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: 66 minutes

Score: /55

Percentage: /100

Grade Boundaries:

| A* | А | В | С | 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..... [2] (NOT any of: "maintains pH"; "keeps pH constant"; "no change in pH")when small amounts of acid/H⁺ or base/OH⁻ are added (both acid and base are needed)
 - (ii) HCO_3^- reacts with H^+ ions as follows: $HCO_3^- + H^+ \longrightarrow H_2CO_3 (or H_2O + CO_2)$ and with OH^- ions thus: $HCO_3^- + OH^- \longrightarrow CO_3^{2-} + H_2O$

(the equation arrows can be equilibrium arrows, as long as HCO₃⁻ is on the left)

(iii)
$$(pK_a = -log(K_a) = 7.21)$$
 [2]
 $pH = pK_a + log([base]/[acid] = 7.21 + log(0.5/0.3)$
 $= 7.43 (7.4)$

- (b) (i) $K_{sp} = [Ag^+]^3[PO_4^{3-}]$ and units: mol^4dm^{-12} [1]
 - (ii) call $[PO_4^{3-}] = x$, then $[Ag^+] = 3x$, and $K_{sp} = 27x^4$ [3] $x = (K_{sp}/27)^{1/4} = (1.25 \times 10^{-20}/27)^{1/4} = 4.64 \times 10^{-6} \text{ mol dm}^{-3}$ $[Ag^+] = 3x = 1.39 \times 10^{-5} \text{ (mol dm}^{-3)} \qquad \text{(allow 1.4} \times 10^{-5})$
- (c) $H_3PO_3 + 2Fe^{3+} + H_2O \longrightarrow H_3PO_4 + 2Fe^{2+} + 2H^+$ [2] $Ee_{cell} = 0.77 - (-0.28) = (+)1.05 V$ or $3H_3PO_3 + 3H_2O + 2Fe^{3+} \longrightarrow 3H_3PO_4 + 6H^+ + 2Fe$

 $E_{\text{Cell}} = -0.04 - (-0.28) = (+)0.24 \text{ V}$

[Total: 12]

| T/chloride/F ⁻ /fluoride | 1 | |
|--|--|---|
| | 1 | |
| | 1 | 3 |
| /iodide | 1 | |
| | 1 | |
| I ⁻ → AgI (or equation with L) ₃ + NaI → AgI + NaNO ₃ (or equation with L) | 1 | 3 |
| nolecular/van der Waals' forces (in Br ₂ /M ₂) weaker than in iodine/stronger than | 1 | 2 |
| | | |
| - | 1 | |
| | 1 | 3 |
| | T/chloride/F⁻/fluoride 1 + 2NaCl → Na ₂ SO ₄ + 2HCl (or equation with F or K for Cl) OR 1 + NaCl → NaHSO ₄ + HCl (or equation with F or K for Cl) m identity of K so long as halide acidic/HK is a gas/an acidic gas is produced //iodide = yellow m identity of L i.e. Cl⁻(white) or Br⁻(cream) I⁻ → AgI (or equation with L) 3 + NaI → AgI + NaNO ₃ (or equation with L) m identity of L so long as halide comine has fewer electrons than iodine/more electrons than chlorine nolecular/van der Waals' forces (in Br₂/M₂) weaker than in iodine/stronger than brine cliorine/Cl₂ cdrogen/H₂ cdium hydroxide/NaOH | $_{3}$ + 2NaC l → Na $_{2}$ SO $_{4}$ + 2HC l (or equation with F or K for C l) OR $_{3}$ + NaC l → NaHSO $_{4}$ + HC l (or equation with F or K for C l) m identity of K so long as halide acidic/HK is a gas/an acidic gas is produced /iodide = yellow m identity of L i.e. Cl^{-} (white) or Br $^{-}$ (cream) I $^{-}$ → AgI (or equation with L) $_{3}$ + NaI → AgI + NaNO $_{3}$ (or equation with L) m identity of L so long as halide romine has fewer electrons than iodine/more electrons than chlorine nolecular/van der Waals' forces (in Br $_{2}$ /M $_{2}$) weaker than in iodine/stronger than lorine 1 alorine/C l_{2} drogen/H $_{2}$ |

| (ii) | anode: $2Cl^- \rightarrow Cl_2 + 2e^-$ | 1 | |
|------|---|---|----|
| | cathode: $2H^{+} + 2e^{-} \rightarrow H_{2}$ OR $2H_{2}O + 2e^{-} \rightarrow 2OH^{-} + H_{2}$ | 1 | 2 |
| | | | 13 |



3 (a $(1s^22s^22p^6)3s^23p^63d^9$

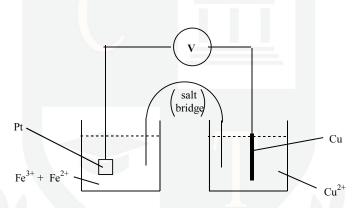
[1]

[Total: 1]

- (b) electron / orbitals near ligands are at a higher energy [1] due to repulsion from ligand lone pairs [1]
 - (ii) when an electron moves to higher orbital / energy level **or** is promoted [1] it absorbs a photon **or** light (mention of light being *emitted* negates this mark) [1]
 - (iii) (different ligands produce) different (sizes of) energy gap or ∆E [1]

