

Pioneer Junior College Higher 2 Chemistry (9647) Physical Chemistry Electrochemistry

References:

1. Longman A-Level Guide, Chemistry – J.G.R. Briggs
2. Chemistry for advanced level – Peter Cann & Peter Hughes

Content

- Redox processes: electron transfer and changes in oxidation number (oxidation state)
- Electrode potentials
 - (i) Standard electrode (redox) potentials, E^\ominus ; the redox series
 - (ii) Standard cell potentials, E^\ominus_{cell} , and their uses
 - (iii) Batteries and fuel cells
- Electrolysis
 - (i) Factors affecting the amount of substance liberated during electrolysis
 - (ii) The Faraday constant; the Avogadro constant; their relationship
 - (iii) Industrial uses of electrolysis

Learning Outcomes

Candidates should be able to:

- (a) describe and explain redox processes in terms of electron transfer and/or of changes in oxidation number (oxidation state)
- (b) define the terms:
 - (i) standard electrode (redox) potential
 - (ii) standard cell potential
- (c) describe the standard hydrogen electrode
- (d) describe methods used to measure the standard electrode potentials of:
 - (i) metals or non-metals in contact with their ions in aqueous solution
 - (ii) ions of the same element in different oxidation states
- (e) calculate a standard cell potential by combining two standard electrode potentials
- (f) use standard cell potentials to:
 - (i) explain/deduce the direction of electron flow from a simple cell
 - (ii) predict the feasibility of a reaction
- (g) understand the limitations in the use of standard cell potentials to predict the feasibility of a reaction
- (h) construct redox equations using the relevant half-equations (see also Section 9.4)
- (i) predict qualitatively how the value of an electrode potential varies with the concentration of the aqueous ion
- (j) state the possible advantages of developing other types of cell, e.g. the H_2/O_2 fuel cell and improved batteries (as in electric vehicles) in terms of smaller size, lower mass and higher voltage
- (k) state the relationship, $F = Le$, between the Faraday constant, the Avogadro constant and the charge on the electron
- (l) predict the identity of the substance liberated during electrolysis from the state of electrolyte (molten or aqueous), position in the redox series (electrode potential) and concentration
- (m) calculate:
 - (i) the quantity of charge passed during electrolysis
 - (ii) the mass and/or volume of substance liberated during electrolysis, including those in the electrolysis of $\text{H}_2\text{SO}_4(\text{aq})$; $\text{Na}_2\text{SO}_4(\text{aq})$
- (n) explain, in terms of the electrode reactions, the industrial processes of:
 - (i) the anodising of aluminium
 - (ii) the electrolytic purification of copper [technical details are not required]

1 Electrochemistry: the study of electron transfer reactions occurring in two types of cells - **electrochemical cell** and **electrolytic cell**.

- (i) **Electrochemical cell / voltaic cell / galvanic cell** : in which the redox reaction is spontaneous and chemical energy is converted to electrical energy.
- (ii) **Electrolytic cell (in electrolysis)**: in which the redox reaction is non-spontaneous and electrical energy is used to cause it to occur. Electrical energy is converted to chemical energy in an electrolytic cell.

1.1 Common terms in Electrochemistry

Electrolyte – a compound in aqueous or molten state with mobile ions

Electrodes – conductors by which current enters or leaves the electrolyte.

- **Anode** – electrode at which **oxidation** occurs
- **Cathode** – electrode at which **reduction** occurs

Half-cell – arrangement of an electrode dipped into a solution of ions.

(Note : A half-equation can be written for the reaction inside a half-cell)

Cell – arrangement of two half-cells joined together and consists of two electrodes (an anode and a cathode) dipped in aqueous or molten solutions.

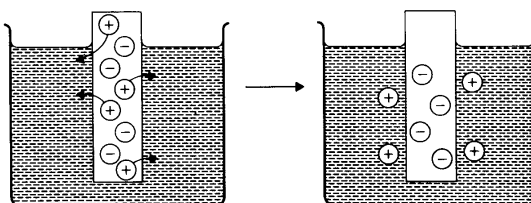
Part 1: The Electrochemical Cell

(b) define the terms: (i) standard electrode (redox) potential

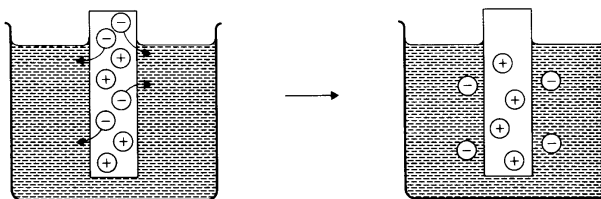
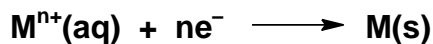
2 Electrode Potentials & Standard Electrode (Redox) Potentials

When a metal is placed in a solution of one of its ions, two processes occur:

(a) Oxidation where the metal atoms lose electrons to form cations in solution. The electrons remain on the electrode, making it negatively charged.



(b) Reduction where the metal ions in solution gain electrons from the metal to form atoms. The cations remain on the metal, making it positively charged.



Hence, when a metal is dipped into its solution, a **reversible** electron transfer reaction occurs:



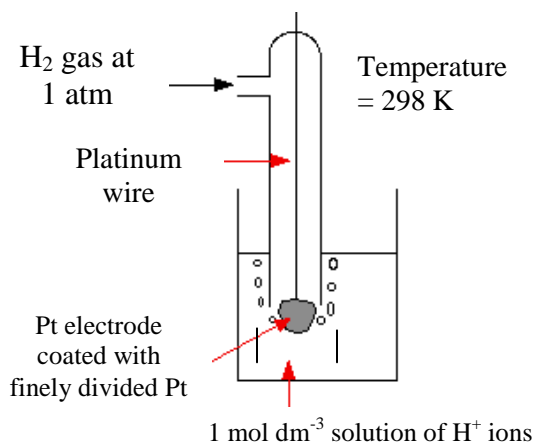
This arrangement of an electrode dipping into a solution of its ions is called a **half cell**.

When the rates of the two reversible reactions are equal, equilibrium is reached.

At equilibrium, there is a **potential difference** between the metal and an aqueous solution of its ions and this is called its **electrode potential**.

(c) describe the standard hydrogen electrode

2.1 The Standard Hydrogen Electrode (S.H.E.)



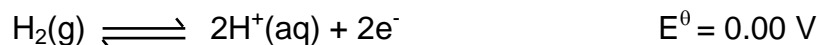
S.H.E. consists of:

- ♦ H₂ gas at 1 atm pressure and 25°C bubbling around a platinum electrode coated with finely divided Pt.
- ♦ The electrode is immersed in a 1 mol dm⁻³ solution of H⁺ ions.

Platinum is chosen for its inert property

so that equilibrium between H₂(g) and H⁺(aq) can be established rapidly

- Chosen as the reference electrode and assigned an electrode potential of 0.00 V under standard conditions.
- Consists of a platinised platinum electrode (to increase surface area of the electrode so as to increase rate at which equilibrium is established) dipped in a 1.0 mol dm⁻³ H⁺ (aq) solution (usually HCl (aq)).
- A slow stream of hydrogen gas at 1 atm pressure and 25°C is bubbled over the platinum electrode so that equilibrium is established.



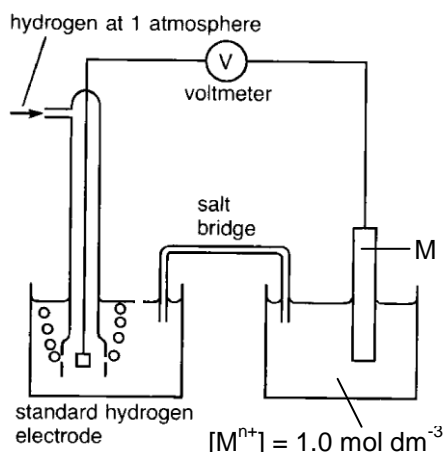
Standard Conditions :

1. temperature : **25°C (298K)**
2. pressure : **1 atm**
3. concentration of H⁺ ions involved: **1.0 mol dm⁻³**

2.2 Half-cell

Half-cell is the term used to describe the arrangement of an electrode dipping into a solution of ions.

2.3 Measuring Standard Electrode (Redox) Potential, E^\ominus



For example, when we join the metal electrode half-cell and the hydrogen electrode together, a potential difference (p.d) or e.m.f is built across them which is measured by a **high resistance voltmeter**.

This p.d is the driving force which forces the electrons to move through the circuit. The reading on the voltmeter gives the **standard electrode potential, E^\ominus** , of the metal under standard conditions at the first instance the voltmeter is connected and read.

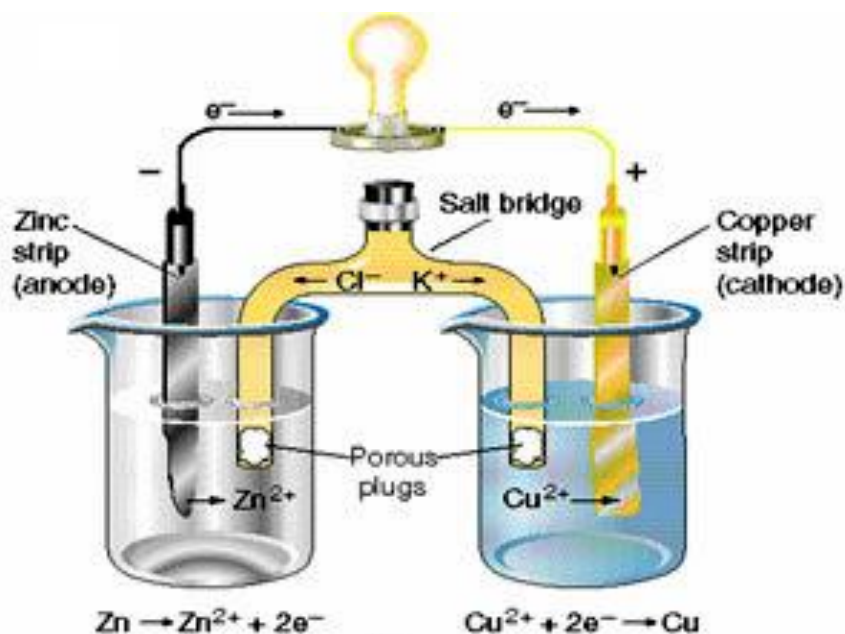
The superscript " \ominus " is used to indicate that measurements are done under standard conditions.

Standard electrode potential, E^\ominus , is defined as:

The potential difference between a standard hydrogen electrode and a half cell under standard conditions of 25°C , 1 atm and concentration of ions is 1 mol dm^{-3} .

2.4 The Set-up of the Galvanic Cell

Galvanic cells (or voltaic cells) are electrochemical cells in which spontaneous redox reactions occur to generate electrical energy.



About the set-up (also known as the Daniell Cell):

- The two reactants, Zn(s) and $\text{Cu}^{2+}(\text{aq})$, are not in direct physical contact.
- Each beaker forms a metal-metal ion half-cell.
- The zinc and copper strips act as electrodes. The electrodes are being connected by an electrical wire.
- The salt bridge consists of an inverted U-tube containing a salt solution, e.g. Na_2SO_4 , KCl , KNO_3 . The salt chosen must not react with the ions in either half-cell. The ends of the bridge are stuffed with porous plugs to prevent direct mixing of the two solutions but allow the passage of ions through them.

Functions of Salt Bridge (contains KCl(aq) or $\text{KNO}_3(\text{aq})$ or $\text{Na}_2\text{SO}_4(\text{aq})$ are:

- To **complete** the circuit allowing the passage of electricity between electrodes but physically **separating** the two half-cells.
- To maintain **electrical neutrality** by providing cations and anions to balance the charges of ions formed from the electrodes.

(b) define the terms (ii) standard cell potential

(e) calculate a standard cell potential by combining two standard electrode potentials

3 Calculation of Standard Cell Potential

E^\ominus_{cell} is the potential difference between two electrodes in an electrochemical cell formed by combining 2 half-cells under standard conditions. It measures the tendency of electrons to flow through the external circuit.

