ANDERSON SERANGOON JUNIOR COLLEGE
JC2 H2 CHEMISTRY
ELECTROCHEMISTRY

Content

I. Overview
II. Electrode Potentials & Electrochemical Cells
III. Electrolysis & Electrolytic Cells
IV. Summary

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 spontaneity of a reaction

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

(h) construct redox equations using the relevant half–equations

(i) state and apply the relationship $\Delta G^{\ominus} = -nFE^{\ominus}$ to electrochemical cells, including the calculation of $E^{\ominus}$ for combined half reactions

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

(k) 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

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

(m) 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

(n) calculate:
  (i) the quantity of charge passed during electrolysis
  (ii) the mass and/or volume of substance liberated during electrolysis

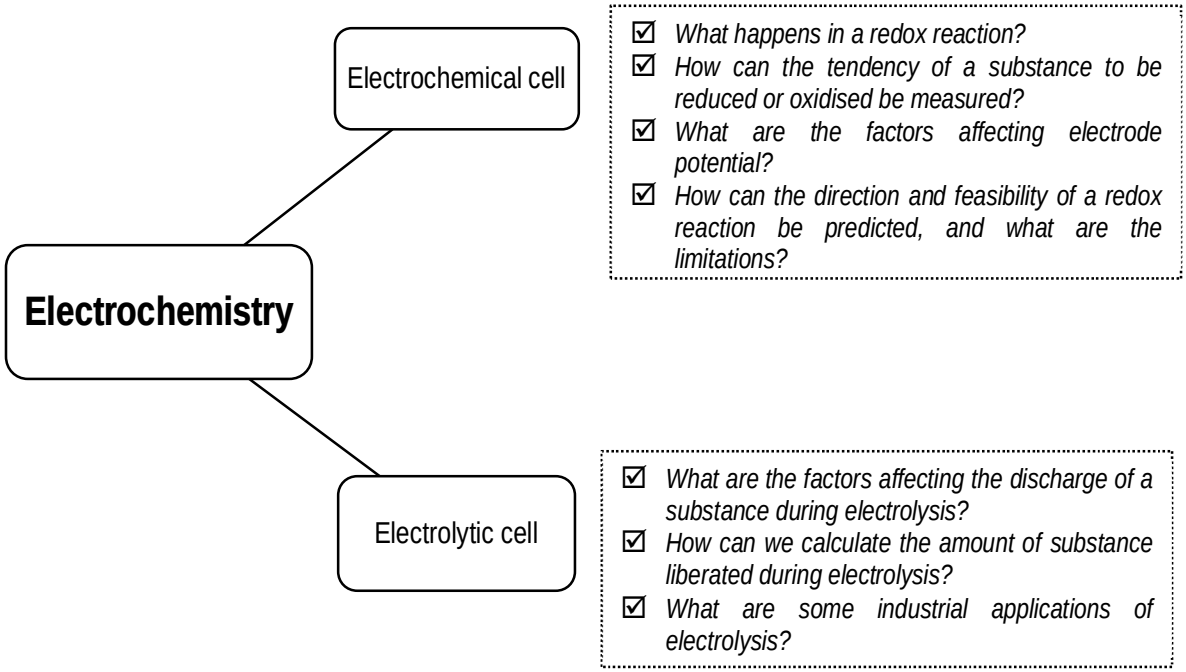
(o) explain, in terms of the electrode reactions, the industrial processes of:
  (i) the anodising of aluminium
  (ii) the electrolytic purification of copper

[technical details are **not** required]

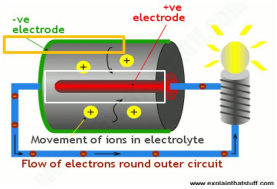
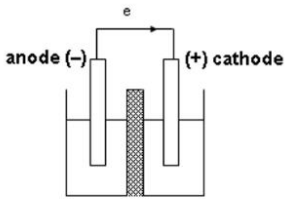
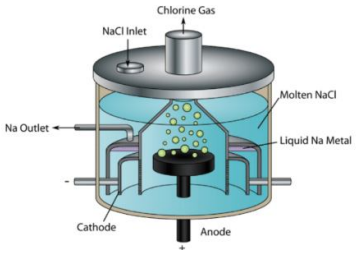
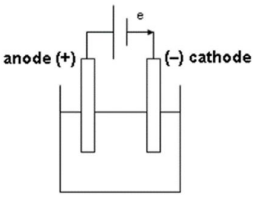
References

1. *Chemistry for Advanced Level*, Cann and Hughes, Murray
2. *Understanding Advanced Physical Inorganic Chemistry*, Jeanne Tan and Kim Seng Chan
3. *Chemistry, The Molecular Nature of Matter and Change (Fourth Edition)*, Silberberg, McGraw Hill
4. *Chemistry The Central Science (Ninth Edition)*, Brown, LeMay, Bursten, Prentice Hall

I. Overview



Electrochemistry is the study of interactions between chemical changes and flow of electrons.
There are two types of cells:

Part 1	**Electrochemical cells** (or Galvanic / Voltaic cells) Example: Alkaline battery 	**chemical reaction ⟶ flow of electrons** • converts chemical energy from a <u>spontaneous reaction</u> to generate electrical energy 
Part 2	**Electrolytic cells** Example: Down Cell (Electrolysis of molten NaCl) 	**flow of electrons ⟶ chemical reaction** • converts electrical energy to cause a <u>non–spontaneous reaction</u> to occur 

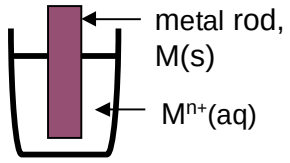
Note that in electrochemistry, we are dealing with **redox reactions**.

II Electrode Potentials & Electrochemical Cells

The tendency of a substance to be oxidised or reduced can be measured by its **electrode potential.**

(A) Electrode Potentials

When a metal rod (called the electrode) is dipped into a solution containing ions, M^{n+}, of the same metal (M), two possible electron transfer reactions can occur: oxidation and reduction



(i) Oxidation: The M atoms have a tendency to lose electrons. Some atoms will go into the solution as M^{n+}. The electrons will be left behind on the metal. As time passes, there will be a build–up of electrons on the M surface.

$$M(s) \longrightarrow M^{n+}(aq) + ne^-$$

(ii) Reduction: The M^{n+} ions on the metal surface may gain electrons, resulting in the regeneration of M.

$$M^{n+}(aq) + ne^- \longrightarrow M(s)$$

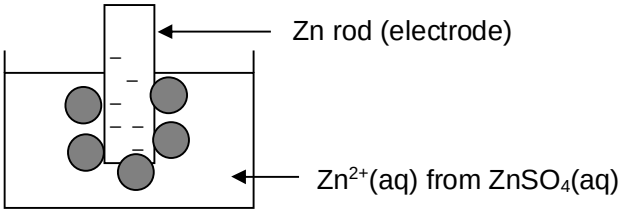
When the rates of oxidation and reduction are equal, **dynamic equilibrium** is established. At this point, there will be a constant negative charge on the metal, and a constant number of ions present in the solution around the metal.

$$M^{n+}(aq) + ne^- \underset{\text{oxidation}}{\overset{\text{reduction}}{\rightleftharpoons}} M(s)$$

For metals that are more reactive (i.e. more readily oxidised) e.g. Zn

Position of **equilibrium lies more to the left**, meaning that Zn tends to dissolve and go into the solution as positively charged Zn^{2+} ions.

