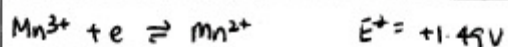
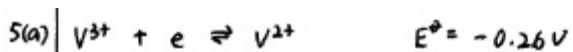
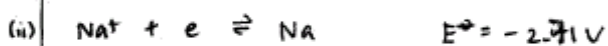
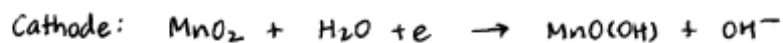


Electrochemistry**1 ACJC2009/P3/Q5(a)-(b)**

Based on E^{\ominus} values, Mn^{3+} has a higher tendency to be reduced compared to V^{3+} and Fe^{3+} . The formation of Mn^{2+} is favourable due to the additional stability associated with the half-filled $3d^5$ configuration. Hence, Mn^{3+} has a higher oxidising power, compared to its adjacent elements.

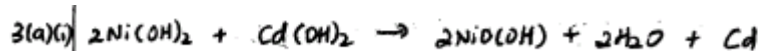
Based on E^{\ominus} values, Fe^{3+} has a lower tendency to be reduced compared to Mn^{3+} and Co^{3+} . The reduction of Fe^{3+} is not favourable due to the additional stability associated with its half-filled $3d^5$ configuration.



$$\text{Now, } 1.0 = E^{\ominus}_{\text{cathode}} - (-2.71)$$

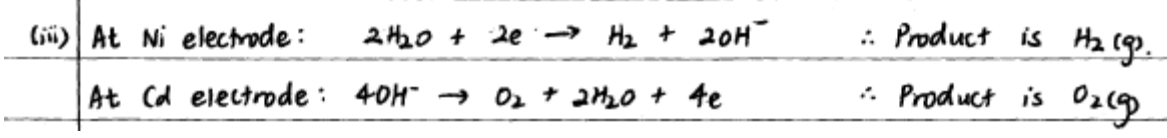
$$\therefore E^{\ominus}_{\text{cathode}} = -1.71V$$

Assume that the cell is working under standard conditions

2 AJC/2009/P3/Q3(a)-(b)

Electrochemistry – Suggested Solutions

(ii) $n_{\text{Cd(OH)}_2} = \frac{3.65}{146} = 0.025 \text{ mol}$
 $\frac{n_e}{n_{\text{Cd(OH)}_2}} = 2 \Rightarrow n_e = 2 \times 0.025 = 0.050 \text{ mol}$
 $Q = n_e \times F = 0.050 \times 96500 = 4825 \text{ C}$
 $Q = It \Rightarrow t = \frac{4825}{2.0} = 1610 \text{ s}$



(b)(i) The oxidation state of Mn decreases from +4 in MnO_2 to +3 in MnO(OH) . Hence, MnO_2 has been reduced and the carbon electrode coated with $\text{MnO}_2(\text{s})$ is the cathode.

(ii) $\text{Zn}^{2+} + 2e \rightleftharpoons \text{Zn} \quad E^\circ = -0.76 \text{ V}$
 Now, $1.60 = E^\circ_{\text{cathode}} - (-0.76)$
 $\therefore E^\circ_{\text{cathode}} = 1.60 + 0.76$
 $= +0.84 \text{ V}$

(iii) The reduction in the size of the Zn electrode has no effect on the emf.

(iv) The use of a dry cell alleviates the problem of electrolyte leaking from the battery.

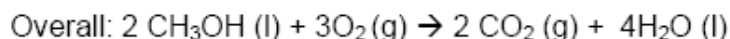
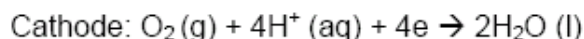
3 CJC/2009/P3/Q3(d)

(d) No. of mols of Ag added = $0.50 / 108 = 4.63 \times 10^{-3}$
 Quantity of charge = $(4.63 \times 10^{-3}) \times 96500 = 447 \text{ C}$
 Time taken = $447 / 0.2 = 2230 \text{ s} = 37.2 \text{ min}$

4 DHS/2009/P2/Q3

(a) Write equations for the reactions which take place for the fuel cell.
 Anode: $\text{CH}_3\text{OH}(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{CO}_2(\text{g}) + 6\text{H}^+(\text{aq}) + 6e^-$

Electrochemistry – Suggested Solutions



(b) Write the cell diagram.



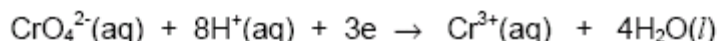
(c) Give an advantage of the fuel cell with methanol as a fuel.

There is no carbon or CO formed in the fuel cell. Or No poisonous gases evolved.

5 HCI/2009/P2/Q6(c)

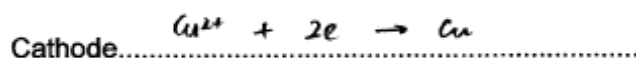
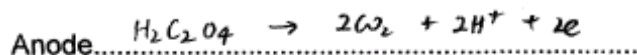
(i) mass of chromium = $\frac{1}{3} \times \frac{3.0 \times 45 \times 60}{96500} \times 52.0 = 1.45 \text{ g}$

(ii) As the $Cr^{3+}(aq)$ ions are discharged at the cathode, they are replenished by reduction of $CrO_4^{2-}(aq)$ ions at the cathode.



6 IJC/2009/P2/Q1(c)

(i) Write the equation at the respective electrodes:



(ii) Calculate the e.m.f of the cell.

$E_{cell}^{\circ} = +0.34 - (-0.49)$
 $= +0.83 \text{ V}$

(iii) State and explain the effect of the E_{cell}° of the reaction on adding aqueous potassium hydroxide to the $CO_2/H_2C_2O_4$ half-cell.

When $KOH(aq)$ is added to the $CO_2/H_2C_2O_4$ half-cell, $[H^+]$ decreases.