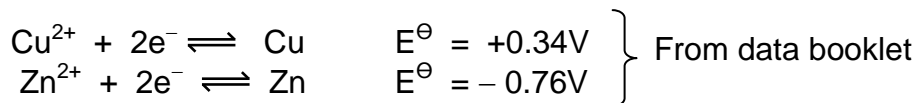
$$E^\ominus_{\text{cell}} = E^\ominus_{\text{red}} + E^\ominus_{\text{ox}}$$

where E^\ominus_{red} is the standard electrode potential of the reduction half-cell
 E^\ominus_{ox} is the standard electrode potential of the oxidation half-cell

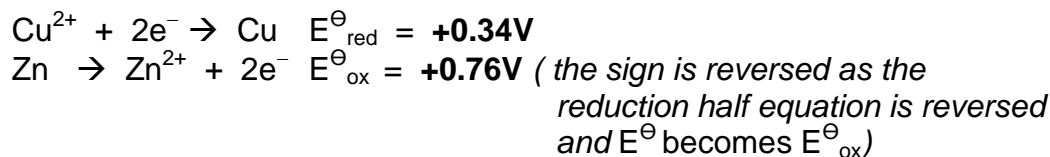
E^\ominus_{cell} also called **electromotive force (e.m.f.) or cell voltage**.

Using the Daniell cell as example: $\text{Cu}^{2+} + \text{Zn} \rightarrow \text{Cu} + \text{Zn}^{2+}$

1. Choose the E^\ominus for the two half-cells:



2. Write down the reactions as they occur in the two half-cells. If the reaction occurs in the opposite direction as the equation stated, the sign of the E^\ominus must be reversed.



Hence,

$$E^{\ominus}_{\text{ox}} = -E^{\ominus}_{\text{red}}$$

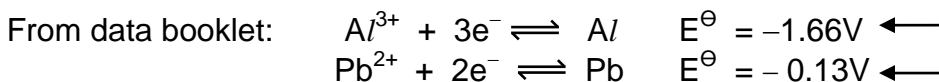
Then calculate standard cell potential:

$$\begin{aligned} \text{Standard Cell Potential : } E^{\ominus}_{\text{cell}} &= E^{\ominus}_{\text{red}} + E^{\ominus}_{\text{ox}} \\ &= (+0.34) + (+0.76) \\ &= +1.10\text{V} > 0 \text{ V (energetically feasible)} \end{aligned}$$

If $E^{\ominus}_{\text{cell}} > 0$	\Rightarrow reaction is energetically feasible and spontaneous
If $E^{\ominus}_{\text{cell}} = 0$	\Rightarrow reaction proceeds until equilibrium is established
If $E^{\ominus}_{\text{cell}} < 0$	\Rightarrow reaction is NOT energetically feasible and non-spontaneous

(h) construct redox equations using the relevant half-equations (see also Section 9.4)

Question 1: An electrochemical cell was set up using a $\text{Al}^{3+} / \text{Al}$ half-cell and a $\text{Pb}^{2+} / \text{Pb}$ half-cell. Find the e.m.f. of the cell (i.e., $E^{\ominus}_{\text{cell}}$) and write the overall cell reaction.



$$\begin{aligned} E^{\ominus}_{\text{cell}} &= E^{\ominus}_{\text{red}} + E^{\ominus}_{\text{ox}} \\ &= -0.13 + (+1.66) \\ &= +1.53\text{V} > 0 \text{ (energetically feasible)} \end{aligned}$$



The reaction at **anode** is chosen from the **more negative E^{\ominus}** or **less positive E^{\ominus}**

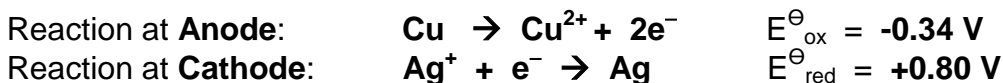
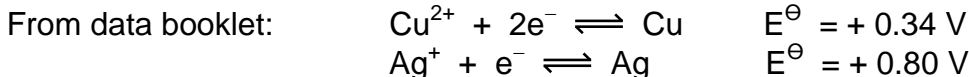
Similarly, the reaction at **cathode** is chosen from the **less negative** or **more positive E^{\ominus}**

Note: E^{\ominus} values are independent of the number of electrons being transferred, so do NOT multiply the E^{\ominus} even if equations are multiplied by a factor.

Common Mistake by Students !

$$E^{\ominus}_{\text{cell}} = E^{\ominus}_{\text{red}} + E^{\ominus}_{\text{ox}} = +3(-0.13) + 2(+1.66) = +2.93 \text{ V} !!$$

Question 2: Calculate the E^\ominus_{cell} of this reaction: $\text{Cu} + 2\text{Ag}^+ \rightarrow \text{Cu}^{2+} + 2\text{Ag}$

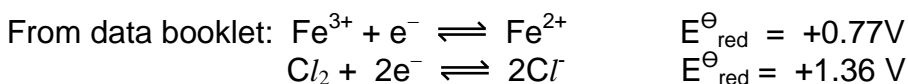


$$\begin{aligned} E^\ominus_{\text{cell}} &= E^\ominus_{\text{red}} + E^\ominus_{\text{ox}} \\ &= +0.80 + (-0.34) \\ &= +0.46\text{V} > 0 \text{ (energetically feasible)} \end{aligned}$$

(f) use standard cell potentials to:

(i) explain/deduce the direction of electron flow from a simple cell

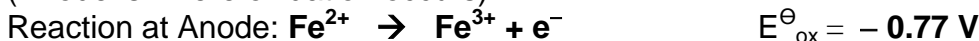
Question 3: An electrochemical cell was set up using a $\text{Fe}^{3+}/\text{Fe}^{2+}$ & Cl_2/Cl^- half-cell. Find the e.m.f. of the cell (i.e., E^\ominus_{cell}) and write the overall cell equation.



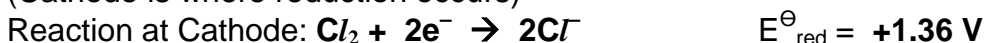
Note: Fe^{2+} must be oxidised to Fe^{3+} , Cl_2 reduced to Cl^-

$$\begin{aligned} E^\ominus_{\text{cell}} &= E^\ominus_{\text{red}} + E^\ominus_{\text{ox}} \\ &= +1.36 + (-0.77) \\ &= +0.59\text{V} > 0 \text{ (energetically feasible)} \end{aligned}$$

(Anode is where oxidation occurs)



(Cathode is where reduction occurs)



Electrons flow from $\text{Fe}^{2+}/\text{Fe}^{3+}$ half cell to Cl_2/Cl^- half cell.

*Electrons always flow through external circuit from **anode to cathode**.*

(d) describe methods used to measure the standard electrode potentials of:

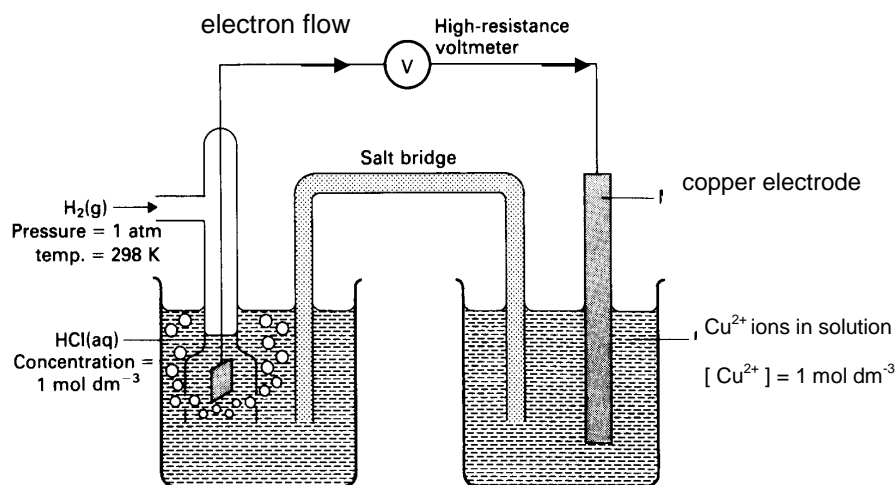
- (i) metals or non-metals in contact with their ions in aqueous solution
- (ii) ions of the same element in different oxidation states

- (f) use standard cell potentials to:
 (i) explain/deduce the direction of electron flow from a simple cell

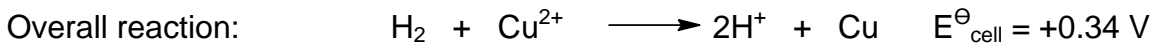
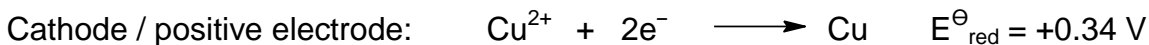
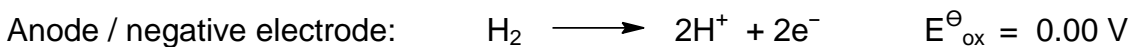
4 Examples of Standard Electrode Potentials

4.1 Metals in contact with their ions in aqueous solution

Example 1: Cu electrode in CuSO_4 solution with respect to standard hydrogen electrode.

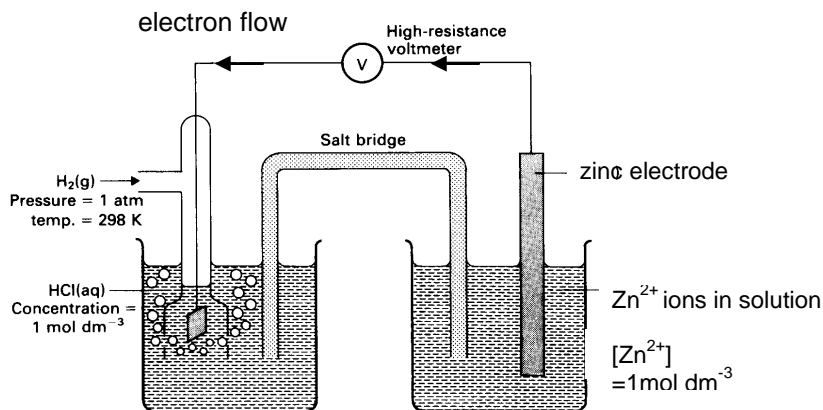


Reactions at the electrodes:

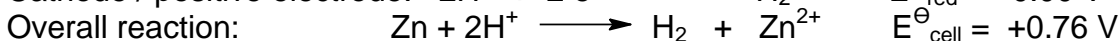
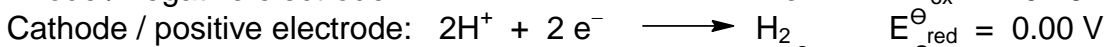
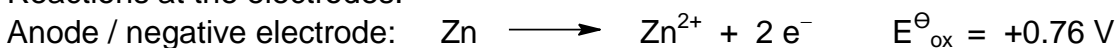


- Electrons flow through external circuit from **anode to cathode** (or Pt / negative electrode to Cu / positive electrode).

Example 2: Zn electrode in $1 \text{ mol dm}^{-3} \text{ ZnSO}_4$ solution with respect to standard H_2 electrode.



Reactions at the electrodes:

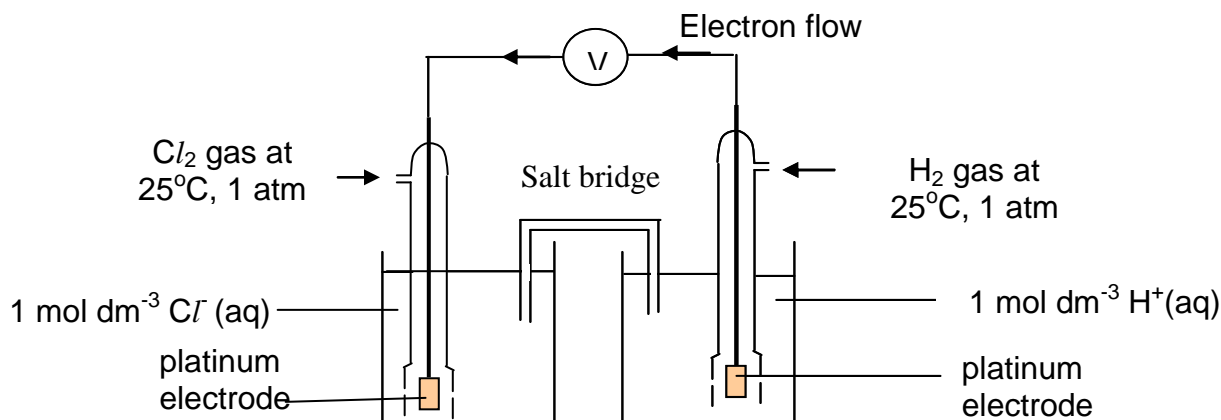


- Electrons flow through external circuit **anode to cathode** (or Zn/negative electrode to Pt/positive electrode).