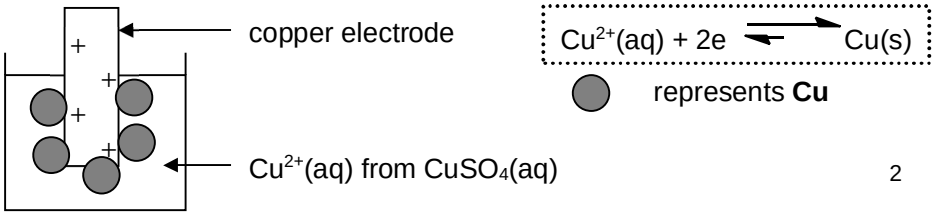
$$Zn^{2+}(aq) + 2e \rightleftharpoons Zn(s)$$



This leaves a surplus of electrons on the metal rod and thus a **negative** charge on the Zn electrode. The negatively charged electrode attracts a layer of positive ions on the metal surface. This results in a separation of charges across the metal–solution interface, creating a **potential difference** between the metal and the solution. This potential difference is known as the absolute **electrode potential, E** of the metal.

For metals that are less reactive (i.e. more readily reduced) e.g Cu

Position of **equilibrium lies more to the right**, meaning that the M^{n+} ions in the solution tend to gain electrons from the metal rod and are thus deposited as metal atoms on the electrode. This results in a net deficit of electrons on the copper rod and thus a **positive** charge on the electrode.



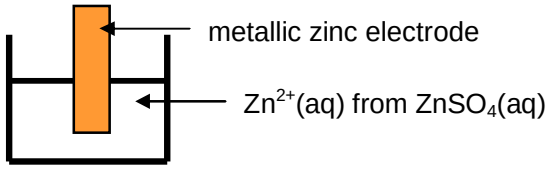
(B) Half–Cells

An electrochemical cell consists of two half-cells.
Half–cells are systems in which the oxidised state is in *equilibrium* with the reduced state.

$$\text{oxidised form} + ne^- \rightleftharpoons \text{reduced form}$$

There are **three main types** of half–cells:

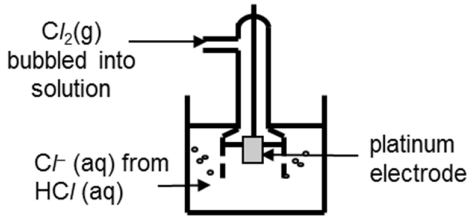
1 Metal and its ion Half–cell
e.g. $Zn^{2+}(aq) \mid Zn(s)$ half–cell



$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$$

The solid Zn metal acts as the electrode when dipped in a solution containing its ions.

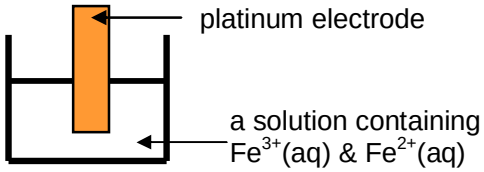
2 Non–metal and its ion Half–cell
e.g. $Cl_2(g) \mid Cl^-(aq)$ half–cell



$$\tfrac{1}{2}Cl_2(g) + e^- \rightleftharpoons Cl^-(aq)$$

An inert electrode (e.g. platinum electrode) dipped in a solution containing Cl^- ions will develop an electrode potential when gaseous Cl_2 is bubbled into the solution.

3 Ion–Ion Half–cell
e.g. $Fe^{3+}(aq)$, $Fe^{2+}(aq)$ half–cell



$$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$$

It consists of an inert electrode (e.g. Pt) dipped into a solution containing ions of the same element in two different oxidation states.

Note: Platinum (Pt) is usually used as the **inert electrode** in half–cells that do not contain a metal.

Reference half-cell: The Standard Hydrogen Electrode (i.e. the H^+/H_2 half–cell under standard conditions)

The electrode potential of half-cells are measured against a **reference half–cell** such as the **Standard Hydrogen Electrode.**

The Standard Hydrogen Electrode is arbitrary assigned a potential of **0.00 V** since the absolute electrode potential of H^+/H_2 half–cell, like any other half-cell, cannot be determined.

It consists of an inert **platinum electrode** (coated with finely divided platinum) dipped into an aqueous solution of H^+ ions at **1 mol dm^{-3}**, with hydrogen gas bubbling in at a pressure of **1 bar** and **298 K**.

$$\mathbf{2H^+(aq) + 2e^- \rightleftharpoons H_2(g)} \quad E^\ominus = \mathbf{0.00\ V}$$

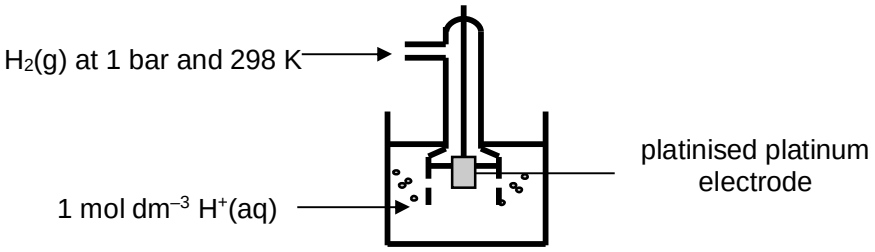


Diagram for **standard hydrogen electrode (S.H.E.)**.

Note: It is **not** possible to measure the absolute electrode potential (with a voltmeter) across the metal–solution interface in a half–cell because it is too narrow for viable electrical contacts to be made.

Hence, a way to overcome this problem is to connect the half-cell with a reference half-cell (i.e. Standard Hydrogen Electrode) to measure the potential difference between the two electrodes. This potential difference is known as the Standard Electrode Potential, ($E^\ominus$).

Note: The standard hydrogen electrode (S.H.E.) is the most commonly quoted reference half–cell. Other reference half-cells also exist e.g. Ag/AgCl half–cell ($E^\ominus$ = +0.199 V) and calomel Hg/Hg_2Cl_2 half-cell ($E^\ominus$ = +0.244 V)

(C) Standard Electrode (or Redox) Potentials, ($E^\ominus$)

Definition

The **standard electrode potential**, $\boldsymbol{E^\ominus}$, of a half–cell is defined as the potential difference between a **standard hydrogen electrode** and the **half–cell** in which the reacting species in the solution are at molar concentrations of **1 mol dm^{-3}**, **298 K** and gaseous species at pressure of **1 bar**.

Note that the standard electrode potentials are measured under **standard conditions**.

Standard conditions are:

- temperature of **298 K** (or 25 ^{o}C)
- concentration of **1 mol dm^{-3}** for **all** aqueous solutions
- pressure (if gases are involved) of **1 bar**
- **platinum** as the electrode when the half–cell system does not contain a metal

Why is it necessary to use standard conditions in measuring electrode potential?
The electrode potential for a half–cell reaction can be affected by: **nature** of the element, **concentration** of ions in solution, **temperature**, **pressure** of gases (if any)

We will elaborate further about the effects under section (G) Non–standard conditions.