Hence, the equilibrium $2CO_2 + 2H^+ + 2e \rightleftharpoons H_2C_2O_4$ shifts to the left to replenish H^+ ions. As a result, $E_{(CO_2/H_2C_2O_4)}^{\circ}$ decreases

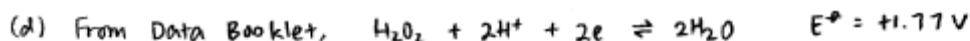
Since $E_{cell}^{\circ} = E_{(Cu^{2+}/Cu)}^{\circ} - E_{(CO_2/H_2C_2O_4)}^{\circ}$, E_{cell}° increases.

Electrochemistry – Suggested Solutions

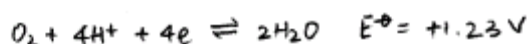
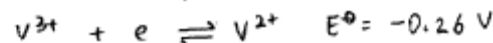
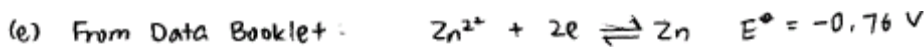
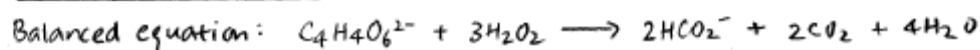
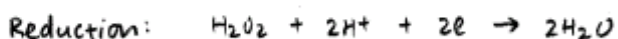
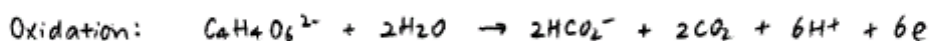
- (iv) Explain why it is not possible to use E^\ominus value reliably to determine if a reaction will occur.

E^\ominus_{cell} can only predict the spontaneity of reactions carried out under standard conditions.

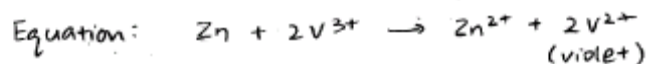
7 IJC/2009/P3/Q1(d)-(e)



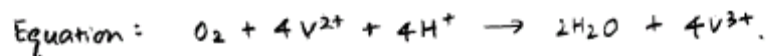
$\therefore E^\ominus_{\text{cell}} = +0.77 - (+0.20) = +0.57\text{V}$ (Reaction is feasible.)



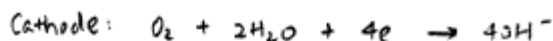
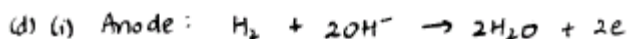
Zn is able to reduce V^{3+} to V^{2+} since $E^\ominus_{\text{cell}} = +0.50\text{V} > 0$



O_2 is able to oxidise V^{2+} back to V^{3+} since $E^\ominus_{\text{cell}} = +1.49\text{V} > 0$



8 IJC/2009/P3/Q3(d)



(ii) $Q = It = 10 \times (24 \times 60 \times 60)$

$= 8.64 \times 10^5\text{C}$

$Q = neF \Rightarrow n_e = \frac{Q}{F} = \frac{8.64 \times 10^5}{9.65 \times 10^4}$

$= 8.95\text{ mol}$

85% $\rightarrow 8.95\text{ mol}$

100% $\rightarrow \frac{100}{85} \times 8.95 = 10.53\text{ mol}$

$n_{\text{H}_2} = \frac{1}{2} \times n_e = \frac{1}{2} \times 10.53 = 5.265\text{ mol}$

\therefore volume of $\text{H}_2 = 5.265 \times 24$

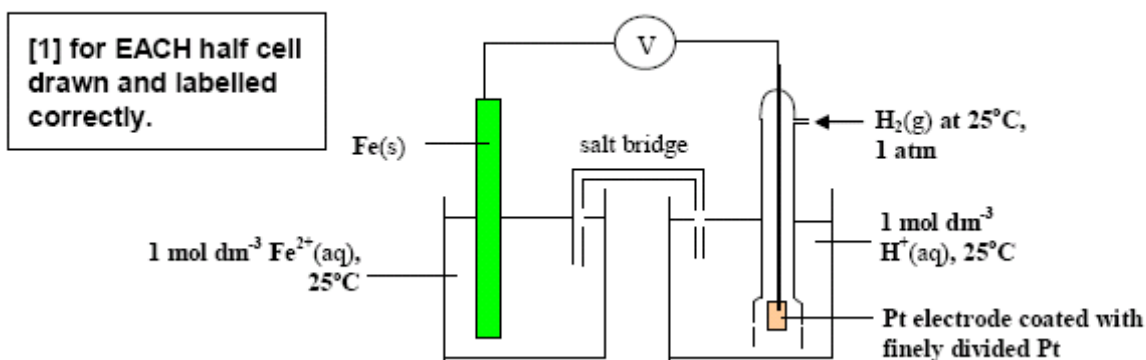
$= 126\text{ dm}^3$

9 JJC/2009/P2/Q4(b)

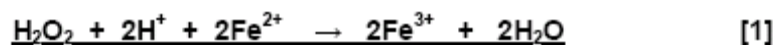

(ii) $E^\circ_{\text{cell}} = E^\circ(\text{MnO}_2/\text{Mn}_2\text{O}_3) - (-0.76) = 1.5$

$E^\circ(\text{MnO}_2/\text{Mn}_2\text{O}_3) = \underline{0.74 \text{ V}}$ [1]

 10 JJC/2009/P3/Q5(a)-(b)

 5. (a) (i) *NO MARKS for (a) if battery is included in the diagram.*


(ii) $E^\circ_{\text{cell}} = +1.77 - (+0.77) = \underline{+1.00 \text{ V}}$ (energetically feasible) [1]



(b) (i) $[\text{Fe}^{2+}] = \underline{1 \text{ mol dm}^{-3}}$ [1]

(ii) $\underline{K_{\text{sp}} = [\text{Fe}^{2+}][\text{OH}^-]^2}$ [1]

(iii) $K_{\text{sp}} = [\text{Fe}^{2+}][\text{OH}^-]^2$

$[\text{OH}^-] = \underline{7.75 \times 10^{-8} \text{ mol dm}^{-3}}$ [1]