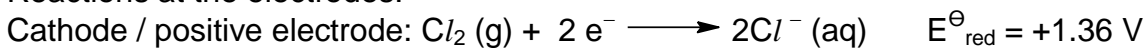
4.2 Non- metals in contact with their ions in aqueous solution

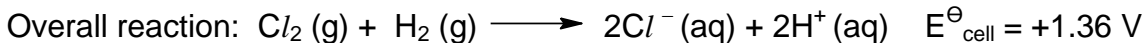
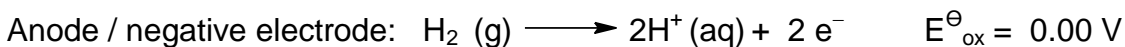
- A gas-ion electrode uses a gas in contact with its anions or anions in solution. The gas is bubbled into the solution.
- An **inert** platinum electrode is dipped into the solution of **anions** under standard conditions as there is no metal to act as electrode in the gas-ion electrode system.

Example 1: Chlorine gas is bubbled into $\text{Cl}^{-}(\text{aq})$ using platinum electrode



Reactions at the electrodes:



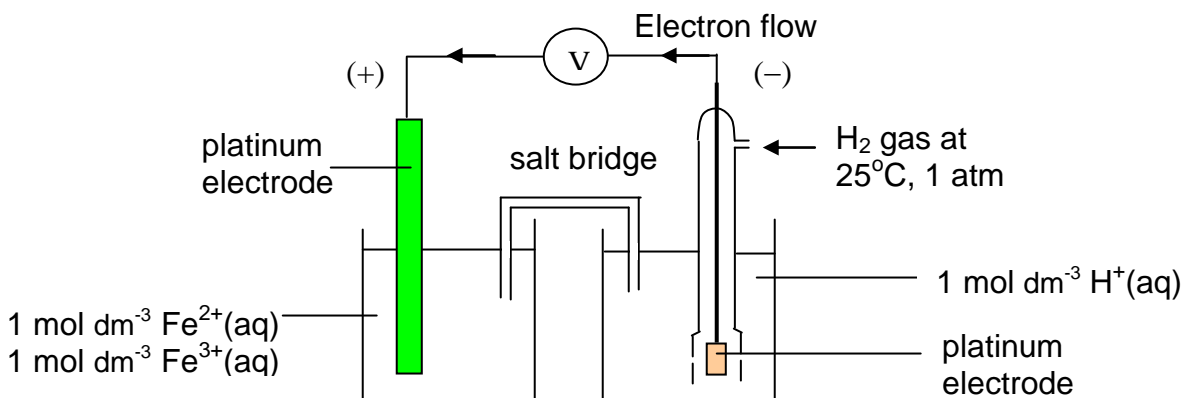


Electrons flow through external circuit from **anode to cathode**

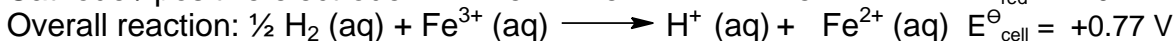
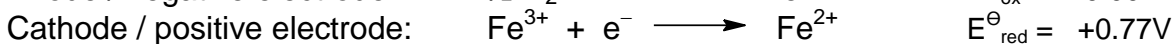
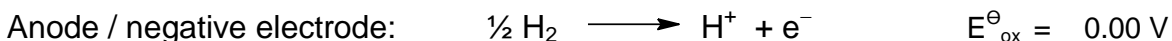
4.3 Ions of the same element in different oxidation states

- Half-cell consisting of ions of same element in **2 oxidation states**.
- An inert electrode such as platinum electrode is essential when the half-cell does not involve a metal.

Example 1: Platinum electrode is immersed in a mixture of $\text{Fe}^{3+}(\text{aq})$ and $\text{Fe}^{2+}(\text{aq})$



Reactions at the electrodes:



Common error made by students who used Fe metal electrode at the cathode instead of Pt electrode.

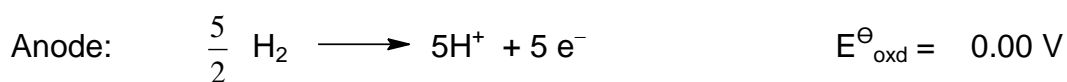
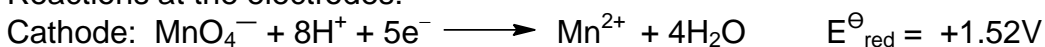
It is wrong because if Fe is used, you will also be measuring the standard electrode potential of **Fe^{2+}/Fe and Fe^{3+}/Fe system as well** instead of the **desired $\text{Fe}^{3+}/\text{Fe}^{2+}$ system only**.

Example 2: Platinum electrode immersed in a mixture of acidified MnO_4^- (aq) and Mn^{2+} (aq)

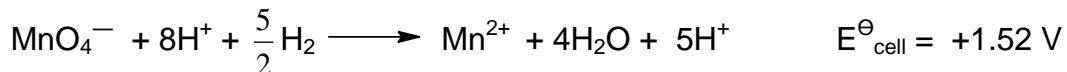
- Set-up is similar to Section 4.3 Example 1 except that **3 types of ions** are used.
- An inert platinum electrode is dipped into a solution of MnO_4^- , Mn^{2+} and H^+ , all of which are 1.00 mol dm^{-3} .

(Please do **NOT** use $8.00 \text{ mol dm}^{-3} \text{H}^+$ as E^\ominus does **NOT** follow the mole ratio of the particles)

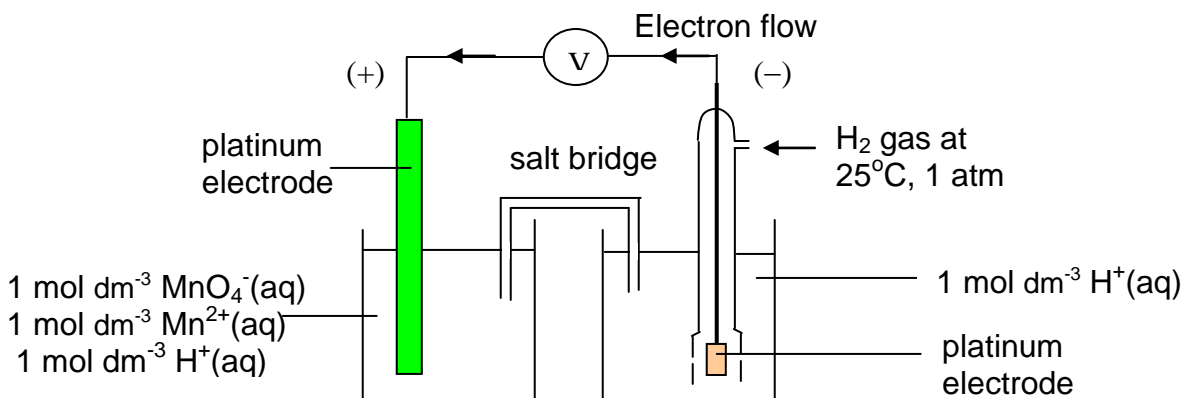
Reactions at the electrodes:



Overall reaction:



- Electrons flow through external circuit from **anode to cathode**.



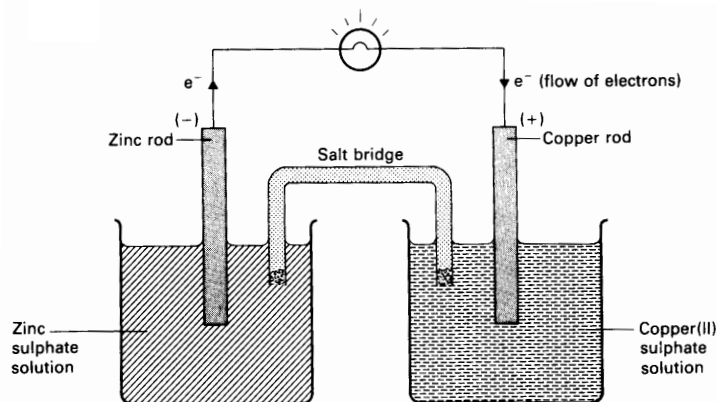
5 Cell Diagram OR Cell Notation

“Cell diagram” aka “Cell Notation” is a convenient method of representing a cell. It is shorthand for writing down a cell formed by connecting two half-cells.

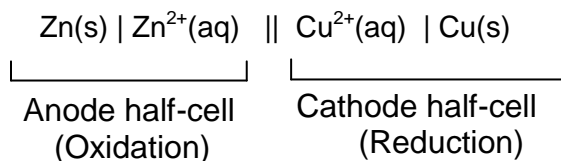
Notation used	Meaning
	boundary between 2 phases which are in contact
or ⋮ or ⋮⋮	salt bridge
,	2 oxidation states sharing the same homogeneous aqueous phase
()	conditions used in measurement, e.g. pressure, concentration

- (a) Anode: **oxidation half-cell** or electrode where oxidation occurs (**-ve** electrode) **MUST** always be on the **LHS**.
- (b) Cathode: **reduction half-cell** or electrode where reduction occurs (**+ve** electrode) **MUST** always be on the **RHS**.
- (c) Cell reaction reads from the left to the right.
- (d) Electrode on the extreme left (for oxidation half-cell) and on the extreme right (for reduction half-cell).

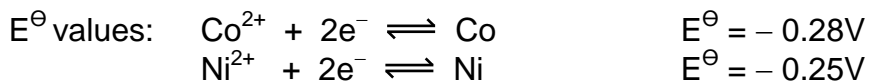
For example,



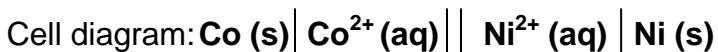
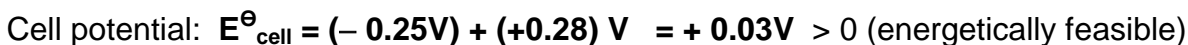
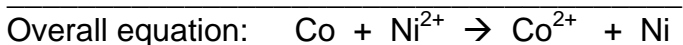
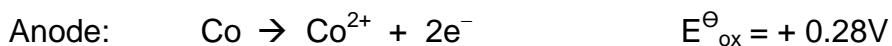
The cell diagram for the cell is:



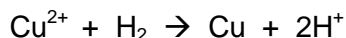
Example 1: Determine the standard cell potential of the following system:



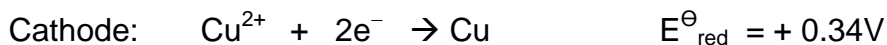
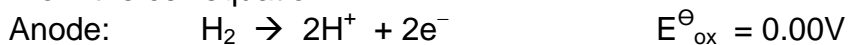
Remember that all standard cell potential for cell must be **positive**.



Example 2: Construct a cell diagram from the overall cell equation given below:



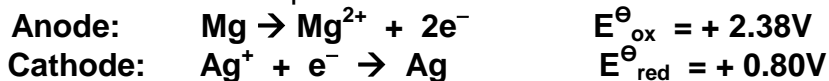
From the cell equation:



Question 3:

Consider $\text{Mg(s)} \mid \text{Mg}^{2+}(\text{aq}) \parallel \text{Ag}^+(\text{aq}) \mid \text{Ag(s)}$ under standard conditions.

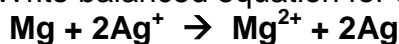
(a) Write ion-electron equations for reactions at the two half-cells.



(b) State the direction of electron flow from which electrode to another.

Electrons flow from Mg electrode to Ag electrode.

(c) Write balanced equation for the overall reaction.