(D) Measuring standard electrode (or redox) potentials ($E^{\ominus}$)

When a half–cell is connected to the standard hydrogen electrode (S.H.E.), electrons flow spontaneously from one electrode to the other due to the potential difference established between the two electrodes.

The standard electrode potential values of some half-cells are listed in the *Data Booklet*. Note that these values are measured against the standard hydrogen electrode and under standard conditions.

Significance of electrode potential values

Electrode (or redox) potential of half–cells is a **measure of how favourable the reduction process is.**

All half–cell reactions (given in the *Data Booklet*) are written in the following format, with electrons on the left (i.e. with reduction as the forward reaction).

oxidised form + **ne**$^-$ $\rightleftharpoons$ **reduced** form $E^{\ominus}$ = **standard** electrode potential

Standard electrode potential, $E^{\ominus}$, may be positive or negative, depending on the position of equilibrium of the half-cell.

- The **more positive** the electrode potential $E^{\ominus}$, the **more likely reduction** will occur.
- The **more negative** the electrode potential $E^{\ominus}$, the **more likely oxidation** will occur.

e.g. $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ $E^{\ominus} = +0.34$ V
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ $E^{\ominus} = -0.76$ V

It is easier to reduce Cu^{2+} ions to Cu atoms than it is to reduce Zn^{2+} ions to Zn atoms. Conversely, it is easier to oxidise Zn atoms to Zn^{2+} ions than it is to oxidise Cu atoms to Cu^{2+} ions.

How to measure standard electrode potentials, $E^{\ominus}$, of half–cells experimentally?

(Note that you need to learn to describe the method, and draw a diagram, to show how electrode potentials are measured.)

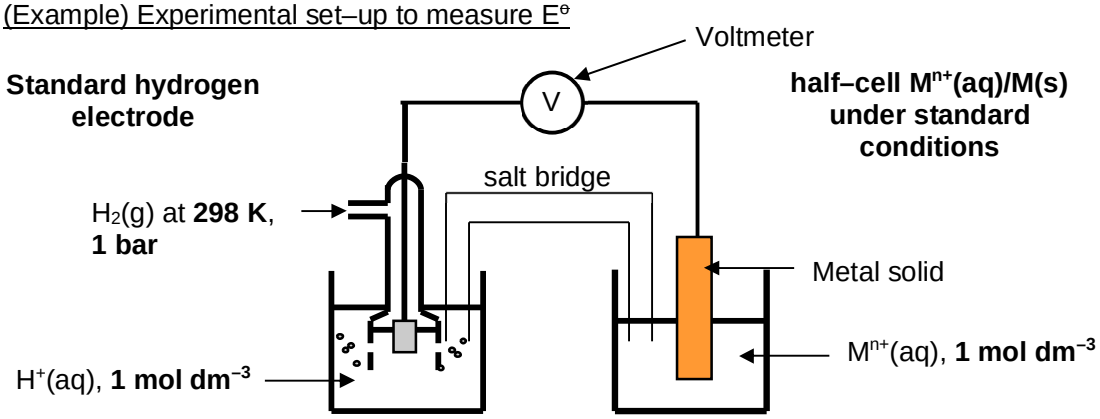
Method

1. Set up an **electrochemical cell** consisting of the given half–cell (e.g. $M^{n+}(aq)/M(s)$ and the standard hydrogen electrode (S.H.E.) as shown below under standard conditions (i.e. concentrations of all solutions = 1 mol dm^{-3}; temperature = 298 K and pressure of gases = 1 bar).

2. Connect the two half–cells via a '**salt bridge**', commonly made up of saturated potassium nitrate solution.

3. Measure the potential difference with a high–resistance **voltmeter**.

(Example) Experimental set–up to measure $E^{\ominus}$



Since the standard hydrogen electrode is arbitrarily assigned a potential of zero, the potential difference between the two half–cells is the **standard electrode potential**, ***E*$^{\ominus}$, of the half–cell $M^{n+}(aq)/M(s)$**.

Key features of an electrochemical cell

1. The electrodes are connected by a **high resistance voltmeter** so that the current in the external circuit is virtually zero and the cell registers its **maximum** potential difference, which is called the electromotive force (e.m.f.) of the cell.

2. Flow of charges in the cell takes place in 2 ways:

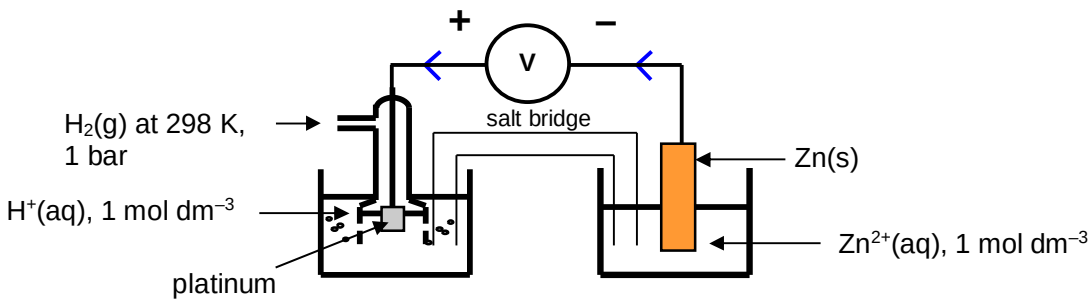
   - **External** circuit
     - Flow of **ELECTRONS** between the 2 half–cells through the wire
     - Electrons **always** flow from the oxid**A**tion half–cell (called the **A**node) to the redu**C**tion half–cell (called the **C**athode)
   - **Internal** circuit
     - Flow of **IONS** between the 2 half–cells through the salt bridge

3. **Polarity** of the electrodes (refer to page 3 of notes):
   - Negative electrode (-) : electrode with accumulation of negative charge (electrons)
   - Positive electrode (+) : electrode with a deficit of electrons

4. The **salt bridge** completes the entire circuit. (It consists of an inverted U–tube containing a saturated solution of a simple salt such as potassium nitrate (KNO_3). Both ends are plugged with porous material.)

   - It allows ions to move between the 2 solutions of the 2 half–cells
   - It prevents build–up of charges in the 2 half–cells, which if allowed to occur, would eventually halt electron flow in the external circuit

Case 1: Standard electrode potential of $Zn^{2+}(aq)/Zn(s)$ half–cell



Since the standard hydrogen electrode is assigned 0.00V, the potential difference shown on the high–resistance voltmeter gives the standard electrode potential for the Zn^{2+}/Zn half–cell.

Standard electrode potential of $Zn^{2+}(aq)/Zn(s)$ half–cell, $\boldsymbol{E^{\ominus}_{Zn^{2+}/Zn} = -0.76\ V}$ (from the Data Booklet)

$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$ $\quad E^{\ominus} = 0.00\ V$
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ $\quad E^{\ominus} = -0.76\ V$

Recall:
The **more positive** the electrode potential $E^{\ominus}$, the **more likely reduction (gain of electrons)** will occur.
The **more negative** the electrode potential $E^{\ominus}$, the **more likely oxidation (lose of electrons)** will occur.