[Total: 5]

(c)



| solutions at 1 mol dm ⁻³ (1 M) and 298(K)/25°C | [1] |
|--|-----|
| salt bridge and voltmeter | [1] |
| platinum/carbon/graphite electrode | [1] |
| (this mark is negated by inclusion of H ₂ around the electrode) | |
| copper electrode | [1] |
| Fe ³⁺ /Fe ²⁺ mixture and Cu ²⁺ or CuSO ₄ etc | [1] |

[Total: 5]

(d) Parts (i) – (iii) have to correspond to each other. either

or

| (i) | ligand exchange/substitution/displacement/replacement | precipitation/acid-base/deprotonation |
|-------|--|--|
| (ii) | $\begin{split} & [\text{Cu}(\text{H}_2\text{O})_6]^{2^+} + 4\text{NH}_3 \rightarrow [\text{Cu}(\text{H}_2\text{O})_2(\text{NH}_3)_4]^{2^+} + 4\text{H}_2\text{O} \\ & \textit{or} \ [\text{Cu}(\text{H}_2\text{O})_6]^{2^+} + 4\text{NH}_3 \rightarrow [\text{Cu}(\text{NH}_3)_4]^{2^+} + 6\text{H}_2\text{O} \\ & \textit{or} \ [\text{Cu}(\text{H}_2\text{O})_6]^{2^+} + \text{nNH}_3 \rightarrow [\text{Cu}(\text{H}_2\text{O})_{6-n}(\text{NH}_3)_n]^{2^+} + \\ & \text{nH}_2\text{O} \end{split}$ | $Cu^{2+} + 2NH_3 + 2H_2O \rightarrow Cu(OH)_2 + 2NH_4^+$ or $Cu^{2+} + 2NH_4OH \rightarrow Cu(OH)_2 + 2NH_4^+$ or $[Cu(H_2O)_6]^{2+} + 2NH_3 \rightarrow [Cu(H_2O)_4(OH)_2]$ $+ 2N_4^+$ |
| (iii) | turns purple or deep/dark/royal blue | forms a pale blue ppt |

[1] + [1] +

- (iv) E° will decrease/ be less positive/more negative... ...because $[Cu^{2^+}]$ decreases or $Cu^{2^+} + 2e^- = Cu$ shifts to the LHS or $E^{\circ}[Cu(NH_3)_4]^{2^+} = -0.05V$ or $[Cu(NH_3)_4]^{2^+}$ is more stable.
- [1]
- [Total: 4]

(e) (i) aldehyde

[1]

(ii) red ppt./solid

[1]

[1]

(iii) $2Cu^{2+} + CH_3CHO + 5OH^- \rightarrow Cu_2O + CH_3CO_2^- + 3H_2O$

[Total: 3]

(f) pH = p K_a + log [salt]/[acid] = -log(9.3 × 10⁻⁴) + log (0.8/0.5) = 3.032 + 0.204 = **3.23/3.24** (3 or more sig. figs.)

[2]

[Total: 2]

- ____
- [TOTAL: 20]

- 4 **(a** The EMF of a cell made up of the test electrode and a standard hydrogen electrode. [1] (or the EMF of the electrode compared to the S.H.E.)
 - EMF measured under standard conditions of T, (P) and concentration. [1] (or at 298K and 1 mol dm⁻³)
 - **(b)** The stronger the halogen is as an oxidising agent, the more positive is its E^e value. [1]

Two examples of F_2/F^- , Cl_2/Cl_1 ; Br_2/Br^- , I_2/I^- quoted [1]

(data:
$$F_2/F^- = +2.87V$$

 $Cl_2/CI = +1.36V$
 $Br_2/Br^- = +1.07V$
 $I_2/I^- = +0.54V$)

(c) $H_2O_2 + 2I^{-} + 2H^{+} \longrightarrow I_2 + 2H_2O$ or $H_2O_2 + 2KI + 2H^{+} \longrightarrow 2K^{+} + I_2 + 2H_2O$ [1

$$E^{\circ} = 1.77 - 0.54 = 1.23 \, \text{V}$$
 [1

(ii) $Cl_2 + SO_2 + 2H_2O \longrightarrow 2Cl^- + SO_4^{2-} + 4H^+$ or $Cl_2 + SO_2 + 2H_2O \longrightarrow 2HCl + H_2SO_4$ [1]

$$E^{\circ} = 1.36 - 0.17 = 1.19 \text{ V}$$
 [1]

(d) since $E^{\theta}(I_2/I^{-})$ is +0.54V, tin will be oxidised to $\mathbf{Sn^{4+}}$ [1] $(E^{\theta} \text{ for } \mathbf{Sn^{2+}/Sn} = -0.14V \text{ and } E^{\theta} \text{ for } \mathbf{Sn^{4}/Sn^{2}} = +0.15V)$

Thus:
$$Sn + 2I_2 \longrightarrow SnI_4$$
 [1]

total: 10

2

2

4

2