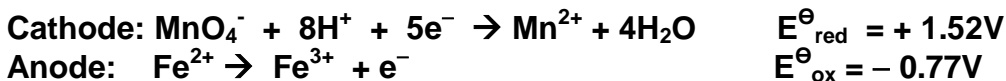
(d) Calculate the e.m.f of the cell.

$$\begin{aligned} E_{\text{cell}}^{\ominus} &= E_{\text{red}}^{\ominus} + E_{\text{ox}}^{\ominus} \\ &= +0.80 + (+ 2.38) \\ &= +3.18\text{V} > 0 \text{ (energetically feasible)} \end{aligned}$$

Question 4: Consider the following standard electrode potentials:

Half-cells: $\text{Fe}^{3+}(\text{aq})/\text{Fe}^{2+}(\text{aq})$ & $\text{MnO}_4^- (\text{aq})/\text{Mn}^{2+} (\text{aq})$

(a) Write the half equation for each electrode reaction.



(b) With reference to the *Data Booklet*, calculate the $E_{\text{cell}}^{\ominus}$ of the reaction and write the balanced redox equation.

$$\begin{aligned} E_{\text{cell}}^{\ominus} &= E_{\text{red}}^{\ominus} + E_{\text{ox}}^{\ominus} \\ &= +1.52 + (- 0.77) \\ &= + 0.75\text{V} > 0 \text{ (energetically feasible)} \end{aligned}$$

Overall equation: $\text{MnO}_4^- + 8\text{H}^+ + 5\text{Fe}^{2+} \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} + 5\text{Fe}^{3+}$

(d) State the direction of electron flow in the external circuit.

Electrons flow from the Pt electrode of $\text{Fe}^{2+}/\text{Fe}^{3+}$ to the Pt electrode of $\text{MnO}_4^- / \text{Mn}^{2+}$

(e) Write the cell diagram of the redox reaction.



6 Uses of E^\ominus values:

When metals are placed in order of their E^\ominus , the **electrochemical series or the Redox series** is obtained.

Reaction	E^\ominus/V
$\text{Li}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Li}(\text{s})$	-3.04
$\text{K}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{K}(\text{s})$	-2.92
$\text{Ca}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Ca}(\text{s})$	-2.87
$\text{Na}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Na}(\text{s})$	-2.71
$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Mg}(\text{s})$	-2.38
$\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \rightleftharpoons \text{Al}(\text{s})$	-1.66
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Zn}(\text{s})$	-0.76
$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Pb}(\text{s})$	-0.13
$\text{H}^+(\text{aq}) + \text{e}^- \rightleftharpoons \frac{1}{2}\text{H}_2(\text{g})$	0.00
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s})$	+0.34
$\frac{1}{2}\text{I}_2(\text{s}) + \text{e}^- \rightleftharpoons \text{I}^-(\text{aq})$	+0.54
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Fe}^{2+}(\text{aq})$	+0.77
$\text{Ag}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s})$	+0.80
$\frac{1}{2}\text{Br}_2(\text{l}) + \text{e}^- \rightleftharpoons \text{Br}^-(\text{aq})$	+1.07
$\frac{1}{2}\text{Cl}_2(\text{g}) + \text{e}^- \rightleftharpoons \text{Cl}^-(\text{aq})$	+1.36
$\frac{1}{2}\text{F}_2(\text{g}) + \text{e}^- \rightleftharpoons \text{F}^-(\text{aq})$	+2.87

The standard electrode potential given in the data booklet is the **reduction potential**

Strength of oxidising agent and reducing agent

- Oxidising agent** is always itself reduced.

The more positive the E^\ominus , the greater the tendency for the substance to be reduced.

- Reducing agent** is always itself oxidised.

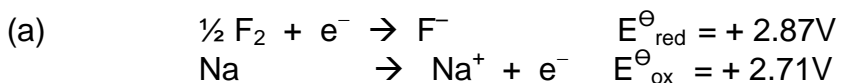
The more negative the E^\ominus , the greater the tendency for the substance to be oxidised.

(f) use standard cell potentials to: (ii) predict the feasibility of a reaction

(h) construct redox equations using the relevant half-equations (see also Section 9.4)

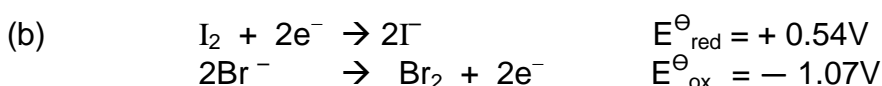
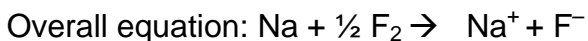
Question 5: With reference to the *Data Booklet*. Predict whether a reaction (usually conducted in test tubes) will occur under standard conditions between:

- F_2 and Na
- I_2 and Br^-
- $\text{Cr}_2\text{O}_7^{2-}$ and F_2
- V^{3+} and Cu^{2+}

Solution:


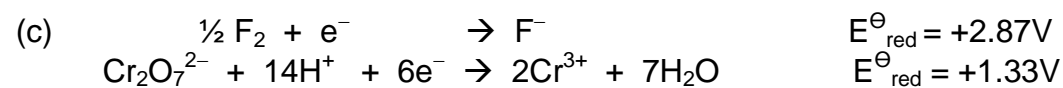
$$\begin{aligned}
 E_{\text{cell}}^{\ominus} &= E_{\text{red}}^{\ominus} + E_{\text{ox}}^{\ominus} \\
 &= +2.87 + (+2.71) = +5.58\text{V} > 0\text{V}
 \end{aligned}$$

Reaction is energetically feasible as the $E_{\text{cell}}^{\ominus}$ is positive.

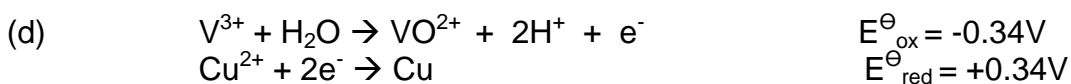


$$\begin{aligned}
 E_{\text{cell}}^{\ominus} &= E_{\text{red}}^{\ominus} + E_{\text{ox}}^{\ominus} \\
 &= (+0.54) + (-1.07) = -0.53\text{V} < 0\text{V}
 \end{aligned}$$

Reaction is not energetically feasible as the $E_{\text{cell}}^{\ominus}$ is negative.



Reaction is not energetically feasible as both F_2 and $\text{Cr}_2\text{O}_7^{2-}$ undergo reduction.
 [Note: No Cr^{3+} and F^- are present in reaction mixture]



$$\begin{aligned}
 E_{\text{cell}}^{\ominus} &= E_{\text{red}}^{\ominus} + E_{\text{ox}}^{\ominus} \\
 &= (+0.34) + (-0.34) = 0\text{V}
 \end{aligned}$$

Reaction proceeds until equilibrium is reached.

(i) predict qualitatively how the value of an electrode potential varies with the concentration of the aqueous ion

7 Effect of Concentration on the electrode potential and cell e.m.f.

E is affected by the concentration of ions and Le Chatelier's Principle is used to predict the effect of changing the concentration of the solution in a half-cell.

Example:


Case 1: Changes in [Mⁿ⁺] → position of equilibrium shifts

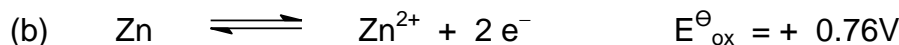
State and explain how the e.m.f. of the cell would change if

- (a) the solution of copper ions were diluted,
(b) the solution of zinc ions were diluted.



When Cu²⁺(aq) is diluted, i.e. [Cu²⁺(aq)] is **decreased**, by Le Chatelier's Principle, the equilibrium position will shift to the **left**, so as to produce more Cu²⁺(aq) so as to re-establish equilibrium. Hence, E_{red}(Cu²⁺/Cu) becomes **less** positive.

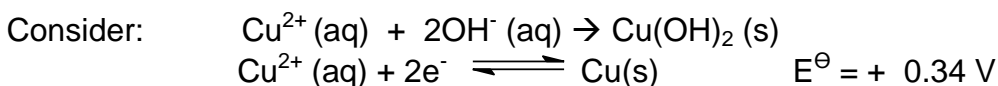
Thus E_{cell} = E_{red}(Cu²⁺/Cu) + E_{ox}(Zn/Zn²⁺) will **decrease to less than +1.10 V**.



When Zn²⁺(aq) is diluted, i.e. [Zn²⁺(aq)] is **decreased**, by Le Chatelier's Principle, the equilibrium position will shift to the **right** to produce more Zn²⁺(aq) so as to re-establish the equilibrium. Hence E_{ox} value becomes **more positive**.

Thus, E_{cell} value **increased** or becomes **more positive than** E_{cell}[⊖] = +1.10 V

Case 2: Precipitation → concentration of aqueous ions changes → position of equilibrium shifts.



When NaOH(aq) is added to the half-cell containing Cu²⁺(aq), Cu(OH)₂ ppt forms
As a result, [Cu²⁺(aq)] decreases.

Position of equilibrium shifts to the left

E_{red}(Cu²⁺/Cu) becomes less positive than E_{red}[⊖] = + 0.34 V

Thus, E_{cell} value **decreased** or becomes **less positive than** E_{cell}[⊖] = +1.10 V

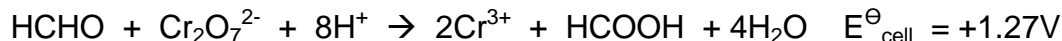
(g) understand the limitations in the use of standard cell potentials to predict the feasibility of a reaction

8 Limitations of E_{cell}[⊖] to predict feasibility of reaction

Reactions with positive E_{cell}[⊖] are energetically feasible. However, this may not occur for all cases due to:

1 Reaction has a very high activation energy

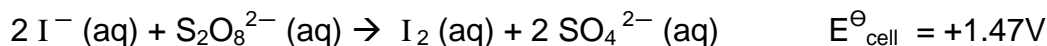
(a) Eg: oxidation of methanal to methanoic acid by acidified potassium dichromate(VI)



Since E^\ominus_{cell} is positive, the reaction should be feasible. However, in practice, there is no reaction at room temperature due to the **high activation energy** needed to **break strong covalent bonds**.

Reaction is too slow to occur. Heating is required to **break covalent bonds** for reaction to occur. Hence, the cell potential indicates **energetically feasibility** of the reaction but **not its kinetic feasibility**.

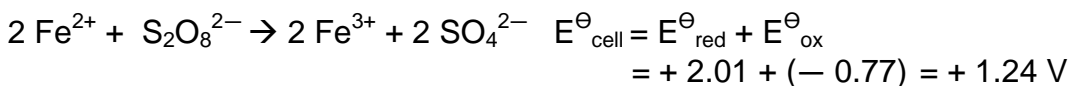
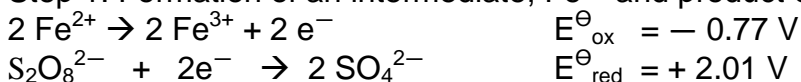
(b) Eg: Oxidation of I^- by peroxodisulfate ion



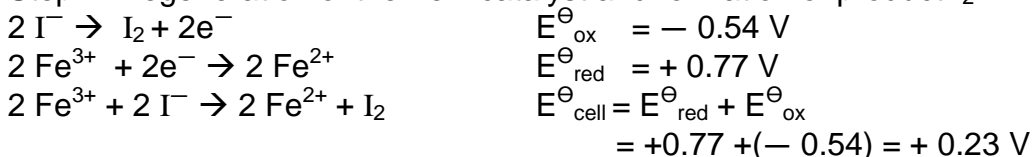
Since E^\ominus_{cell} is positive, the reaction should be feasible. However, the rate of the reaction is found to be very low due to **high activation energy needed to overcome repulsion** involving collisions between **two (similarly charged) negatively charged ions**.

An opposite positively charged Fe^{2+} or Fe^{3+} catalyst is used to **increase the rate of the reaction**.

Step 1: Formation of an intermediate, Fe^{3+} and product SO_4^{2-}



Step 2: Regeneration of the Fe^{2+} catalyst and formation of product I_2



Each of these 2-steps in the alternative pathway has a **positive E^\ominus_{cell}** hence each step is energetically feasible.

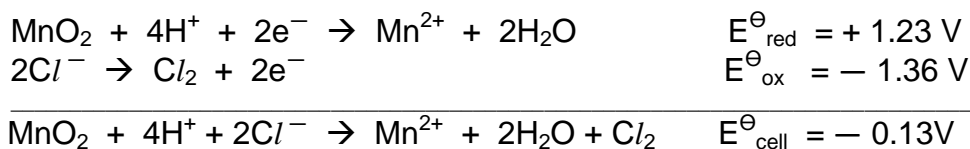
The rate of the reaction is high as both steps require a **lower activation energy due to collision between two oppositely charged ions**.