What do the $E^{\ominus}$ values tell us about

1. Reactions occurring at the electrodes

Cathode: $2H^+ + 2e^- \longrightarrow H_2$ (H^+ is _____ to H_2)
Anode: $Zn \longrightarrow Zn^{2+} + 2e^-$ (Zn is _____ to Zn^{2+})

2. Polarity of electrodes:

Anode: **Negative** (electrode with accumulation of negative charge - electrons)
Cathode: **Positive** (electrode with a deficit of electrons)

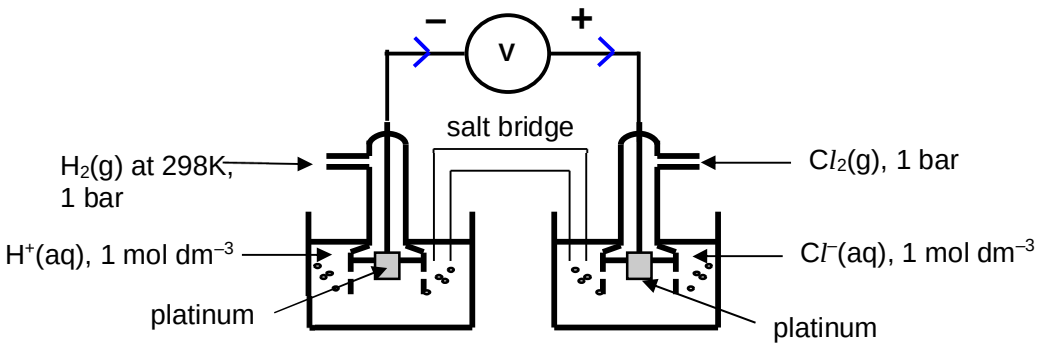
Zinc electrode is the negative electrode and the Standard Hydrogen Electrode is the positive electrode in this electrochemical cell

3. Direction of electron flow in the external circuit of the electrochemical cell

Since the **Zn^{2+}/Zn half–cell will undergo oxidation** and the **H^+/H_2 half–cell will undergo reduction,** we can then imply that **electrons flow from the Zn^{2+}/Zn half–cell to the H^+/H_2 half–cell**, via the external circuit.

Quick Summary
Electrons always flow in the external circuit from
- oxid**A**tion half–cell to the redu**C**tion half–cell
- **A**node to **C**athode
- (-) electrode to (+) electrode

Case 2: Standard electrode potential of $Cl_2(g)/Cl^-(aq)$ half–cell



(From Data Booklet) $E^{\ominus}_{Cl_2/Cl^-}$ = _____ V

1. Reactions occurring at the electrodes

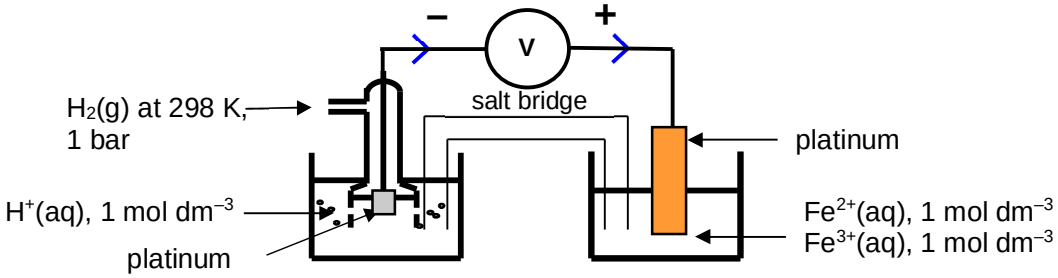
Cathode: _____ (reduction)

Anode: _____ (oxidation)

2. Standard Hydrogen Electrode is the **negative** electrode in this electrochemical cell

3. Electrons flow from the **H^+/H_2** half–cell to the **Cl_2/Cl^-** half–cell, via the external circuit.

Case 3: Standard electrode potential of $Fe^{3+}(aq)/Fe^{2+}(aq)$ half–cell



(From Data Booklet) $E^{\ominus}_{Fe^{3+}/Fe^{2+}} = +0.77$ V

1. Name of electrodes

_____ : $H_2 \longrightarrow 2H^+ + 2e^-$

_____ : $2Fe^{3+} + 2e^- \longrightarrow 2Fe^{2+}$

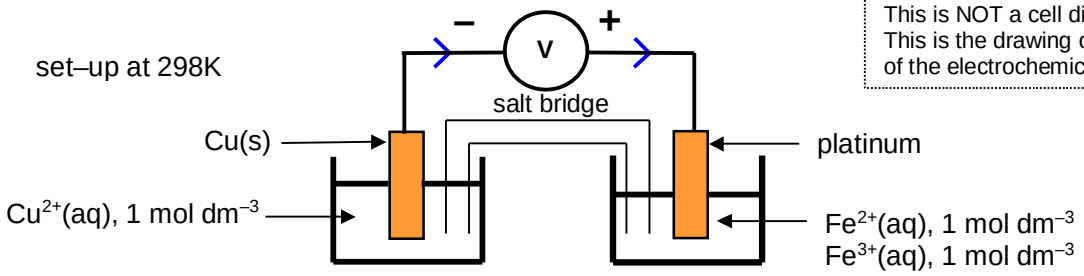
2. Standard Hydrogen Electrode is the **negative** electrode in this electrochemical cell.

3. Electrons flow from the H^+/H_2 half–cell to the Fe^{3+}/Fe^{2+} half–cell, via the external circuit.

(E) Writing a Cell Diagram / Cell Notation for Electrochemical cells

(Recall) An **electrochemical cell** consists of two half–cells. Oxidation takes place in one half–cell and reduction takes place at the other half-cell.

Example of a fully labelled set–up of an electrochemical cell



Note:
This is NOT a cell diagram.
This is the drawing of a set-up of the electrochemical cell.

As a convenient substitution for the above drawing, we use a **cell diagram** to show the parts of an electrochemical cell. A cell diagram is a **written notation** that represents the different components of an electrochemical cell.

1 A **cell diagram/cell notation** can be used to represent an electrochemical cell as follows:

oxidation half–cell ll reduction half–cell

Cell diagram of example above is,

$$Cu(s)\ |\ Cu^{2+}(aq)\ ||\ Fe^{3+}(aq),\ Fe^{2+}(aq)\ |\ Pt(s) \qquad E^{\ominus}_{cell} = +0.43\ V$$

2 Common cell notations in cell diagrams are:

- ll represents salt bridge
- l represents phase boundary
- , represents species boundary (in same phase)

Note: State symbols must be included in a cell diagram

3 The half–cell with the **more positive $E^{\ominus}$** value appears on the **Right** hand side of the cell diagram. **Reduction** occurs in this half–cell.

In the above example, $E^{\ominus}_{Cu^{2+}/Cu} = +0.34\ V$ and $E^{\ominus}_{Fe^{3+}/Fe^{2+}} = +0.77\ V$.
Hence, the Fe^{3+}/Fe^{2+} half–cell appears on the right hand side of the cell diagram. The two electrodes are Cu and Pt (inert electrode).