$\text{pOH} = 7.11$

Electrochemistry – Suggested Solutions

$$\text{pH} = x = \underline{6.89} \quad [1]$$

5. (b) (iv) With $\text{pH} > x$, $[\text{OH}^-] > 7.75 \times 10^{-8} \text{ mol dm}^{-3}$ and **$[\text{Fe}^{2+}]$ concentration will decrease**.

equilibrium position of $\text{Fe}^{2+} + 2\text{e}^- \rightleftharpoons \text{Fe}$ shifts left, favouring the oxidation process and leading to a decreasing $E(\text{Fe}^{2+}/\text{Fe})$. [1]

- (c) (i) To **reduce** any **Fe^{3+}** present in tea leaves **to Fe^{2+}** [1]

- (ii) Amt of Fe^{2+} in 10 cm^3 solution = **Error! Objects cannot be created from editing field codes.** $= 1.34 \times 10^{-4} \text{ mol}$ [1]

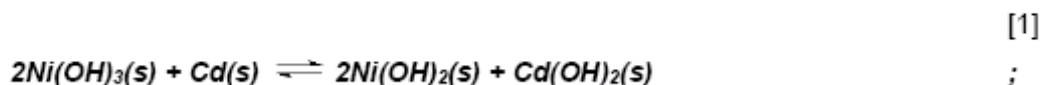
$$\text{Amt of } \text{Fe}^{2+} \text{ in } 100 \text{ cm}^3 \text{ solution} = 1.34 \times 10^{-4} \times 10 = 1.34 \times 10^{-3} \text{ mol}$$

Mass of iron (per gram of dry tea leaves) = **Error! Objects cannot be created from editing field codes.**

$$= \underline{1.50 \times 10^{-4} \text{ g}} \quad [1]$$

11 **MI/2009/P2/Q1**

- (a) Write a balanced equation that shows the reaction that occurs as the cell discharges.

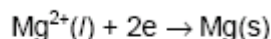


- (b) Using the information given above and the Data Booklet, can a nicad battery be used to drive the electrolytic decomposition of molten MgCl_2 into Mg metal and Cl_2 gas, i.e.



$$\begin{array}{ll} E_{\text{cell}}^{\ominus} = 0.49 - (-0.81) & E_{\text{cell}}^{\ominus} = -2.38 + (-1.36) \\ = +1.30 \text{ V} & = -3.74 \text{ V} \end{array} \quad ;$$

- (c) If the nicad battery can deliver 0.1A for 12 hours, what is the mass of Mg can be produced from MgCl_2 by electrolysis? [2]



$$\begin{array}{l} Q = It \\ = 0.1 \times 12 \times 60 \times 60 \\ = 4320 \text{ C} \end{array} \quad [4]$$

Electrochemistry – Suggested Solutions

$$\begin{aligned} \text{Amount of electrons} &= \frac{4320}{96500} && [1/4] \\ &= 0.04477 \text{ mol} \end{aligned}$$

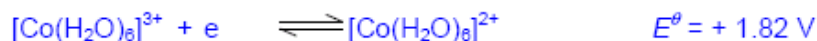
$$\begin{aligned} \text{Amount of Mg} &= 0.04477 \div 2 && [1/4] \\ &= 0.02238 \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{Mass of Mg} &= 0.02238 \times 24.3 && [1/4] \\ &= 0.544 \text{ g} \end{aligned}$$

- (d) The voltage delivered by a nicad battery does not change significantly as the battery discharges. Briefly explain why this is true. [1]

In the above equilibrium, all the substances present are in solid state and concentration of solids are considered to be constant, hence the equilibrium position of the half cells in the battery do not change as the battery discharges and use up the solid reactants, i.e. E^\ominus_{cell} remains the same. ;

12 MJC/2009/P2/Q3(a)



In water, the highly positive E^\ominus indicates that Co^{3+} is unstable with respect to Co^{2+} and should be spontaneously reduced to Co^{2+}



In the presence of $\text{C}_2\text{O}_4^{2-}$ ligands, the reduction potential decreases significantly to $E^\ominus [\text{Co}(\text{C}_2\text{O}_4)_3]^{3-} / [\text{Co}(\text{C}_2\text{O}_4)_3]^{4-} = +0.57$ meaning that $\text{C}_2\text{O}_4^{2-}$ ligand stabilises the +3 oxidation state of Co with respect to the +2 oxidation state

Conclusion

$[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$ is less readily reduced compared to Co^{3+} , rendering $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$ less oxidising.

13 MJC/2009/P3/Q2(b)

(bi) E^\ominus_{cell} for Rxn 1 = 0.36 V

E^\ominus_{cell} for Rxn 2 = 0.30 V

$E^{\ominus}_{\text{cell}}$ for Reaction I > $E^{\ominus}_{\text{cell}}$ for Reaction II, hence reaction I is more feasible. The decomposition will follow that of Reaction I.

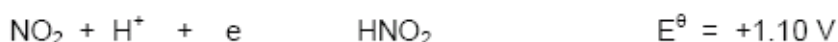
(ii) Reagent HClO_3 or KClO_3 or NaClO_3 eg

14 **NYJC/2009/P2/Q1(a)**

(i) Write a balanced equation for the disproportionation reaction.



(ii) Use the data below and any other relevant data in the Data Booklet to determine if this disproportionation reaction would actually occur under standard conditions



$$E^{\ominus}_{\text{cell}} = (+1.10) - (+0.81) = +2.9 \text{ V}$$

Hence disproportionation is favourable

15 **NYJC/2009/P2/Q2(b)-(c)**

(i) Copper corrodes in moist air to first give a thin layer of copper(II) oxide and this process happens much more slowly than the rusting of iron to form the iron(III) oxides. With the use of relevant data from the *Data Booklet*, explain this difference.



$$E^{\ominus}_{\text{cell}} = +0.40 - (+0.34) = +0.06 \text{ V (close to 0) (feasible)}$$



$$E^{\ominus}_{\text{cell}} = +0.40 - (-0.04) = +0.44 \text{ V} > 0 \text{ (feasible)}$$

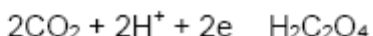
- $E^{\ominus}_{\text{cell}}$ for the oxidation of Fe is much more positive than that for the oxidation of Cu, hence more spontaneous.

