecf from identity of $\mathbf{K}$ so long as halide HK is acidic/HK is a gas/an acidic gas is produced | 1 1 1 | 3 |
| :---: | :---: | :---: | :---: |
| (ii) | $\begin{aligned} & \mathrm{L}=\mathrm{I}^{-} / \text {iodide } \\ & \text { colour }=\text { yellow } \\ & \text { ecf from identity of } \mathrm{L} \text { i.e. } \mathrm{Cl}^{-}(\text {white }) \text { or } \mathrm{Br}^{-}(\text {cream }) \\ & \mathrm{Ag}^{+}+\mathrm{I}^{-} \rightarrow \mathrm{AgI} \text { (or equation with } \mathrm{L} \text { ) } \\ & \left.\mathrm{AgNO}_{3}+\mathrm{NaI} \rightarrow \mathrm{AgI}+\mathrm{NaNO}_{3} \text { (or equation with } \mathrm{L}\right) \\ & \text { ecf from identity of } \mathrm{L} \text { so long as halide } \end{aligned}$ | 1 1 1 | 3 |
| (iii) | $\mathrm{Br}_{2} /$ bromine has fewer electrons than iodine/more electrons than chlorine intermolecular/van der Waals' forces (in $\mathrm{Br}_{2} / \mathbf{M}_{2}$ ) weaker than in iodine/stronger than in chlorine | 1 1 | 2 |
| (b) (i) | $\begin{aligned} & \mathrm{B}=\text { chlorine } / \mathrm{Cl}_{2} \\ & \mathbf{C}=\text { hydrogen } / \mathrm{H}_{2} \\ & \mathbf{D}=\text { sodium hydroxide } / \mathrm{NaOH} \end{aligned}$ | 1 1 1 | 3 |

$\left.\begin{array}{|c|l|c|c|}\hline \text { (ii) } & \text { anode: } 2 \mathrm{Cl}^{-} \rightarrow \mathrm{Cl}_{2}+2 \mathrm{e}^{-} \\ \text {cathode: } 2 \mathrm{H}^{+}+2 \mathrm{e}^{-} \rightarrow \mathrm{H}_{2} \mathrm{OR} \\ 2 \mathrm{H}_{2} \mathrm{O}+2 \mathrm{e}^{-} \rightarrow 2 \mathrm{OH}^{-}+\mathrm{H}_{2}\end{array}\right)$

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) 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 $\Delta \mathrm{E}$
[Total: 5]
(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
(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> $\mathrm{or}\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}+4 \mathrm{NH}_{3} \rightarrow\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\right]^{2+}+6 \mathrm{H}_{2} \mathrm{O}$ <br> or $\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}+\mathrm{nNH}_{3} \rightarrow\left[\mathrm{Nu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6-n}\left(\mathrm{NH}_{3}\right)_{n}\right]^{2+}+$ <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 Cu+ $\mathrm{Cu}^{2+}+2 \mathrm{NH}_{4} \mathrm{OH} \rightarrow \mathrm{Cu}(\mathrm{OH})_{2}+2 \mathrm{NH}_{4}^{+}$ <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> $+2 \mathrm{~N}_{4}^{+}$ |
| turns purple or deep/dark/royal blue | forms a pale blue ppt |

(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 $E^{\circ}\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\right]^{2+}=-0.05 \mathrm{~V}$ or $\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\right]^{2+}$ is more stable.
(e) (i) aldehyde ..... [1]
(ii) red ppt./solid ..... [1](iii) $2 \mathrm{Cu}^{2+}+\mathrm{CH}_{3} \mathrm{CHO}+5 \mathrm{OH}^{-} \rightarrow \mathrm{Cu}_{2} \mathrm{O}+\mathrm{CH}_{3} \mathrm{CO}_{2}^{-}+3 \mathrm{H}_{2} \mathrm{O}$
(f) $\mathrm{pH}=\mathrm{p} K_{\mathrm{a}}+\log [$ salt $] /[$ acid $]=-\log \left(9.3 \times 10^{-4}\right)+\log (0.8 / 0.5)$

$$
=3.032+0.204=3.23 / 3.24 \text { ( } 3 \text { or more sig. figs.) }
$$

[2]

4 (a The EMF of a cell made up of the test electrode and a standard hydrogen electrode. (or the EMF of the electrode compared to the S.H.E.)

EMF measured under standard conditions of $\mathrm{T},(\mathrm{P})$ and concentration. (or at 298 K and $1 \mathrm{~mol} \mathrm{dm}^{-3}$ )
(b) The stronger the halogen is as an oxidising agent, the more positive is its $\mathrm{E}^{\ominus}$ value.

Two examples of $\mathrm{F}_{2} / \mathrm{F}, \mathrm{Cl}_{2} / \mathrm{CT} ; \mathrm{Br}_{2} / \mathrm{Br}^{r}, \mathrm{I}_{2} / \mathrm{I}^{\text {q }}$ quoted

$$
\text { (data: } \begin{aligned}
& \mathrm{F}_{2} / \mathrm{F}^{-}=+2.87 \mathrm{~V} \\
& \mathrm{Cl}_{2} / \mathrm{C} \mathrm{C}=+1.36 \mathrm{~V} \\
& \mathrm{Br}_{2} / \mathrm{Br}=+1.07 \mathrm{~V} \\
&\left.\mathrm{I}_{2} / \mathrm{I}=+0.54 \mathrm{~V}\right)
\end{aligned}
$$

(c) $\quad \mathrm{H}_{2} \mathrm{O}_{2}+2 \mathrm{I}^{-}+2 \mathrm{H}^{+} \longrightarrow \mathrm{I}_{2}+2 \mathrm{H}_{2} \mathrm{O}$

$$
\text { or } \quad \mathrm{H}_{2} \mathrm{O}_{2}+2 \mathrm{KI}+2 \mathrm{H}^{+} \longrightarrow 2 \mathrm{~K}^{+}+\mathrm{I}_{2}+2 \mathrm{H}_{2} \mathrm{O}
$$

$$
E^{\ominus}=1.77-0.54=1.23 \mathrm{~V}
$$

(ii)
$+4 \mathrm{H}^{+}$ or $\mathrm{Cl}_{2}+\mathrm{SO}_{2}+2 \mathrm{H}_{2} \mathrm{O} \longrightarrow 2 \mathrm{HCl}+\mathrm{H}_{2} \mathrm{SO}_{4}$

$$
\begin{equation*}
E^{\ominus}=1.36-0.17=1.19 \mathrm{~V} \tag{1}
\end{equation*}
$$

(d) since $\mathrm{E}^{\circ}\left(\mathrm{I}_{2} / \mathrm{I}\right)$ is +0.54 V , tin will be oxidised to $\mathrm{Sn}^{4+}$

$$
\left(E^{\circ} \text { for } \mathrm{Sn}^{2+} / S n=-0.14 \mathrm{~V} \text { and } \mathrm{E}^{\ominus} \text { for } \mathrm{Sn}^{4} / \mathrm{Sn}^{2}=+0.15 \mathrm{~V}\right)
$$

Thus: $\mathrm{Sn}+2 \mathrm{I}_{2} \longrightarrow \mathrm{SnI}_{4}$