In a cell diagram	
LHS half–cell (cell with more –ve $E^{\ominus}$ value) **Oxid**ation occurs **A**node $Cu \longrightarrow Cu^{2+} + 2e^-$	RHS half–cell (cell with more +ve $E^{\ominus}$ value) **R**edu**C**tion occurs **C**athode $2Fe^{3+} + 2e^- \longrightarrow 2Fe^{2+}$
overall cell reaction: $2Fe^{3+} + Cu \longrightarrow 2Fe^{2+} + Cu^{2+}$	

Exercise 1

A current is produced in the following cell.

$Pt(s) \mid Y^{2+}(aq), Y^{3+}(aq) \parallel XO_4^-(aq), X^{2+}(aq), H^+(aq) \mid Pt(s)$

When a current is flowing, which one of the following species is oxidised?

(**A**) H^+ (**B**) XO_4^- (**C**) X^{2+} (**D**) Y^{3+} (**E**) Y^{2+} **Ans:** _____

(F) Uses of $E^\ominus$ and $E^\ominus_{cell}$ values

- To determine the relative strengths of oxidising and reducing agents
- To predict the direction of electron flow in an electrochemical cell
- To calculate the $E^\ominus_{cell}$ value
- To predict the spontaneity of a redox reaction

1. $E^\ominus$ values may be used to determine the relative strengths of oxidising and reducing agents

The more positive the $E^\ominus$ value, the greater the tendency for the half–reaction to undergo reduction, that is, proceed in the forward direction.

Strength of oxidising agents

Here are some half–equations with $E^\ominus$ values taken from the *Data Booklet*.

$\mathbf{MnO_4^-} + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	$E^\ominus = +1.52$ V
$\mathbf{Cr_2O_7^{2-}} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	$E^\ominus = +1.33$ V
$\mathbf{Fe^{3+}} + e^- \rightleftharpoons Fe^{2+}$	$E^\ominus = +0.77$ V
$\mathbf{I_2} + 2e^- \rightleftharpoons 2I^-$	$E^\ominus = +0.54$ V

Oxidising agents undergo reduction by gaining electrons.
They are thus found on the LHS of the half–equations in the Data Booklet.
The most powerful oxidising agent is the one that has the greatest tendency to undergo reduction, i.e. the one with the **most positive $E^\ominus$ value**.

Oxidising power: $MnO_4^- > Cr_2O_7^{2-} > Fe^{3+} > I_2$

Strength of reducing agents

$K^+ + e^- \rightleftharpoons \mathbf{K}$	$E^\ominus = -2.92$ V
$Ca^{2+} + 2e^- \rightleftharpoons \mathbf{Ca}$	$E^\ominus = -2.87$ V
$Zn^{2+} + 2e^- \rightleftharpoons \mathbf{Zn}$	$E^\ominus = -0.76$ V
$I_2 + 2e^- \rightleftharpoons \mathbf{2I^-}$	$E^\ominus = +0.54$ V

Reducing agents undergo oxidation by losing electrons.
They are thus found on the RHS of the half–equations in the Data Booklet.
The most powerful reducing agent is the one that has the greatest tendency to undergo oxidation, i.e. the one with the **most negative $E^\ominus$ value**.

Reducing power: $K > Ca > Zn > I^-$

2. $E^{\ominus}$ values may be used to predict the direction of electron flow in an electrochemical cell

In the external circuit, **electrons flow from** the negative electrode (where **oxidAtion** occurs i.e. **A**node) **to** the positive electrode (where **reduCtion** occurs i.e. **C**athode).

E.g. For the electrochemical cell comprising 2 half–cells with

$E^{\ominus}$ (Fe^{3+}/Fe^{2+}) = +0.77 V (Reduction half-cell)
$E^{\ominus}$ (Zn^{2+}/Zn) = –0.76 V (Oxidation half-cell)

Electrons flow from the zinc electrode in the Zn^{2+}/Zn half–cell (i.e. oxidation half–cell; half–cell with more negative $E^{\ominus}$ value) to the platinum electrode in the Fe^{3+}/Fe^{2+} half–cell (i.e. reduction half–cell; half–cell with more positive $E^{\ominus}$ value) in the external circuit.

3. $E^{\ominus}$ values may be used to calculate the $E^{\ominus}_{cell}$ value

The **standard cell potential (or e.m.f. of a cell), E^{o}_{cell}**, is the maximum potential difference between the two half–cells which are operated under standard conditions.

$E^{\ominus}_{cell}$ is calculated by: $\boldsymbol{E^{\ominus}_{cell} = E^{\ominus}_{reduction\ half\text{–}cell} - E^{\ominus}_{oxidation\ half\text{–}cell}}$

Example:
If the Zn^{2+}/Zn and Fe^{3+}/Fe^{2+} half–cells above are connected to form an electrochemical cell,

$E^{\ominus}$ (Fe^{3+}/Fe^{2+}) = +0.77 V $E^{\ominus}$ (Zn^{2+}/Zn) = –0.76 V

$\boldsymbol{E^{\ominus}_{cell}} = E^{\ominus}_{reduction} - E^{\ominus}_{oxidation}$ = +0.77 – (–0.76) = **+1.53 V**

Note that the **sign** and **units** must be included in the value of $E^{\ominus}_{cell}$.

Important: We should **NOT** alter the value of $E^{\ominus}$ when multiplying a half–equation by any factor!

e.g. $Fe^{3+}(aq) + e^{-} \rightleftharpoons Fe^{2+}(aq)$ $E^{\ominus}$ = +0.77 V
$2Fe^{3+}(aq) + 2e^{-} \rightleftharpoons 2Fe^{2+}(aq)$ $\boldsymbol{E^{\ominus}}$ **= +0.77 V** *Not 2 x +0.77 V!

**Volt (V) is defined as Joules per Coulomb – the amount of energy obtained from one Coulomb of charge. When the half–cell equation is multiplied by any factor, the number of electrons will be greater (greater Coulombic charge), but at the same time, the amount of energy obtained will also increase proportionally. Hence, the amount of energy per Coulomb remains the same (i.e. voltage is independent of number of electrons in the equation).*

Exercise 2

The two half–cells below are connected to form an electrochemical cell.

electrode reaction in half–cell	$E^{\ominus}$ / V
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.77

(i) write down the cell diagram for the electrochemical cell formed
(ii) state the direction of electron flow in the external circuit
(iii) calculate the cell e.m.f.
(iv) write the overall cell reaction

4. ***E^{o}_{cell} or E^{o} values may be used to predict the spontaneity of a redox reaction***

Recall from *Thermodynamics* that the spontaneity of a reaction is dependent on $\Delta G^{\ominus}$.

Similarly, in electrochemical cells, the change in Gibbs free energy for a redox reaction is related to the cell potential:

$$\Delta G^{\ominus} = -nFE^{\ominus}_{cell}$$

$\Delta G^{\ominus}$ = change in Gibbs free energy in **J mol^{-1}**
n = number of moles of electrons transferred during the redox reaction
F = Faraday's constant, 96500 C mol^{-1}, i.e. total charge of a mole of electrons

Hence, under standard conditions,
when $E^{\ominus}_{cell} > 0$, $\Delta G^{\ominus} < 0$ and the redox reaction is **spontaneous**
when $E^{\ominus}_{cell} < 0$, $\Delta G^{\ominus} > 0$ the redox reaction is **NOT spontaneous**

Exercise 3

(a) State, with reasons, whether the following reaction is spontaneous.