- (ii) Another possible oxidation state that copper can have is +1, such as in copper(I) sulphate, Cu_2SO_4 . When this sulphate is added to water, blue solution of copper(II) sulphate and pink deposit of copper metal forms. Write a balanced equation for this process and using relevant data from the *Data Booklet*, show that this reaction is feasible.



$$E^\ominus = + 0.52 - (+ 0.15) = + 0.37 \text{ V} > 0 \text{ (feasible)}$$

- (iii) A copper metal plate was dipped into an aqueous solution of 1.0 mol dm^{-3} copper(II) sulphate solution and this half-cell was connected via a salt bridge, to the following half-cell,



The **overall cell e.m.f** was found to be $+0.83 \text{ V}$ and the size of the copper plate *increased* after some time.

Give the cell notation and hence, calculate the reduction potential, E^\ominus ($\text{CO}_2 / \text{H}_2\text{C}_2\text{O}_4$)

The size of Cu increased shows that Cu^{2+} ions is reduced to Cu. Hence oxidation must be occurring at the other CO_2 half-cell.



$$E^\ominus = E^\ominus_{\text{R}} - E^\ominus_{\text{O}}$$

$$+0.83 = +0.34 - E^\ominus_{\text{O}}$$

$$E^\ominus_{\text{O}} = - 0.49 \text{ V} = E^\ominus (\text{CO}_2 / \text{H}_2\text{C}_2\text{O}_4)$$

- (i) Write balanced half-equations, with state symbols, for the reactions at the anode and the cathode.



- (ii) Calculate the current used during electrolysis.

$$Q = nzF = (0.04/63.5)(2)(96500) = 121.6 \text{ C}$$

$$I = Q / t = 121.6 / (20 \times 60) = 0.101 \text{ A}$$

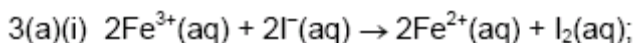
- (iii) It is not always possible to accurately predict the electrode reactions that occur during electrolysis. Suggest a reason for this.

Electrolysis may not occur at standard conditions. OR

Rate of reaction may be too slow. OR

The reaction has a high activation energy.

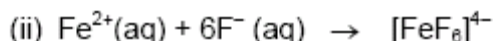
16 PJC/2009/P2/Q3(a)



$$E^{\ominus}_{\text{cell}} = +0.76 + (-0.54) \text{ V}$$

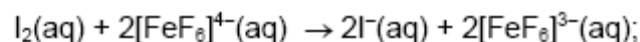
$$= +0.22 \text{ V}$$

The reaction is energetically feasible and produces $\text{I}_2(\text{aq})$ which forms $\text{I}_3^{-}(\text{aq})$ – the brown solution.



Ligand exchange takes place. F^{-} ligands replace water ligands in the iron(II) complex ion.

The $[\text{FeF}_6]^{4-}(\text{aq})$ ion then reduces the brown iodine to colourless iodide. Thus the brown colour fades.



$$E^{\ominus}_{\text{cell}} = +0.54 + (-0.40) \text{ V} = +0.14 \text{ V}$$

17 PJC/2009/P3/Q2

- 2(a)(i)** At the cathode,

Due to the high negative reduction potential of Na^{+} , H_2O is preferentially discharged, producing H_2 and NaOH which turns litmus blue at region Y.

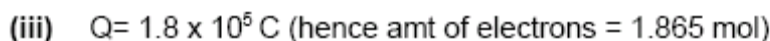
At the anode,

Although the oxidation of water is more favourable based on the oxidation potential, Cl^{-} is discharged in preference due to its high concentration, thus liberating Cl_2 at the anode.

Region X becomes red initially due to formation of HOCl and eventually becomes white due to the bleaching action of HOCl .



Chlorine is produced at the anode while the $[\text{OH}^-]$ in the electrolyte will increase as the electrolysis proceeds. As a result, Cl_2 will react with the OH^- in the electrolyte to produce NaClO_3 .



Since $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$ and



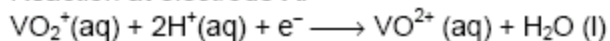
$$n(\text{e}^-) \equiv \frac{1}{2}n(\text{Cl}_2) \equiv \frac{1}{3}n(\text{NaClO}_3)$$

$$\text{Hence } n(\text{NaClO}_3) = 0.3109 \text{ mol}$$

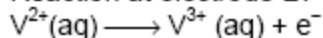
$$[\text{NaClO}_3] = 0.3109 / 2 = \mathbf{0.155 \text{ mol dm}^{-3}}$$

18 RI/2009/P3/Q3(c)-(d)

(c)(i) Reaction at electrode A:



Reaction at electrode B:



$$E_{\text{cell}}^{\ominus} = 1.00 - (-0.26) = +1.26\text{V}$$

- (ii) Electrode A is the **positive electrode as electrons are consumed** in the reaction due to reduction of VO_2^+ to VO^{2+} .
- (iii) To **increase the total surface area of the electrodes** so that the reactions at the electrodes proceed rapidly.
- (iv) As the reaction proceeds, the **electrolyte in tank A becomes increasingly negative** (due to consumption of H^+) while the **electrolyte in tank B becomes increasingly positive** (due to a more highly positively charged ion being formed). The membrane **allows selective ions to pass through** (eg H^+ to migrate via membrane from tanks B to A) **to maintain electrical neutrality**.

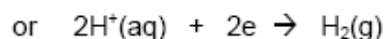
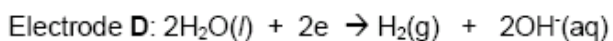
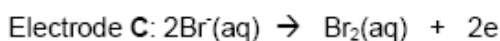
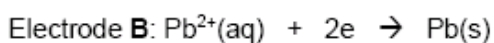
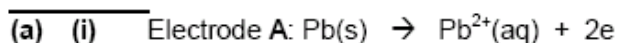
Electrochemistry – Suggested Solutions

- (v) Spent electrolyte may be replaced by fresh electrolyte so that the battery does not run out of power.