Fe^{2+} is regenerated at the end of the reaction.

If Fe^{3+} is used, these 2 steps will just be reversed in sequence. (this will be discussed under Transition elements).

2 Reaction not under standard conditions

(a) Eg. Oxidation of concentrated HCl by MnO_2



Since E_{cell}^\ominus is **negative**, the reaction should **not be feasible**.

However, Cl_2 can be prepared by **heating** MnO_2 with **concentrated** HCl .

The prediction fails because E^\ominus values do not apply when **non standard conditions** are used. (Here $[\text{HCl}] > 1 \text{ mol dm}^{-3}$ and temperature is not at 25°C)

(b) For Oxidation of Fe^{2+} by Ag^+



Since E_{cell}^\ominus is **positive**, the reaction should be energetically feasible.

However, when concentration of reactants used is lower than 1.00 mol dm^{-3} , the position of equilibrium will shift to the left and E_{cell} **will decrease to a negative value** and the reaction becomes **energetically not feasible**.

Note: As discovered by scientists, if E_{cell}^\ominus is about **less than + 0.20 V**, a fairly small change in concentration could make the E_{cell} become negative and the reaction becomes energetically not feasible.

(j) state the possible advantages of developing other types of cell, e.g. the H_2/O_2 fuel cell and improved batteries (as in electric vehicles) in terms of smaller size, lower mass and higher voltage

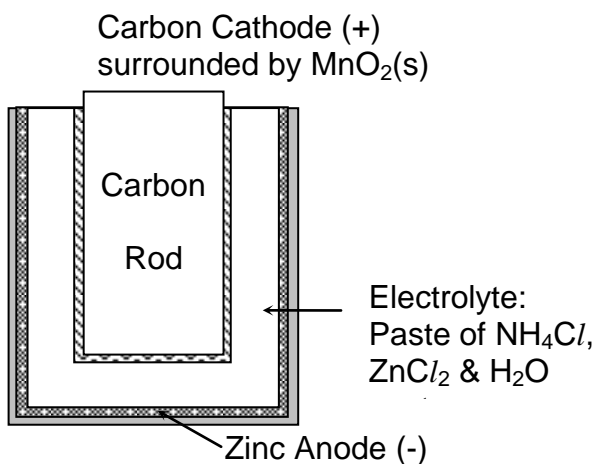
9 Batteries, Fuel Cells and Electric Cars

- A battery is made up of a few electrochemical cells in series and supplies direct electric current at a constant voltage. It is self-contained and portable.
- Electrochemical cells can be classified as primary or secondary.

(a) Primary Cells

- A primary cell may be used only once as it is **not rechargeable**.
- Examples : Dry cell (Leclanche Cell), Alkaline dry cell

Dry cell (Leclanche Cell)



Advantages :

Cheap and very portable

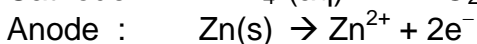
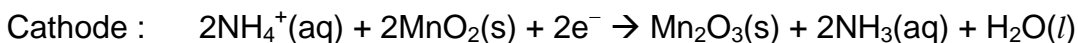
Disadvantages:

Non-rechargeable

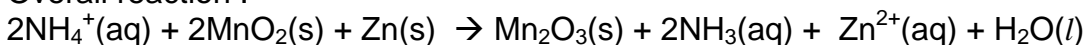
Paste is acidic (causes rust if leaking)

Limited shelf-life

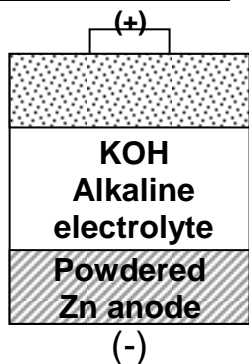
Delivers very low current and voltage drops during rapid discharge



Overall reaction :



Alkaline dry cell



Advantages :

Very portable

Delivers much greater current than dry cell

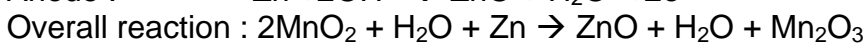
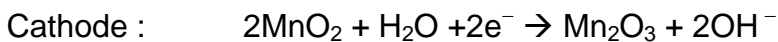
Voltage of 1.5 V remains fairly constant

Disadvantages:

Non-rechargeable

Limited shelf-life

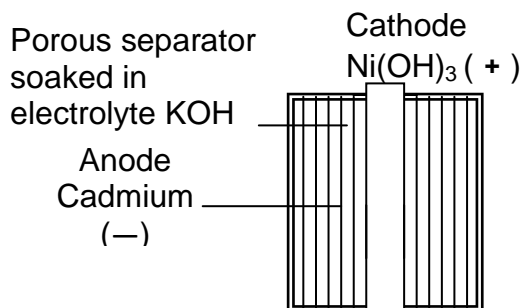
More expensive than dry cell



(b) Secondary Cells

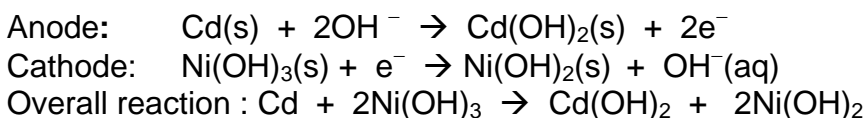
- Can be **recharged** by passing a current in opposite direction to the current flow during discharge.
- Examples : Nickel–cadmium cell, lead-acid accumulator

Nickel-Cadmium Cell (used in laptops and mobile phones)



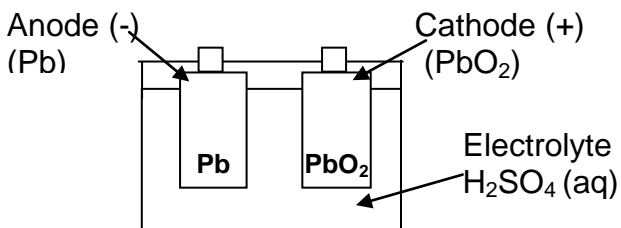
Advantages :
Rechargeable
Sealed to prevent leakage

Disadvantages:
Expensive
Low Voltage: 1.25 V



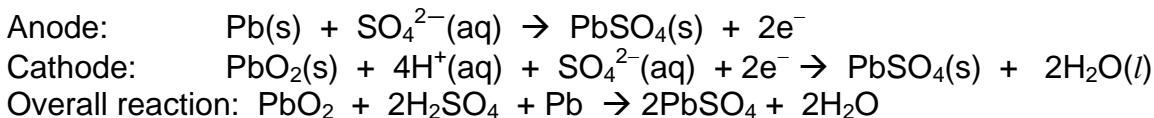
Lead-Acid Cell (Lead Accumulator)

The lead-acid accumulator is used in cars and normally consists of six cells arranged in series to provide 12 V.



Advantages :
Rechargeable
Delivers large **current** to start car

Disadvantages:
Heavy due to lead



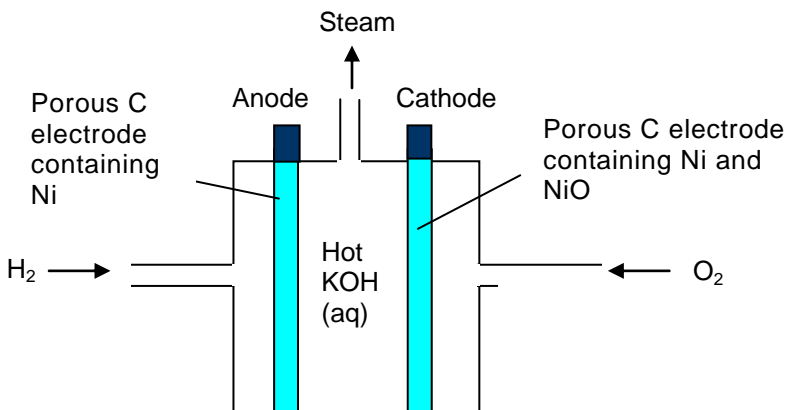
(j) state the possible advantages of developing other types of cell, e.g. the H₂/O₂ fuel cell and improved batteries (as in electric vehicles) in terms of smaller size, lower mass and higher voltage.

Fuel Cells (Used in spacecrafts)

- Converts **chemical energy** of conventional fuels (such as hydrogen or methane) into **electrical energy** by direct oxidation with oxygen from air.

Hydrogen-Oxygen Fuel Cell

- The negative and positive terminals are porous graphite coated with Ni or Pt catalysts.
- H₂(g) is passed into the negative compartment (anode) and O₂(g) into the positive compartment (cathode) of the cell.
- Under pressure, the gases diffuse through the porous graphite terminals into the electrolyte (either an acid or an alkali)



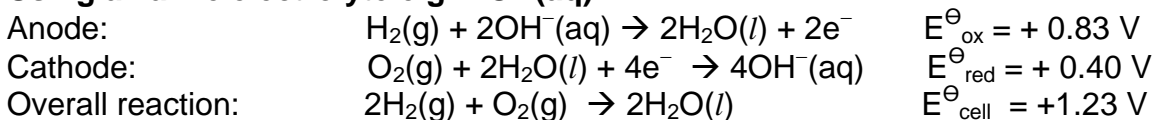
Advantages :

Pollution free (water is the only by-product)
Work indefinitely as long as the reactants are supplied

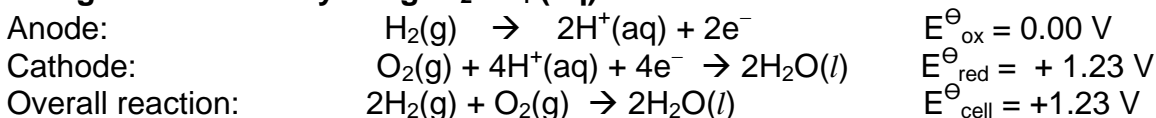
Disadvantages:

Expensive as large amount of platinum is used
Bulky storage of fuels

Using alkaline electrolyte e.g. KOH(aq)



Using acidic electrolyte e.g. H₂SO₄ (aq)



At the negative electrode (anode), released electrons flow through an external circuit towards the positive electrode (cathode).

Electric Cars

An **electric car** uses electric motors instead of an internal combustion engine. Electrical power is derived from battery packs carried on board the vehicle.

Advantages: noiseless, pollution-free, higher fuel efficiency than petrol

Disadvantages: high mass of batteries, short driving ranges, need to recharge batteries (time-consuming), high replacement costs of batteries

For a viable electric car, batteries that are of smaller size, lower mass and higher voltage are being developed.

Part 2: Electrolysis

When electricity from an **external voltage supply** is passed through an electrolyte, a chemical reaction called **electrolysis** occurs.

An electrolytic cell contains an electrolyte with two electrodes (anode and cathode) connected to a direct current supply.