$2Ag^+ + Zn \longrightarrow 2Ag + Zn^{2+}$

$Ag^+ + e^- \rightleftharpoons Ag$ +0.80 V $Zn^{2+} + 2e^- \rightleftharpoons Zn$ –0.76 V

E^{o}_{cell} = +0.80 – (–0.76)
= +1.56 > 0 (hence reaction is spontaneous)

(b) Predict whether I^- can reduce $Fe^{2+}(aq)$ to metallic iron.

$Fe^{2+} + 2e^- \rightleftharpoons Fe$ –0.44 V $I_2 + 2e^- \rightleftharpoons 2I^-$ +0.54 V

$E^{\ominus}_{cell}$ = –0.44 – 0.54 = –0.98 < 0 (hence reaction is not spontaneous). Hence, I^- cannot reduce Fe^{2+} to metallic iron.

(c) Calculate the e.m.f for the reaction of acidified aqueous hydrogen peroxide with aqueous iron(II) sulfate solution and hence, predict the products of the reaction. Hence, determine the $\Delta G^{\ominus}$ of the reaction.

Approach:

⇨ Select half-cell reactions in the Data Booklet that contain the reactant species.

$\mathbf{Fe^{2+}} + 2e^- \rightleftharpoons Fe$	–0.44 V
$Fe^{3+} + e^- \rightleftharpoons \mathbf{Fe^{2+}}$	+0.77 V
$\mathbf{H_2O_2} + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	+1.77 V
$O_2 + 2H^+ + 2e^- \rightleftharpoons \mathbf{H_2O_2}$	+0.68 V

⇨ Select the relevant pair of half-cell reactions, bearing in mind:

- o one half-cell must undergo oxidation (reactant should be on the right of equilibrium) and the other must undergo reduction (reactant should be on the left of equilibrium)
- o the e.m.f. (or $\boldsymbol{E^{\ominus}_{cell}}$) should be positive, $\boldsymbol{E^{\ominus}_{cell} > 0}$

Hence the relevant half-cell reactions are,

_____ +1.77 V

_____ +0.77 V

$E^{\ominus}_{cell}$ =

Since $\boldsymbol{E^{\ominus}_{cell}}$ ___ **0**, we can say that this reaction is _____.

$\boldsymbol{\Delta G^{\ominus} = -nFE^{\ominus}_{cell}}$ =

Overall equation: _____

Products of reaction: _____

Note:
If the two half-cell reactions chosen are,

$O_2 + 2H^+ + 2e^- \rightleftharpoons \mathbf{H_2O_2}$	+0.68 V
$\mathbf{Fe^{2+}} + 2e^- \rightleftharpoons Fe$	–0.44 V

Then,

$E^{\ominus}_{cell} = -0.44 - (+0.68) = -1.12$ V

$E^{\ominus}_{cell} < 0$, not spontaneous

(G) Non–standard conditions – FYI

The electrode potential, E, under *non–standard conditions* can be related to standard electrode potential, $E^{\ominus}$, by the **Nernst equation**:

$$E = E^{\ominus} - \frac{RT}{nF} \ln Q$$

where n is the no. of electrons transferred
F is the Faraday constant,
Q is the reaction quotient which describes the relative amount of reactants and products at a particular point in time

Similarly, the Nernst equation for the cell potential is

$$E_{cell} = E^{\ominus}_{cell} - \frac{RT}{nF} \ln Q$$

From this, we can see that the value of E_{cell} is dependent on a few factors:

- temperature (as reflected in T)
- concentration or pressure (for gas) of reactants and products (as reflected in Q)

Therefore, **a non–spontaneous reaction under standard conditions can be made spontaneous under non–standard conditions by changing the temperature, concentration or pressure** – *See Section (H)*.

Note also that the equilibrium constant, K, for a redox reaction can be determined from the $E^{\ominus}_{cell}$ value as shown:

At equilibrium, $E_{cell} = 0$ V and Q = K (equilibrium constant) and we get:

$$E^{\ominus}_{cell} = \frac{RT}{nF} \ln K$$

Example

Under standard conditions, an electrochemical cell formed by connecting a zinc half–cell to a copper half–cell will give $E^{\ominus}_{cell} = +1.10$ V.

$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ $\quad E^{\ominus} = -0.76$ V
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ $\quad E^{\ominus} = +0.34$ V

If $[Zn^{2+}]$ in the zinc half–cell is increased (i.e. $[Zn^{2+}]$ now exceeds 1 mol dm^{-3}), how will the following be affected?

(i) electrode potential of the zinc half–cell,
(ii) the cell e.m.f.

Answer
(i) In the zinc half–cell,
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ $\quad E^{\ominus} = -0.76$ V

When $[Zn^{2+}]$ is increased, position of equilibrium _____.

_____ of $Zn^{2+}(aq)$ to $Zn(s)$ _____.

Electrode potential ($E^{\ominus}_{Zn^{2+}/Zn}$) becomes _____ (or _____).

(ii) Since $E_{cell} = E_{Cu^{2+}/Cu} - E_{Zn^{2+}/Zn}$, E_{cell} becomes _____.

Exercise 4

A cell with $E^{\ominus}_{cell} = +1.53$ V is shown below.

$$Zn(s) \mid Zn^{2+}(aq) \parallel Fe^{3+}(aq), Fe^{2+}(aq) \mid Pt(s)$$

Which of the following changes, when made separately to the set–up above, will the $E^{\ominus}_{cell}$ be more positive?

1 Adding aqueous iron(III) chloride to the Fe^{3+}/ Fe^{2+} half–cell
2 Adding water to the Zn^{2+}/Zn half–cell
3 Adding water to the Fe^{3+}/Fe^{2+} half–cell

Ans: _____

(H) Limitations of the standard electrode potential approach to determine spontaneity of reaction

Predictions on spontaneity of reaction **may not** always be true.

- $E^{\ominus}_{cell} > 0$ (i.e. $\Delta G < 0$) might not mean that a reaction will occur
- $E^{\ominus}_{cell} < 0$ (i.e. $\Delta G > 0$) might not mean that a reaction will not occur

Two possible reasons to explain this:

- Non–standard conditions
- High activation energy of some reactions

1) Non–standard conditions

When determining $E^{\ominus}_{cell}$, all solutions have a concentration of 1 mol dm^{-3} and a temperature of 298 K. The actual conditions for a reaction either in a lab or in the industry are unlikely to be standard. As such, the actual cell e.m.f. may not be the same as the calculated $E^{\ominus}_{cell}$.

Example

$MnO_2 + 4H^+ + 2e^- \rightleftharpoons Mn^{2+} + 2H_2O$ $\quad E^{\ominus} = +1.23$ V
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ $\quad E^{\ominus} = +1.36$ V

$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$ $\quad E^{\ominus}_{cell} = -0.13$ V < 0 assuming standard conditions

However, such a reaction actually occurs when conc. HC*l* is used instead of 1 mol dm^{-3} HC*l*.