(Other acceptable answers: Storage of chemicals in conventional battery lead to loss of power/ environment aspect due to battery being thrown away etc.)

- (d) $\text{VO}_2^+(\text{aq}) + 2\text{H}^+(\text{aq}) + \text{e}^- \longrightarrow \text{VO}^{2+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
Change in amount of VO_2^+ required = $(0.90 - 0.10) \times 3 \times 2.00 \text{ mol} = 4.80 \text{ mol}$
Amount of electrons needed = 4.80 mol
Quantity of electricity required = $4.80 \times 96500 \text{ C} = 4.632 \times 10^5 \text{ C}$
Time required = $\frac{Q}{I} = \frac{4.6320 \times 10^5}{12} + 3600 \text{ h} = 10.7 \text{ h}$

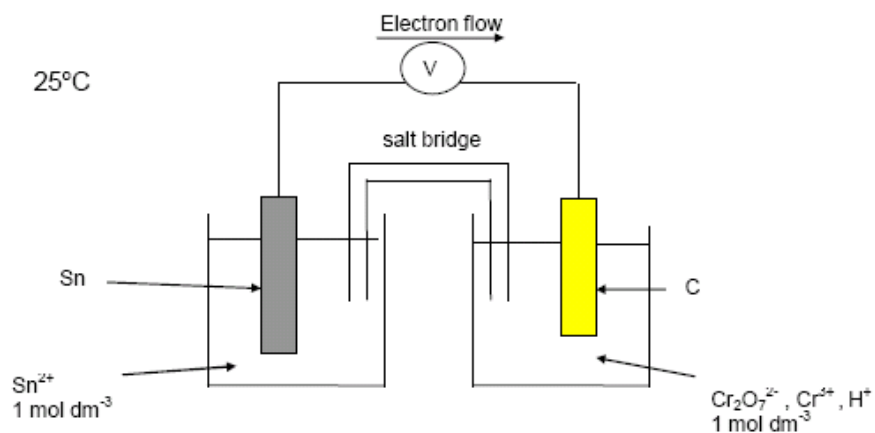
19 SAJC/2009/P2/Q5



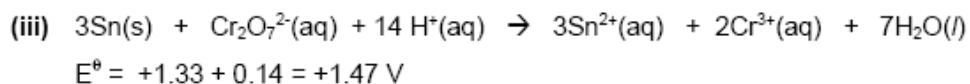
- (ii) No of moles of X = $1/119 = 8.40 \times 10^{-3} \text{ mol}$
3240 C gives $8.40 \times 10^{-3} \text{ mol}$ of X
 $3240 / 8.40 \times 10^{-3} = 385560 \text{ C}$ of electricity gives 1 mol of X
 $385560 / 96500 = 4 \text{ F}$ gives 1 mol of X
 $n = 4$

20 SAJC/2009/P3/Q2

(a) (i)



- (ii)
- **Complete** the circuit by allowing the **ions** to flow through
 - maintain **electrical neutrality** by supplying ions to neutralize any built up of c solution;
 - **prevent** mixing of the two solutions in the half-cells. [Any one]



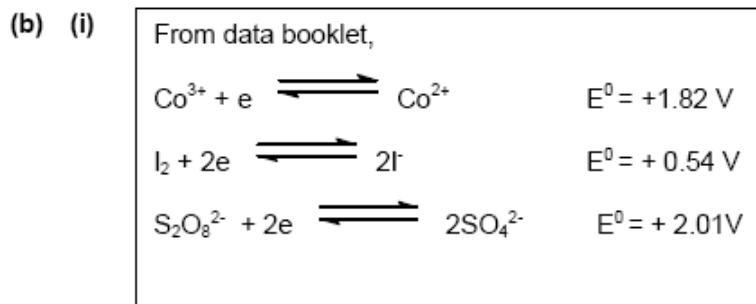
(iv) $Q = It$

$$= 0.2 \times 9000 = \mathbf{1800\text{ C}}$$

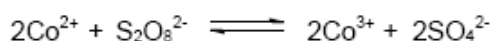
Since 96500 x 2 C of electricity consumes 1 mole of Sn,

193000 C of electricity consumes 119 g of Sn

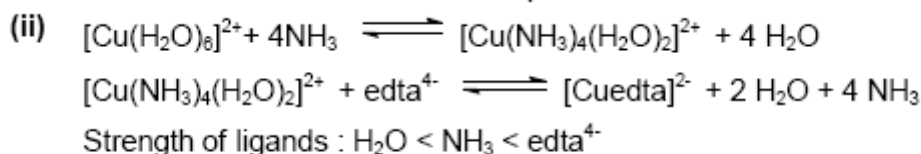
1800 C of electricity consumes **1.11 g** of Sn



$$E^{\circ} = +1.82 - 0.54 = +1.28 \text{ V} > 0$$



$$E^{\circ} = +2.01 - 1.82 = +0.19 \text{ V} > 0$$



21 SRJC/2009/P2/Q5(c)

(i) State what would be observed at the anode, cathode and the electrolyte after some time.

Anode: bubbles of oxygen gas is seen **[1/2 M]**

Cathode: pink solid of copper metal deposited **[1/2 M]**

Electrolyte: Blue solution decolourised or blue color of the solution becomes lighter.

[1/2 M]

(ii) Explain why bubbles of gas are produced at the cathode when the power supply is turned on for a prolonged period of time.