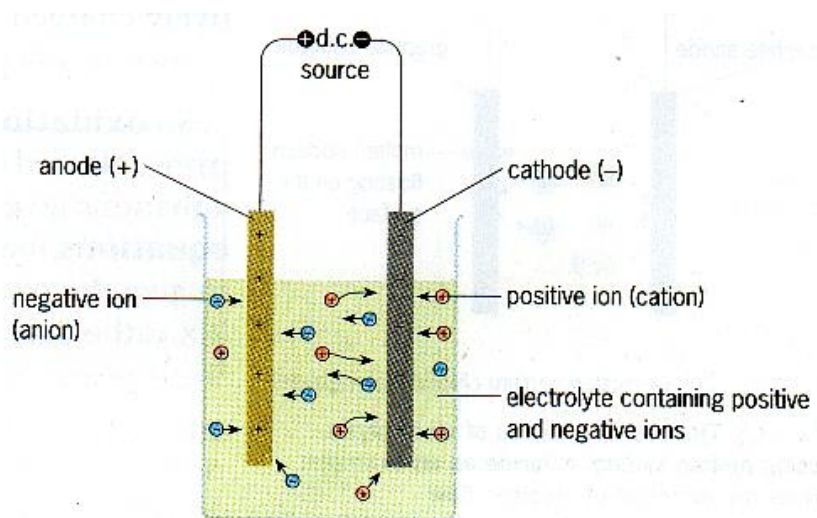
Electrolytes (compounds that conduct electricity and are decomposed by it)

E.g. **molten ionic compounds** such as $\text{NaCl}(l)$
aqueous solutions such as dilute sulfuric acid or aqueous CuSO_4

Mechanism of Electrolysis

The mechanism involves 2 main steps:

- (1) **Migration of ions** (cations move to cathode and anions move to anode)
 (Note: There are some particles which have net zero charge like $\text{H}_2\text{O}(l)$, they will **not migrate** to any electrode. For these $\text{H}_2\text{O}(l)$ molecules, it is the **surrounding** H_2O molecules that will be oxidised or reduced at the electrodes.)
- (2) **Electron transfer at the electrodes** (discharge of species - oxidation at anode and reduction at cathode)





(I) predict the identity of the substance liberated during electrolysis from the state of electrolyte (molten or aqueous), position in the redox series (electrode potential) and concentration

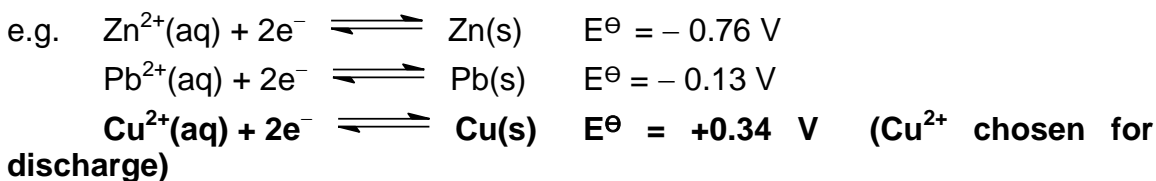
1. Factors Affecting the Selective Discharge of Ions at the Electrodes

In an electrolytic cell, different ions are found at the electrodes and the ion discharged is the one that requires the least energy. This is termed **selective discharge** and is dependent on the following factors:

1.1 Position in the Redox or Electrochemical Series

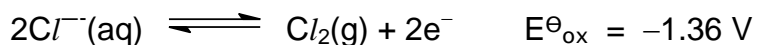
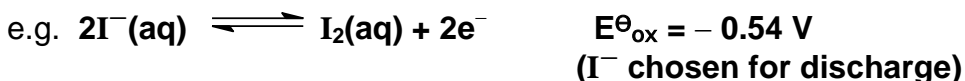
At the Cathode (Reduction)

Cation with the most positive E^{\ominus}_{red} values will be preferentially discharged/reduced.



At the Anode (Oxidation)

Anions with the most positive E^{\ominus} (oxidation) values will be preferentially discharged/oxidised.



Recall:

$E^{\ominus}_{\text{ox}} = -E^{\ominus}_{\text{red}}$

Example 1: Electrolysis of molten salts

Consider the electrolysis of **molten** lead(II) bromide using Pt electrode,

- a) Ions present : Pb^{2+} , Br^-
 b) At the anode (**positive** electrode)
 - **anions** are attracted to it and are discharged:

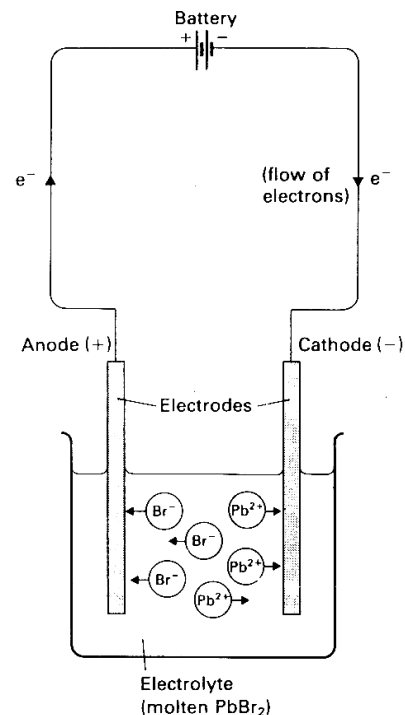
$$2 \text{Br}^- (l) \rightarrow \text{Br}_2 (g) + 2e^-$$

- c) At the cathode (**negative** electrode)
 - **cations** are attracted to it and are discharged:

$$\text{Pb}^{2+} (l) + 2e^- \rightarrow \text{Pb} (s)$$

Results: Reddish brown fumes of Br_2 is observed at anode and **molten lead** is deposited at cathode.

NOTE: High temperature is required to maintain the molten state. Since the melting point of PbBr_2 is higher than melting point of Pb, molten lead is collected at the cathode.



Example 2: Electrolysis of Aqueous Solutions (H_2O to be considered too)

Electrolysis of aqueous Na_2SO_4 using inert electrodes

- At the cathode Species : Na^+ and H_2O

Consider:

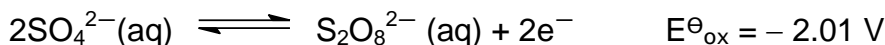
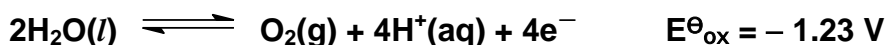


Process occurred: $2\text{H}_2\text{O}(\text{l}) + 2e^- \longrightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$

Hydrogen gas is liberated due to reduction of water molecules.

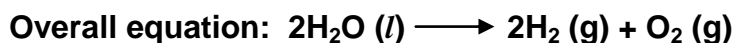
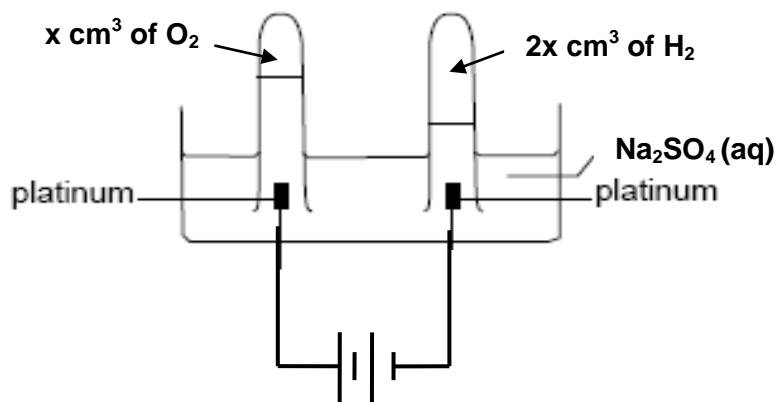
- At the anode Species : SO_4^{2-} and H_2O

Consider:



Process occurred: $2\text{H}_2\text{O}(\text{l}) \longrightarrow \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4e^-$

Oxygen gas is liberated due to oxidation of water molecules.



Example 3: Electrolysis of dilute H_2SO_4 using inert electrodes.

- At the cathode Species : H^+ and H_2O
 Consider:
 $2\text{H}_2\text{O}(l) + 2e^- \rightleftharpoons \text{H}_2(g) + 2\text{OH}^-(aq) \quad E^{\ominus}_{\text{red}} = -0.83 \text{ V}$
 $2\text{H}^+(aq) + 2e^- \rightleftharpoons \text{H}_2(g) \quad E^{\ominus}_{\text{red}} = 0.00 \text{ V}$

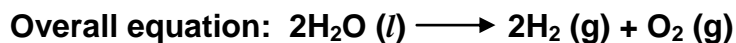
Process occurred: $2\text{H}^+(aq) + 2e^- \longrightarrow \text{H}_2(g)$

Hydrogen gas is liberated due to reduction of hydrogen ions.

- At the anode Species : SO_4^{2-} and H_2O
 Consider:
 $2\text{H}_2\text{O}(l) \rightleftharpoons \text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \quad E^{\ominus}_{\text{ox}} = -1.23 \text{ V}$
 $2\text{SO}_4^{2-}(aq) \rightleftharpoons \text{S}_2\text{O}_8^{2-}(aq) + 2e^- \quad E^{\ominus}_{\text{ox}} = -2.01 \text{ V}$

Process occurred: $2\text{H}_2\text{O}(l) \longrightarrow \text{O}_2(g) + 4\text{H}^+(aq) + 4e^-$

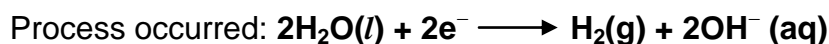
Oxygen gas is liberated due to oxidation of water molecules.



Example 4: Electrolysis of aqueous NaCl solution using graphite or inert electrodes

- At the cathode Species : Na^+ and H_2O

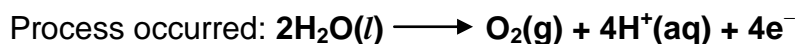
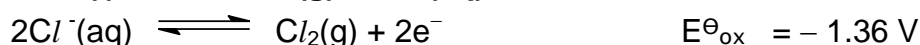
Consider:



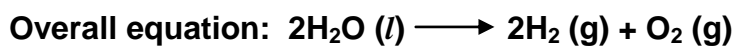
Hydrogen gas is liberated due to reduction of water molecules.

- At the anode Species : Cl^- and H_2O

Consider:



Oxygen gas is liberated due to oxidation of water molecules.



Note: O_2 liberated can oxidise C anode to a mixture of CO and CO_2 gases



1.2 Concentration of the Electrolyte

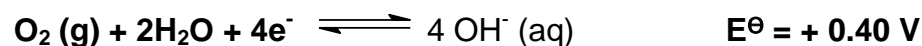
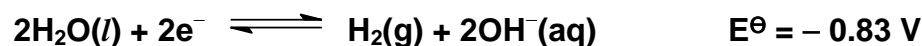
- Ions of higher concentration may be discharged in preference to those of lower concentration although their E^\ominus values may be less positive or more negative.

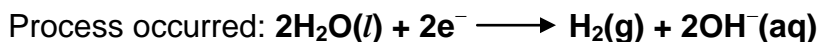
Electrolysis of concentrated brine(saturated NaCl solution) using inert electrodes

Purpose: To manufacture NaOH (aq) and Chlorine gas

At the cathode: Na^+ and H_2O

Consider:



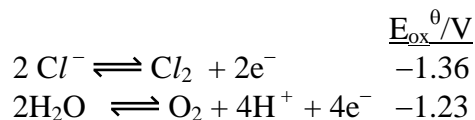
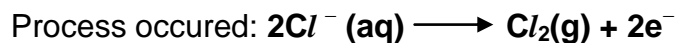
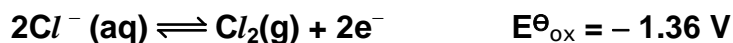
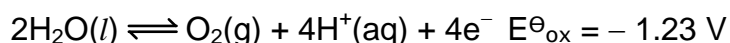


Hydrogen gas is liberated despite high $[\text{Na}^+]$. Na^+ ion is not reduced because its E^\ominus_{red} value is too negative.

Despite a **positive $E^\ominus = +0.40 \text{ V}$** for $\text{O}_2(g) + 2\text{H}_2\text{O} + 4e^- \rightleftharpoons 4\text{OH}^-(aq)$ it does not occur because this reaction shows that O_2 (but not H_2O) is reduced, but there is no oxygen gas pumped into the brine solution.

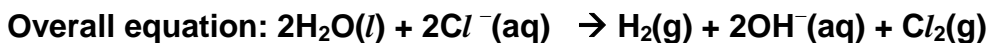
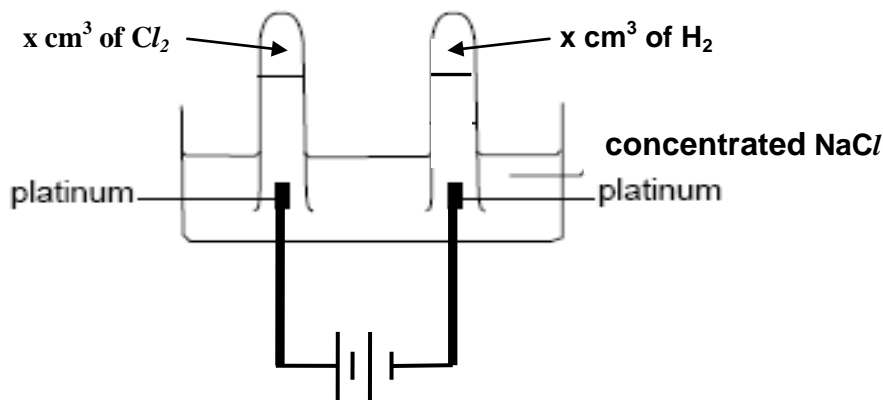
At the anode: Cl^- and H_2O

Consider:



High $[\text{Cl}^-]$ shifts position of the 1st eqm to the right, making $E^\ominus(\text{Cl}^-/\text{Cl}_2)$ less negative such that it becomes less negative than $E^\ominus(\text{H}_2\text{O}/\text{O}_2) = -1.23 \text{ V}$

Due to the **high** concentration of $\text{Cl}^-(aq)$, **chlorine gas** is liberated. Chloride ions are preferentially discharged (oxidised) even though its $E^\ominus(\text{oxidation})$ is less positive than H_2O .