Comments:
Since conc. HC*l* is used, [H^+] and [Cl^-] will be above 1 mol dm^{-3}.
Under such conditions, the E values *might* be

$MnO_2 + 4H^+ + 2e^- \rightleftharpoons Mn^{2+} + 2H_2O$ $\quad E = +1.40$ V
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ $\quad E = +1.30$ V

giving $E_{cell} = +1.40 - (+1.30)$ V > 0 such that the reaction becomes spontaneous (as observed).

2 High Activation Energy

Many reactions, particularly those involving gases and solutions, have high activation energy. Although the $E^{\ominus}_{cell} > 0$, indicating that the reaction is spontaneous, it is so **slow** that no change is observed.

Reaction might have a **high activation energy** that is not overcome under standard conditions.

Example

$3HCHO + Cr_2O_7^{2-} + 8H^+ \longrightarrow 2Cr^{3+} + 3HCO_2H + 4H_2O$ $\quad E^{\ominus}_{cell} = +1.27$ V

Since $E^{\ominus}_{cell} > 0$, acidified dichromate is expected to oxidise methanal to methanoic acid.

However, in practice, the reaction is not observed at room temperature due to the high activation energy, i.e. the reaction is too slow. Heating is required for the reaction to occur.

$E^{\ominus}_{cell}$ values do not give any information about the rate of the reaction.

(I) Types of Electrochemical (or Galvanic/Voltaic) Cells [SDL]

In electrochemical cells, a chemical reaction produces an electric current. There are three types: *primary*, *secondary* and *fuel cells*.

(i) Primary Cell

- ☑ stored chemical energy is simply used up
- ☑ cannot be recharged because electrodes and electrolyte cannot be restored to their original states by an external electrical potential.
- ☑ provides a low voltage and a *very low* current

Examples

flashlight batteries (Leclanche cell), mercury cell – for cameras, digital calculators

Advantages: light and portable
sealed and does not leak

Disadvantage: not rechargeable – to be discarded when supply of electricity is exhausted

(ii) Secondary Cell

Can be recharged by passing a current of electricity (from an external source) through the cell in the reverse direction to that of discharge.

Example

lead–acid accumulator (the traditional "car battery")

Advantages:

- ☑ relatively inexpensive
- ☑ reliable
- ☑ has an adequate life (can be recharged 500–800 times)
- ☑ produces very large currents (around 30 amp) required to start a car engine

Disadvantage

- ☑ has a LOW energy/mass ratio (stores about only 40–50 watt hours of electrical energy per kg of battery weight)

IMPORTANCE OF THE DEVELOPMENT OF IMPROVED BATTERIES (e.g. for electric cars)

Reasons for electric car: shrinking oil supplies
concern about atmospheric pollution

The lead–acid accumulator is not well adapted to electric cars because it is heavy in relation to the energy stored.

Heavy weight of battery power pack requires a great deal of energy to move it over the ground.
∴ Much of the energy is used in moving the battery itself.

Car has (a) short range (< 160 km)
(b) poor acceleration and performance

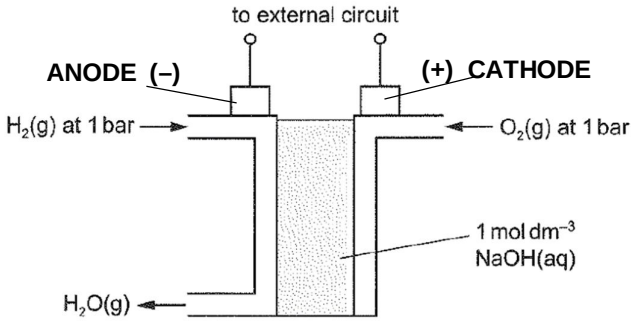
What is needed:

Continued research in order to develop improved batteries of
⊕ smaller size ⊕ lower mass ⊕ higher energy/mass ratio (higher voltage)

(iii) <u>Fuel Cells</u>

A fuel cell is an electrochemical cell that converts the chemical energy of a **continuous supply** of fuel (e.g. hydrogen) and an oxidising agent (usually oxygen) into electrical energy.
The most common type of fuel cell is the **hydrogen–oxygen fuel cell**. This has been used in space and conveniently produces not only **electricity** but also **water**.

<u>A (alkaline) hydrogen-oxygen (H_2/O_2) Fuel Cell</u>



In this cell, there are three compartments separated from one another by porous **carbon electrodes** (with a sprinkling of platinum to act as a catalyst). **Hydrogen** gas is fed into one compartment and **oxygen** gas into another. These gases diffuse (not bubble) slowly through the electrodes and react with an electrolyte in the centre compartment.

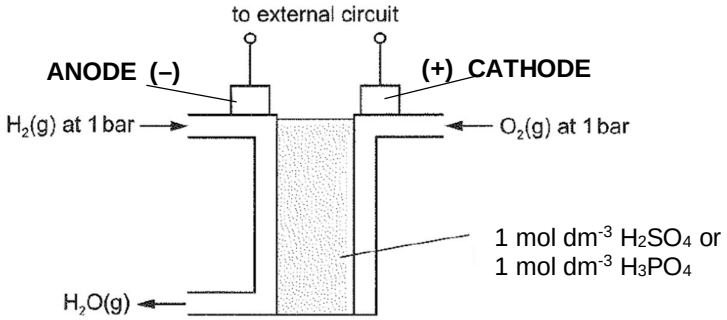
cathode (+) : $\mathbf{O_2}(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$ (reduction)

anode (–) : $2\mathbf{H_2}(g) + 4OH^-(aq) \longrightarrow 4H_2O(l) + 4e^-$ (oxidation)

overall reaction: $\mathbf{2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)}$ **(redox)**

The fuel cell is operated at a high temperature so the water that is formed as a product of the cell reaction evaporates and may be condensed and used as drinking water for astronauts.

<u>A (acidic) hydrogen-oxygen (H_2/O_2) Fuel Cell</u>



In this cell, there are three compartments separated from one another by porous **carbon electrodes** (with a sprinkling of platinum to act as a catalyst). **Hydrogen** gas is fed into one compartment and **oxygen** gas into another. These gases diffuse (not bubble) slowly through the electrodes and react with an electrolyte in the centre compartment.

cathode (+) : $\mathbf{O_2}(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$ (reduction)

anode (–) : $\mathbf{H_2}(g) \longrightarrow 2H^+(aq) + 2e^-$ (oxidation)

overall reaction: $\mathbf{2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)}$ **(redox)**

Advantages of the Fuel Cell [SDL]

1. **High efficiency**
   Electric current is produced directly from the reaction of hydrogen and oxygen without the inherently wasteful intermediate conversion of chemical energy to heat.

2. **No pollution / No Greenhouse Effect**
   Chemical product is water.