After a prolonged period of time, all $\text{Cu}^{2+}(\text{aq})$ in the electrolyte at the cathode region has undergone reaction completely/ reduced to Cu. **[1/2 M]**

H_2O will undergo reduction to H_2 at the cathode which explains the gas produced at the cathode. **[1 M]**

22 SRJC/2009/P3/Q4(a)

(a)	<p>(i) Given the following half cells:</p> <p>$\text{H}_2\text{O} (l) / \text{H}_2 (g)$ $\text{PbO}_2 (s) / \text{Pb}^{2+}(\text{aq})$ $\text{MnO}_4^- (\text{aq}) / \text{MnO}_2 (s)$</p> <p>Suggest the half cell which, when combined with the $\text{Cu}^{2+}(\text{aq}) / \text{Cu} (s)$ half cell, will generate the highest E^\ominus_{cell}. State the anode and the cathode of the electrochemical cell, indicating the direction of electron flow in the external circuit.</p>
<p>1 m $\frac{1}{2}$ m 1m $\frac{1}{2}$ m</p>	<p>$\text{Cu}^{2+}(\text{aq}) / \text{Cu} (s) \quad (+0.34 \text{ V})$</p> <p>$\text{H}_2\text{O} (l) / \text{H}_2 (g) \quad (-0.83 \text{ V})$ $\text{PbO}_2 (s) / \text{Pb}^{2+}(\text{aq}) \quad (+1.47 \text{ V})$ $\text{MnO}_4^- (\text{aq}) / \text{MnO}_2 (s) \quad (+1.67 \text{ V})$</p> <p>From $E^\ominus_{\text{cell}} = E^\ominus_{\text{red}} - E^\ominus_{\text{oxd}}$ Combination which will result in highest voltage is when Cu^{2+}/Cu half cell undergo oxidation and when $\text{MnO}_4^-/\text{MnO}_2$ undergo reduction</p> <p>For choosing $\text{MnO}_4^-/\text{MnO}_2$ Anode: Cu^{2+}/Cu Cathode: $\text{MnO}_4^-/\text{MnO}_2$</p> <p>$E^\ominus_{\text{cell}} = +1.67 - 0.34 = +1.33 \text{ V}$ <i>(ecf $\frac{1}{2}$ m if chose wrong half cell)</i></p> <p>Electron flow from Cu^{2+}/Cu half cell to $\text{MnO}_4^-/\text{MnO}_2$ half cell</p>
	<p>(ii) The set up from a(i) was then used as the battery in the electrolysis of a solution of copper (II) sulphate with inert platinum electrodes. An ammeter showed a reading of 0.45 A in the external circuit of a cell. 0.30 g of copper metal was deposited at the cathode after 30 minutes. Determine the actual current used in the electrolysis process. Hence, determine the percentage error (if any) of the ammeter reading.</p> <p>At the cathode, $\text{Cu}^{2+} + 2e \rightarrow \text{Cu}$</p> <p>$\frac{1}{2}$m Amount of copper deposited = $\frac{0.30}{63.5} = 4.724 \times 10^{-3} \text{ mol}$</p> <p>Amt of copper deposited = $\frac{Q}{2F}$</p> <p>$\frac{1}{2}$m $Q = 4.724 \times 10^{-3} \times 2 \times 96500 = 911.732 \text{ C}$ <i>(Allow ECF)</i></p> <p>$\frac{1}{2}$m $I = \frac{Q}{t} = \frac{911.732}{30 \times 60} = 0.506 \text{ A}$ <i>(Allow ECF)</i></p> <p>$\frac{1}{2}$m % error = $\frac{0.506 - 0.450}{0.506} \times 100\% = 11.1\%$</p>

Electrochemistry – Suggested Solutions

(iii) A student carried out a reaction involving potassium dichromate (VI) with an unknown half cell which consists of transition metal ions. The Gibbs Free Energy of the reaction was known to be -324 kJ mol^{-1} and the procedure involved transfer of 6 mol of electrons from the unknown solution to potassium dichromate (VI).
Using the expression of $\Delta G = -nFE_{\text{cell}}^{\ominus}$, where n is the number of electrons transferred, F is the Faraday constant and $E_{\text{cell}}^{\ominus}$ is the overall cell potential, determine the $E_{\text{cell}}^{\ominus}$ value and hence deduce the identity of the unknown half cell. [8]

1m Using $\Delta G = -nFE_{\text{cell}}^{\ominus}$
 $-324 \times 10^3 = -6 (96500) E_{\text{cell}}^{\ominus}$
 $E_{\text{cell}}^{\ominus} = +0.5595 \text{ V}$

Since procedure involved transfer of 6 mol of electrons from potassium dichromate (VI) to the unknown solution,

Reduction: $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e} \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \quad (+1.33)$
 $E_{\text{red}} = +1.33 \text{ V}$

Using $E_{\text{cell}}^{\ominus} = E_{\text{red}}^{\ominus} - E_{\text{oxd}}^{\ominus}$
 $0.5595 = +1.33 - E_{\text{oxd}}^{\ominus}$

1m $E_{\text{oxd}}^{\ominus} = -(0.5595 - 1.33) = +0.77 \text{ V}$
 1m The E_{oxd}^{\ominus} tally with the $\text{Fe}^{3+}/\text{Fe}^{2+}$ half cell

23 TJC/2009/P2/Q2

- (i) In the table below, indicate the polarity (+/-) of the electrodes and write the half-equations for the electrode processes that occur when the battery discharges.

Electrode	Polarity	Half-equation
Zinc		• $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}$
Carbon		• $\text{Br}_2(\text{aq}) + 2\text{e} \rightarrow 2\text{Br}^-(\text{aq})$

- (ii) 4.2 g of bromine is formed in the cell when a current of 2.0 A is passed through it during charging. Determine the length of time required to form 4.2 g of bromine.

- **Number of moles of electrons passed = $2 \times (4.2 / 159.8)$
= 0.0526 mol**

- **Quantity of charge required = 0.0526×96500
= 5076 C
= $I \times t$**
- **\therefore time required = $5076 \div 2.0$
= 2538 s**

- (iii) In a research laboratory, a research worker first charged a zinc-bromine battery fully before adding 10 cm³ of 0.2 mol dm⁻³ sodium bromide solution to each of the two electrode chambers.