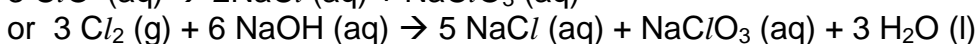


Note:

1. When the products: Cl_2 gas at the anode and $\text{NaOH}(aq)$ at the cathode are mixed, disproportionation occurs to produce chlorate(I) ClO^- and Cl^- ions



2. If the resulting mixture solution is **heated**, ClO^- undergoes further disproportionation.



1.3 Type of Anode Electrode Used

- If the anode electrode is not inert, it may be **preferentially oxidised**.
E.g. an anode metal immersed in its metal ions becomes active and dissolves to form ions.

Electrolysis of copper(II) sulfate solution

- The following species are present at the cathode and anode:
 - Cathode: $\text{Cu}^{2+}(\text{aq}), \text{H}_2\text{O}(\text{l})$ Anode: $\text{SO}_4^{2-}(\text{aq}), \text{H}_2\text{O}(\text{l}), \text{Cu}(\text{s})$
- The relevant E^\ominus values are as follows (from the Data Booklet)
 - Cathode: $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s})$ $E^\ominus_{\text{red}} = + 0.34 \text{ V}$
 - Cathode: $2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$ $E^\ominus_{\text{red}} = - 0.83 \text{ V}$
 - Anode: $2\text{SO}_4^{2-}(\text{aq}) \rightleftharpoons \text{S}_2\text{O}_8^{2-}(\text{aq}) + 2\text{e}^-$ $E^\ominus_{\text{ox}} = - 2.01 \text{ V}$
 - Anode: $2\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^-$ $E^\ominus_{\text{ox}} = - 1.23 \text{ V}$

If Cu anode is used, consider also:

- Anode: $\text{Cu}(\text{s}) \rightleftharpoons \text{Cu}^{2+}(\text{aq}) + 2\text{e}^-$ $E^\ominus_{\text{ox}} = - 0.34 \text{ V}$
- At the cathode:

Type of electrode	Platinum	Copper
Observations	Cu is deposited	Cu is deposited
Half-Equation	$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Cu}(\text{s})$	

- At the anode:

Type of electrode	Platinum (inert anode)	Copper (active anode)
Observations	Oxygen gas is liberated	Cu^{2+} is formed from the anode. * Mass of Cu anode <u>decreases</u> .
Half-Equation	$2\text{H}_2\text{O}(\text{l}) \rightarrow \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^-$	$\text{Cu}(\text{s}) \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{e}^-$

There will be a net transfer of Cu from the anode to the cathode and concentration of CuSO_4 remains unchanged.

(k) state the relationship, $F = Le$, between the Faraday constant, the Avogadro constant and the charge on the electron

2. Quantitative aspects of electrolysis - Faraday's Laws of Electrolysis

Faraday's first law states that the mass of a substance liberated or dissolved at an electrode is directly proportional to the quantity of electricity passed.

$$\underline{m \propto Q} \quad \text{or} \quad \underline{m \propto It}$$

If m : mass in grams, g

Q : quantity of electricity in coulombs, C

I : current in amperes, A

t : time in seconds, s

n_e : number of moles of electrons passed through the circuit

$$Q = It = n_e F$$

Faraday's second law states that the number of Faradays required to discharge one mole of an ion at an electrode is equal to the number of charges on the ion.



1 **Faraday** (Faraday constant) = charge carried by 1 mol of electrons

$$F = Le$$

From the Data Booklet:

F : Faraday constant = $96\,500 \text{ C mol}^{-1}$

e : electronic charge = $1.60 \times 10^{-19} \text{ C}$ L : Avogadro constant = $6.02 \times 10^{23} \text{ mol}^{-1}$

$F = 6.02 \times 10^{23} \times 1.60 \times 10^{-19} \approx 96\,500 \text{ C mol}^{-1}$ of electrons

(m) calculate:

(i) the quantity of charge passed during electrolysis

(ii) the mass and/or volume of substance liberated during electrolysis, including those in the electrolysis of $\text{H}_2\text{SO}_4(\text{aq})$; $\text{Na}_2\text{SO}_4(\text{aq})$

General Steps for Calculations involving electrolysis

- I. Write the **balanced redox equation** for the reaction occurring at the electrode.
- II. Determine the **number of Faradays** needed to produce **one mole** of the substance.
- III. Calculate the quantity of electricity, $Q = It = n_e F = n_e Le$
- IV. Calculate the mass or volume of substance produced at the electrode.

Example 1

A current of 3 A is passed into molten aluminium oxide for 2 hours.

- (a) What mass of aluminium is produced?
 (b) Calculate the volume of oxygen gas liberated at r.t.p.
- (a) Quantity of electricity passed, $Q = I \times t = 3 \times 2 \times 60 \times 60 = 21\,600\text{ C}$
 Cathode reaction: $\text{Al}^{3+} + 3\text{e}^- \longrightarrow \text{Al}$

$3\text{ F} \equiv 3 \times 96\,500\text{ C}$ are required to produce 1 mol of Al

$$\text{Amount of aluminium produced} = \frac{21\,600}{96\,500 \times 3} \text{ mol} = 0.07461 \text{ mol}$$

$$\text{Mass of aluminium} = 0.07461 \times 27.0 = 2.01 \text{ g}$$

- (b) At the anode: $2\text{O}^{2-}(\text{l}) \longrightarrow \text{O}_2(\text{g}) + 4\text{e}^-$

$4\text{ F} \equiv 4 \times 96\,500\text{ C}$ are required to produce 1 mol $\equiv 24\text{ dm}^3$ of O_2

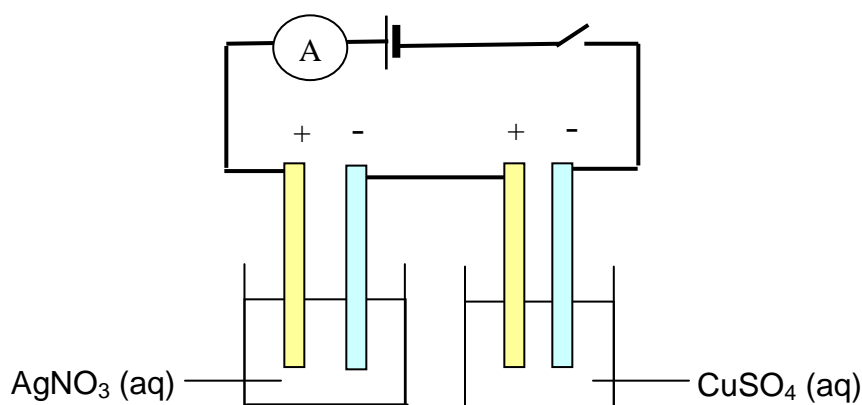
$$21\,600\text{ C will produce } \frac{21\,600}{4 \times 96\,500} \times 24 = 1.34\text{ dm}^3 \text{ O}_2 \text{ at r.t.p.}$$

Example 2

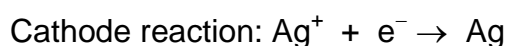
A current of 1 A was passed into 2 cells, containing silver nitrate and copper(II) sulfate solutions connected in series for 30 minutes.

- (a) Draw a diagram for the electrolytic process.
 (b) Calculate the masses of copper and silver deposited.

(a)



- (b) Quantity of electricity passed, $Q = I \times t = 1 \times (30 \times 60) = 1\,800\text{ C}$



2 Faradays $\equiv 2 \times 96500$ C are required to produce 1 mol of Cu.

$$\begin{aligned}\text{Amount of Cu deposited} &= \frac{1800}{96500 \times 2} \\ &= 9.33 \times 10^{-3} \text{ mol}\end{aligned}$$

$$\text{mass of Cu} = 9.33 \times 10^{-3} \times 63.5 = 0.592 \text{ g}$$

1 Faraday $\equiv 96500$ C are required to produce 1 mol of Ag.

$$\begin{aligned}\text{Amount of Ag deposited} &= \frac{1800}{96500} \\ &= 0.01865 \text{ mol}\end{aligned}$$

$$\text{mass of Ag} = 0.01865 \times 108 = 2.01 \text{ g}$$

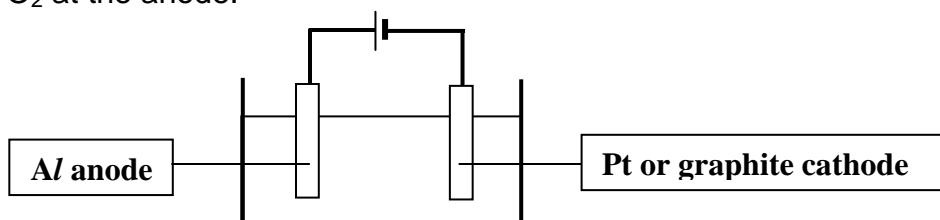
(n) explain, in terms of the electrode reactions, the industrial processes of:
(i) the anodising of aluminium

3. Uses of Electrolysis

3.1 Anodising of aluminium

Purpose: Aluminium has a thin layer of oxide that prevents it from further oxidation. This layer can be enhanced by an anodising process which forms a stronger and thicker layer of aluminium oxide, thereby improving corrosion resistance.

Set up: The natural oxide layer is first removed to expose the aluminium metal. Aluminium is then made the anode in an electrolyte of dilute sulfuric acid. Hence the electrolyte is chosen such that water is to be oxidised to give O_2 at the anode.



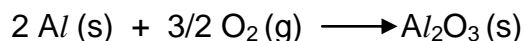
Electrolytes chosen : **dilute sulfuric acid**

Particles present : H^+ , SO_4^{2-} , H_2O

Electrodes: **aluminium anode, platinum or graphite cathode**

Anode (Aluminium): $2 \text{H}_2\text{O} (l) \longrightarrow \text{O}_2(g) + 4\text{H}^+(aq) + 4e^-$

O_2 released reacts with Al to form a thick porous layer of oxide.
The pores can be filled with dye and then sealed by dipping in hot water.



Cathode (Inert Platinum or Graphite): $2\text{H}^+(aq) + 2e^- \longrightarrow \text{H}_2(g)$ $E^\ominus = 0 \text{ V}$

Overall equation: $2 \text{Al} (s) + 3\text{H}_2\text{O} (l) \longrightarrow \text{Al}_2\text{O}_3 (s) + 3\text{H}_2 (g)$

Uses: window grilles, lighting appliances and small ornaments.

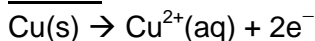
(ii) the electrolytic purification of copper [technical details are not required]

3.2 Purification of copper

Purpose: To extract pure copper from crude copper anode (obtained by roasting its ore ore (copper pyrites CuFeS_2) with silica) and deposit it on pure copper cathode.

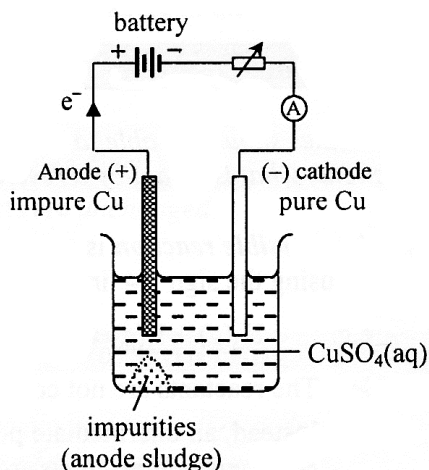
Set Up: Electrolysis is then used to obtain pure copper with $\text{CuSO}_4(\text{aq})$ as electrolyte.