What is the effect on the electrical output of the battery when it is discharged?

[8]

- **There is no effect to the position of equilibrium in the chamber containing Zn electrode and Zn²⁺(aq). Hence $E_{\text{Zn}^{2+}/\text{Zn}}$ remains as -0.76 V.**



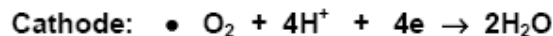
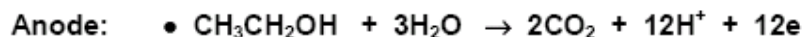
When the concentration of Br⁻(aq) increases in the chamber containing Br₂(aq) and Br⁻(aq), by Le Chatelier's Principle, the system will try to remove the excess Br⁻ by pushing the position of equilibrium to the left, hence making the E_{red} less positive than +1.07 V.

- **$E_{\text{cell}} = E_{\text{Br}_2/\text{Br}^-} - E_{\text{Zn}^{2+}/\text{Zn}}$**

Hence the emf of the cell is reduced which reduces the amount of electrical energy produced.

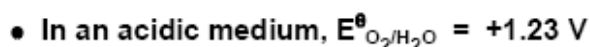
Electrochemistry – Suggested Solutions

- (i) Write the half-equations taking place at each of the electrode:



- (ii) Use appropriate data from the *Data Booklet* to explain why an acidic electrolyte is often preferred to an alkaline or neutral electrolyte.

[4]



- Hence oxygen is a stronger oxidising agent in an acidic medium.

24 TJC/2009/P3/Q5(d)

- (v) • Number of moles of silver produced = $1.08 / 108 = 1.00 \times 10^{-2} \text{ mol}$
 Since $\text{Ag} \equiv \text{e}^-$, number of moles of electrons transferred = $1.00 \times 10^{-2} \text{ mol}$
- $Q = I \times \text{time} = n \times F$
 $10 \times (\text{t} \times 60) = 1.00 \times 10^{-2} \times 96500$
 $\text{t} = 1.61 \text{ min}$

Number of moles of **manganese** produced = $0.183 / 54.9$
 $= 0.00333 \text{ mol}$



$1.00 \times 10^{-2} \text{ mol}$ of electrons liberated 0.00333 moles of Mn
 $x \text{ mol}$ of electrons liberated one mole of Mn.

- therefore $x = 1.00 \times 10^{-2} / 0.00333$
 $= 3$

25 TPJC/2009/P3/Q5

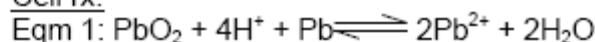
- (i) Cathode (Reduction)
 $\text{PbO}_2 + 4\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Pb}^{2+} + 2\text{H}_2\text{O} \quad E^\ominus = +1.47\text{V}$

Electrochemistry – Suggested Solutions

Anode (Oxidation)

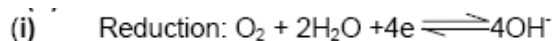


Cell rx:

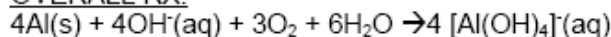


$$E^\ominus_{\text{CELL}} = +1.47 - (-0.13) = \underline{+1.60\text{V}}$$

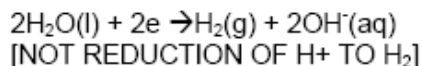
- (ii) White ppt = PbSO_4
 Precipitation of PbSO_4 resulted in a decrease in $[\text{Pb}^{2+}]$;
 According to LCP, system will try to produce more Pb^{2+} , hence favouring the cell reaction (or forward rx or eqm 1 will shift to the right)
 Hence E^\ominus_{cell} becomes more positive.
 OR
 Decrease in $[\text{Pb}^{2+}]$, according to LCP, results in the favoring of the reduction rx at the cathode leading to a more +ve E^\ominus reduction process; while at the anode, it also result in the favoring the oxidation of Pb hence the E^\ominus of oxidation process becomes more -ve.
 As $E^\ominus_{\text{cell}} = E^\ominus_{\text{R}} - E^\ominus_{\text{O}}$, it results in a more +ve value.



OVERALL RX:



- (ii) Oxygen supply is hindered when the pores are clogged up, so that the reduction process of H_2O to H_2 occurred instead.



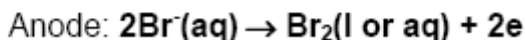
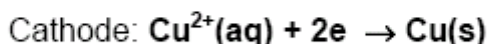
H_2 is potentially explosive OR

Gas is produced in a sealed container, so it is potentially explosive due to extremely high pressure.

- (iii) White ppt = Aluminium hydroxide.
 It is formed as there are insufficient OH^- to dissolved the amphoteric aluminium hydroxide.

26 VJC/2009/P2/Q2(c)

- (i) Using E^\ominus values, write ion-electron equations, for the reactions occurring at the cathode and anode in **Cell 1** during electrolysis. Include state symbols.



After a current was passed through the saturated solution of CuBr_2 in **Cell 1** for 10 minutes, the solution surrounding the anode was removed and it was found to require 35.50 cm^3 of $0.500 \text{ mol dm}^{-3}$ of sodium thiosulphate solution for complete reaction.

(ii) Determine the number of moles of $\text{Na}_2\text{S}_2\text{O}_3$ used.

$$\begin{aligned} \text{No. of moles of thiosulphate solution} &= 35.50/1000 \times 0.500 \\ &= 0.0178 \text{ mol} \end{aligned}$$

(iii) Calculate the number of moles of electrons transferred.

$$\begin{aligned} \text{For } 5\text{H}_2\text{O} + \text{S}_2\text{O}_3^{2-} &\rightarrow 2\text{SO}_4^{2-} + 10\text{H}^+ + 8\text{e} \\ \text{Hence, no. of moles of electrons transferred} & \\ &= 8 \times \text{no. of moles } \text{S}_2\text{O}_3^{2-} \\ &= 8 \times 0.0178 \\ &= 0.142 \end{aligned}$$

(iv) Hence, determine the current that flows through the circuit.

$$\begin{aligned} \text{Quantity of charge transferred} &= I \times t \\ 0.142 \times 96500 &= I \times 10 \times 60 \\ I &= 22.8 \text{ A} \end{aligned}$$

(d) A halogen is evolved at one of the electrodes in **Cell 2** after passing the current through it for 10 minutes and it is found that the mass of the syringe increased by 5.04 g. Identify X by calculating the M_r of the halogen produced.

Since two half cells are connected in series, the current passed through the Cell 2 is also 22.8 A.

$$\text{No. of moles of electrons transferred} = 0.142$$

$$\begin{aligned} \text{From } 2\text{X}^- &\rightarrow \text{X}_2 + 2\text{e}, \\ \text{Hence, no. of moles of the gas produced in Cell 2} & \\ &= \frac{1}{2} \times 0.142 \\ &= 5.04 / M_r \end{aligned}$$

$$M_r \text{ of the gas, } \text{X}_2 = 71.0$$

Hence, X is Cl.

27 VJC/2009/P3/Q1(e)

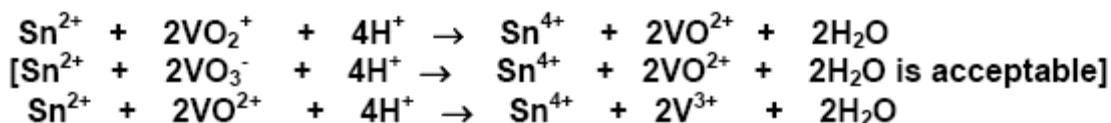
Data	E^\ominus/V
(yellow) $\text{VO}_2^+/\text{VO}^{2+}$	+1.00
(blue) $\text{VO}^{2+}/\text{V}^{3+}$	+0.34
$\text{Sn}^{4+}/\text{Sn}^{2+}$	+0.15
(green) $\text{V}^{3+}/\text{V}^{2+}$ (violet)	-0.26

$$E_{\text{cell}} = +1.00 - 0.15 = +0.85\text{V} > 0 \text{ feasible}$$

$$E_{\text{cell}} = +0.34 - 0.15 = +0.19\text{V} > 0 \text{ feasible}$$

$$E_{\text{cell}} = -0.26 - 0.15 = -0.41\text{V} < 0 \text{ not feasible}$$

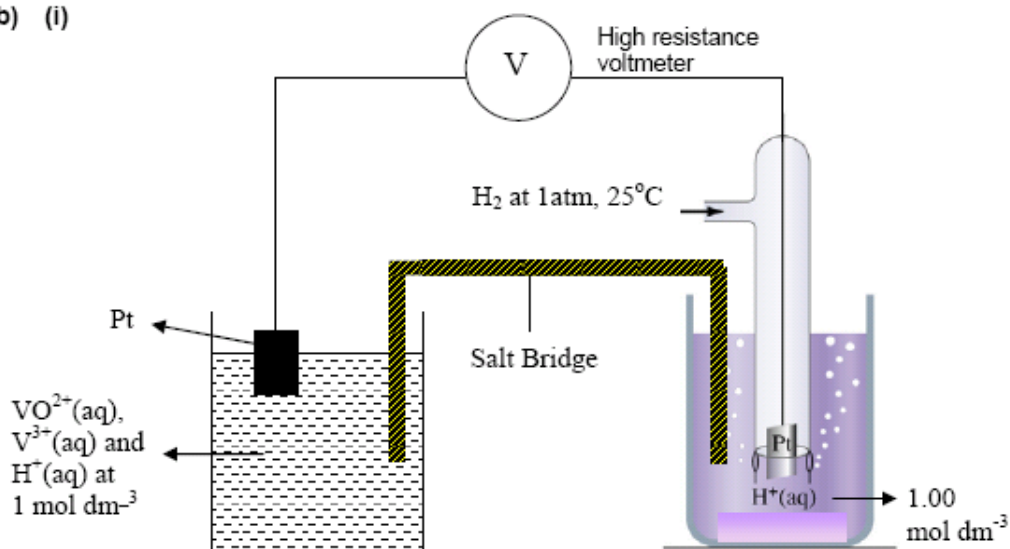
$\text{Sn}^{2+}(\text{aq})$ is powerful enough to reduce VO_3^- to V^{3+} . Hence, green solution is expected to form.



[3]

28 YJC/2009/P3/Q1(b)

(b) (i)



(ii) Stable oxidation state = +5

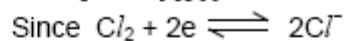
$$\text{V}^{3+} \rightarrow \text{VO}^{2+} \quad E^\ominus_{\text{cell}} = (+0.98) - (-0.50) = +1.48 \text{ V, reaction is feasible}$$

$$\text{VO}^{2+} \rightarrow \text{VO}_2^+ \quad E^\ominus_{\text{cell}} = (+0.98) - (+0.16) = +0.82 \text{ V, reaction is feasible}$$

(iii) Electrode potential values depend on the ligands present in the complex

29 YJC/2009/P3/Q4(d)

(d) (i) $n_{e^-} = \frac{Q}{F} = \frac{2.0 \times 30 \times 60}{96500} = 0.0373 \text{ mol}$



$$n_{\text{Cl}_2} = \frac{1}{2} \times n_{e^-} = \frac{1}{2} \times 0.0373 = 0.01865 \text{ mol}$$

Using $pV = nRT$,

$$V = \frac{(0.01865)(8.31)(27 + 273)}{1.5 \times 1.01 \times 10^5}$$

correct substitution of quantities into equation, and correct conversion of either temperature or pressure.

$$V = 3.07 \times 10^{-4} \text{ m}^3 = 307 \text{ cm}^3$$

(ii) High temperature and low pressure



$E_{\text{red}}^\ominus (\text{F}_2 / \text{F}^-)$ is much more positive than $E_{\text{red}}^\ominus (\text{O}_2 / \text{H}_2\text{O})$

O_2 will always be preferentially discharged (rather than F_2 gas).