Anode:

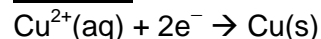


Metals higher than Cu in the electrochemical series are also oxidised and dissolved as cations.

Metals below Cu (such as Ag, Au) remain undissolved as "anode sludge" and can be recovered.



Cathode:

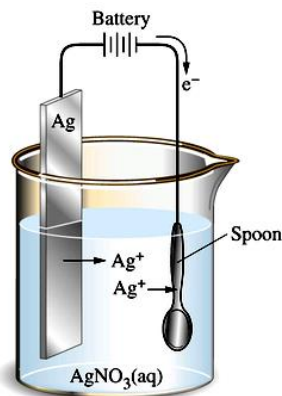


Ions above Cu remain in the solution. Concentration of electrolyte of $\text{CuSO}_4(\text{aq})$ remains unchanged.

2.3 Electroplating (Coating of objects with a thin layer of metal)

Purpose: To coat jewellery and tableware with gold or silver and car bumpers/bicycle parts made of stainless steel with chromium(to prevent rust and improve appearance)

Set Up: Electrolysis is then used with $\text{AgNO}_3(\text{aq})$ as the electrolyte and pure silver anode and object to be electroplated as the cathode.

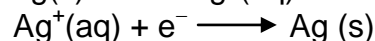


Example of silver plating

Anode: pure plating metal (Ag)



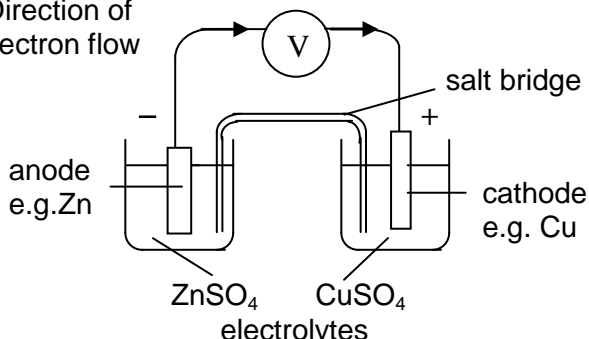
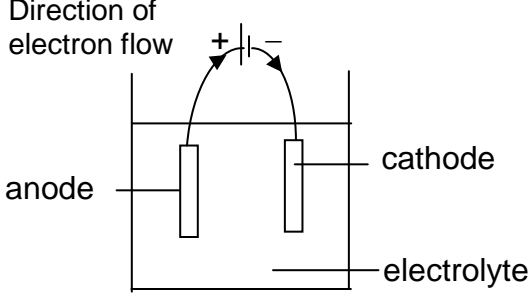
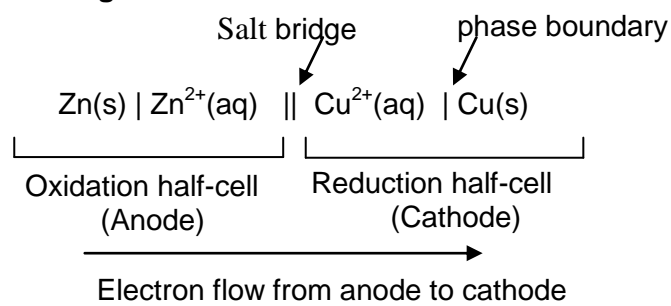
Cathode: object to be electroplated:



Note:

- (1) Object is totally immersed in the solution in order to be fully electroplated.
- (2) If object is not electrically conducting, it will be coated with conducting solid.
Eg: non conducting plastic spoon is coated with a layer of graphite powder.

Summary: Comparison of Electrochemical cell and Electrolytic cell

<div style="text-align: center; border: 1px solid black; padding: 5px; margin: 0 auto; width: 100px;">Electrochemistry</div>	
Electrochemical or Galvanic/Voltaic Cell	Electrolytic Cell
Convert chemical energy to electrical energy	Convert electrical energy to chemical energy
A spontaneous reaction	Non-spontaneous reaction
A spontaneous redox reaction generates an electric current. (the cell itself is a battery)	External electric current is applied to drive (force) the otherwise non-spontaneous redox reaction to occur.
<p>Direction of electron flow</p>  <p style="text-align: center;">Note: Voltmeter and salt bridge in the set-up</p>	<p>Direction of electron flow</p>  <p style="text-align: center;">Note: Battery or power source in set-up.</p>
<p>Cell diagram</p> <div style="text-align: center;">  </div>	-
<p>Anode is negative electrode (more reactive metal) Cathode is positive electrode (less reactive metal)</p> <p>More reactive metal anode loses electrons which move out into the wire, to the cathode which gains the electrons.</p> <p>Anode – electrode where oxidation occurs; half-cell with more negative E^{\ominus}_{red} value OR more positive E^{\ominus}_{ox} undergoes oxidation.</p> <p>Cathode – electrode where reduction occurs; half-cell with more positive E^{\ominus}_{red} value undergoes reduction.</p>	<p>Anode is positive electrode Cathode is negative electrode</p> <p>External d.c power supply pushes electrons to the cathode, making it negative and takes electrons from the anode making it positive</p> <p>Anode – electrode where oxidation occurs; species (look on RHS of half-equations in the Data booklet) with most negative E^{\ominus}_{red} OR most positive E^{\ominus}_{ox} value is preferentially oxidised.</p> <p>Cathode – electrode where reduction occurs; species (look on LHS of half-equations in the Data booklet) with most positive E^{\ominus}_{red} value is preferentially reduced.</p>

Electrochemical or Galvanic/Voltaic Cell	Electrolytic Cell
<p><u>Calculating standard cell potential and using E^\ominus_{cell} to predict feasibility of a reaction</u></p> <ol style="list-style-type: none"> From the data booklet, consider the possible relevant half-equations involving the 2 species stated in question. Decide which species undergoes reduction, which undergoes oxidation? Decide on which half-equations to use. Calculate E^\ominus_{cell} $E^\ominus_{\text{cell}} = E^\ominus_{\text{red}} + E^\ominus_{\text{ox}}$ <ol style="list-style-type: none"> Combine the 2 half-equations to write the overall equation. <p>If $E^\ominus_{\text{cell}} > 0$: reaction is energetically feasible and spontaneous.</p> <p>If $E^\ominus_{\text{cell}} = 0$: reaction proceeds until equilibrium is established</p> <p>If $E^\ominus_{\text{cell}} < 0$: reaction is NOT energetically feasible and non-spontaneous</p>	<p><u>Predicting what substance gets discharged at each electrode during electrolysis</u></p> <ol style="list-style-type: none"> List ALL species present in the electrolyte Decide on what species is present at each electrode. Consider and apply factors affecting selective discharge & predict the products formed at the respective electrodes <ol style="list-style-type: none"> Comparison of E^\ominus_{red} values Concentration of ion in electrolyte Type of anode used. <p><u>For electrolysis of Aqueous electrolytes: consider also if $\text{H}_2\text{O}(l)$ (not $\text{H}^+(\text{aq})$ or $\text{OH}^-(\text{aq})$ will be preferentially discharged.</u></p> <p><u>Calculations in electrolysis using Faraday's laws of electrolysis</u></p> <ol style="list-style-type: none"> Consider & apply factors affecting selective discharge and predict the products formed at the respective electrodes Write the <u>balanced redox equation</u> for the reaction occurring at the electrode. Determine the <u>number of Faradays</u> needed to produce <u>one mole</u> of the substance. Calculate the quantity of electricity, $Q = It = n_e F = n_e Le$ Calculate the mass or volume of substance produced at the electrode.
<p><u>Accounting for the discrepancies in E^\ominus_{cell} and actual E_{cell}</u></p> <p>E^\ominus_{cell} values do not give information about the rate of reaction / cannot predict the rate of a redox reaction.</p> <p>An energetically feasible reaction with $E^\ominus_{\text{cell}} > 0$ may not necessarily occur spontaneously in reality due to:</p> <ol style="list-style-type: none"> high activation energy of the redox reaction The reaction is carried out under non-standard condition. <p>Effect of concentration of ions and pressure (gaseous species) changes on the position of equilibrium of the redox equilibrium, and hence effect the E^\ominus, and E^\ominus_{cell}, can be deduced qualitatively using Le Chatelier's principle.</p>	<p><u>Industrial Applications of the Electrolytic cell</u></p> <ol style="list-style-type: none"> Anodising of aluminium Electrolytic purification of copper Electroplating

Standard electrode potential and redox potentials, E^\ominus at 298 K (25°C)					
For ease of reference, two tabulations are given:					
(a) an extended list in alphabetical order;					
(b) a shorter list in decreasing order of magnitude, ie a redox series.					
(a) E^\ominus in alphabetical order					
Electrode reaction		E^\ominus/V			
$\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag}$		+0.80	$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$		+1.77
$\text{Al}^{3+} + 3\text{e}^- \rightleftharpoons \text{Al}$		-1.66	$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$		+1.23
$\text{Ba}^{2+} + 2\text{e}^- \rightleftharpoons \text{Ba}$		-2.90	$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightleftharpoons 4\text{OH}^-$		+0.40
$\text{Br}_2 + 2\text{e}^- \rightleftharpoons 2\text{Br}^-$		+1.07	$\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2\text{O}_2$		+0.68
$\text{Ca}^{2+} + 2\text{e}^- \rightleftharpoons \text{Ca}$		-2.87	$2\text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{H}_2 + 2\text{OH}^-$		-0.83
$\text{Cl}_2 + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-$		+1.36	$\text{Pb}^{2+} + 2\text{e}^- \rightleftharpoons \text{Pb}$		-0.13
$2\text{HOCl} + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Cl}_2 + 2\text{H}_2\text{O}$		+1.64	$\text{Pb}^{4+} + 2\text{e}^- \rightleftharpoons \text{Pb}^{2+}$		+1.69
$\text{Co}^{2+} + 2\text{e}^- \rightleftharpoons \text{Co}$		-0.28	$\text{PbO}_2 + 4\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Pb}^{2+} + 2\text{H}_2\text{O}$		+1.47
$\text{Co}^{3+} + \text{e}^- \rightleftharpoons \text{Co}^{2+}$		+1.82	$\text{SO}_4^{2-} + 4\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{SO}_2 + 2\text{H}_2\text{O}$		+0.17
$[\text{Co}(\text{NH}_3)_6]^{2+} + 2\text{e}^- \rightleftharpoons \text{Co} + 6\text{NH}_3$		-0.43	$\text{S}_2\text{O}_8^{2-} + 2\text{e}^- \rightleftharpoons 2\text{SO}_4^{2-}$		+2.01
$\text{Cr}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cr}$		-0.91	$\text{S}_4\text{O}_6^{2-} + 2\text{e}^- \rightleftharpoons 2\text{S}_2\text{O}_3^{2-}$		+0.09
$\text{Cr}^{3+} + 3\text{e}^- \rightleftharpoons \text{Cr}$		-0.74	$\text{Sn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Sn}$		-0.14
$\text{Cr}^{3+} + \text{e}^- \rightleftharpoons \text{Cr}^{2+}$		-0.41	$\text{Sn}^{4+} + 2\text{e}^- \rightleftharpoons \text{Sn}^{2+}$		+0.15
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightleftharpoons 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$		+1.33	$\text{V}^{2+} + 2\text{e}^- \rightleftharpoons \text{V}$		-1.20
			$\text{V}^{3+} + \text{e}^- \rightleftharpoons \text{V}^{2+}$		-0.26
			$\text{VO}^{2+} + 2\text{H}^+ + \text{e}^- \rightleftharpoons \text{V}^{3+} + \text{H}_2\text{O}$		+0.34
			$\text{VO}_2^+ + 2\text{H}^+ + \text{e}^- \rightleftharpoons \text{VO}^{2+} + \text{H}_2\text{O}$		+1.00
			$\text{VO}_3^- + 4\text{H}^+ + \text{e}^- \rightleftharpoons \text{VO}_2^+ + 2\text{H}_2\text{O}$		+1.00
			$\text{Zn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Zn}$		-0.76

All ionic states refer to aqueous ions but other state symbols have been omitted.

(b) E^\ominus in decreasing order of oxidising power

JC2 H2 Chemistry (9647)

Electrochemistry

Tutorial