3. **High energy/mass ratio** compared to car batteries
   Smaller size, lower mass, higher voltage – more efficient
   ∴ used in space shuttles

Difference between fuel cell and other cells

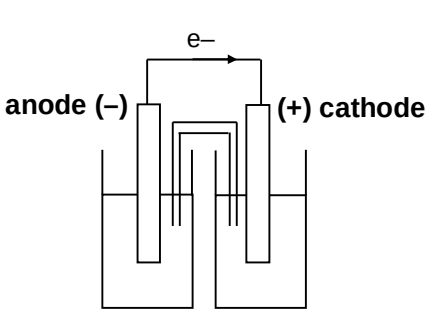
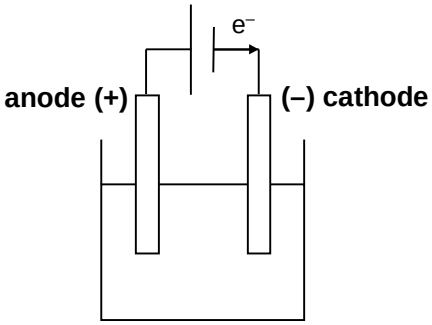
type of cell	characteristics
primary cell (dry)	limited capacity, discard when exhausted
secondary cell (storage)	can be recharged, has storage capacity
fuel cell	reactants (H_2 & O_2) continuously supplied, product (H_2O) continuously removed, energy can be obtained "indefinitely" as long as supply of reactants is maintained.

III. Electrolysis & Electrolytic Cells

(A) Electrolysis: An Introduction

Electrolysis is the process whereby an electric current is passed through an **electrolyte**, resulting in chemical reactions taking place at each of the **electrodes**. The cell in which electrolysis occurs is called the **electrolytic cell**.

Comparison of Electrochemical Cell and Electrolytic Cell

<table>
<tr><td rowspan="2">TYPE</td><td colspan="2">Part 1: ELECTROCHEMICAL CELL</td><td colspan="2">Part 2: ELECTROLYTIC CELL</td></tr>
<tr><td colspan="2">Spontaneous redox reaction resulting in flow of electrons (electricity produced)
 
</td><td colspan="2">Flow of electrons (electricity) from external source to drive a non–spontaneous redox reaction
 
</td></tr>
<tr><td>Electrode</td><td>Anode</td><td>Cathode</td><td>Anode</td><td>Cathode</td></tr>
<tr><td>Sign</td><td>–</td><td>+</td><td>+</td><td>–</td></tr>
<tr><td>Half–reaction</td><td>oxidAtion</td><td>reduCtion</td><td>oxidAtion</td><td>reduCtion</td></tr>
<tr><td>Electron Flow in the External Circuit</td><td colspan="2">anode to cathode</td><td colspan="2">anode to cathode</td></tr>
</table>

(B) Factors affecting Selective Discharge of Substances

Before we can determine what chemical reaction takes place and hence what substances are formed at each electrode during an electrolysis, we need to know what **species/ions are present** at the electrode (e.g. positive ions migrate to the cathode, negative ions migrate to the anode, and for electrolysis of aqueous solutions, H_2O will be present at both electrodes).

The **order in which ions or species are discharged** at the electrodes during electrolysis is determined by a number of factors including:

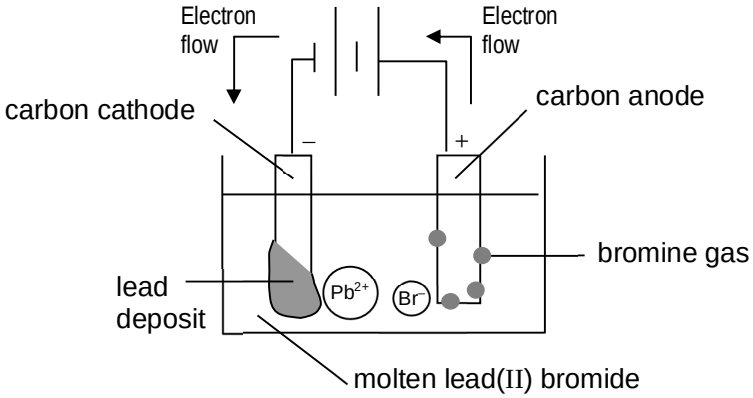
1. **state of electrolyte (molten or aqueous)**
2. **electrode potential**
3. **relative concentration of the ions**
4. **nature of the electrode**

1. State of Electrolyte

Electrolysis of **molten** salts

In a molten electrolyte e.g. $PbBr_2(\boldsymbol{l})$, only one type of cation and anion is present.

Cathode (Reduction)	Anode (Oxidation)
Pb^{2+} (**cation**) migrates to the **cathode** (negative electrode) and is discharged, i.e. Pb^{2+} gains electrons and is reduced to Pb **Reduction half–equation :** $Pb^{2+} + 2e^- \longrightarrow Pb$	Br^- (**anion**) migrates to the **anode** (positive electrode) and is discharged, i.e. Br^- loses electrons and is oxidised to Br_2. **Oxidation half–equation :** $2Br^- \longrightarrow Br_2 + 2e^-$



Electrolysis of **aqueous** solutions

Unlike molten salts, for aqueous electrolytes, there will also be water present. Hence, we need to also consider H_2O as a possible species to be discharged at EACH electrode.

E.g. in the electrolysis of $PbBr_2$(**aq**),

Cathode (Reduction)	Anode (Oxidation)
Pb^{2+} and H_2O will migrate to the cathode. *Which species (Pb^{2+} or H_2O) will be **preferentially** discharged?*	**Br^- and H_2O** will migrate to the anode. *Which species (Br^- or H_2O) will be **preferentially** discharged?*

For the electrolysis of **aqueous solutions, the species that is preferentially discharged (or, **selectively discharged**) will **depend on several factors, such the electrode potentials, relative concentrations of the ions and the nature of the electrode**. These will be discussed in the following sections.

2. Electrode Potential

At the **cathode**, the **species** with the **most positive (or least negative) $E^{\ominus}$** will be preferentially discharged (i.e. reduced).

E.g. In an electrolyte containing Zn^{2+}, Cu^{2+} and Ag^{+}, Ag^{+} has the most positive $E^{\ominus}$, Ag^{+} will be discharged first. When all Ag^{+} has been reduced to Ag, Cu^{2+} will then start to discharge.

$\mathbf{Ag^{+}} + e^{-} \rightleftharpoons Ag$ $\quad E^{\ominus} = +0.80$ V
$\mathbf{Cu^{2+}} + 2e^{-} \rightleftharpoons Cu$ $\quad E^{\ominus} = +0.34$ V
$\mathbf{Zn^{2+}} + 2e^{-} \rightleftharpoons Zn$ $\quad E^{\ominus} = -0.76$ V

At the **anode**, the **species** with the **most negative (or least positive)** $E^{\ominus}$ will be preferentially discharged (i.e. oxidised).

E.g. In an electrolyte containing Cl^{-} and OH^{-} in approximately equal concentrations, OH^{-} will be discharged first as it has a less positive $E^{\ominus}$. When all OH^{-} has been oxidised to O_2, Cl^{-} will then start to discharge as chlorine gas.

$Cl_2 + 2e^{-} \rightleftharpoons 2\mathbf{Cl^{-}}$ $\quad E^{\ominus} = +1.36$ V
$O_2 + 2H_2O + 4e^{-} \rightleftharpoons 4\mathbf{OH^{-}}$ $\quad E^{\ominus} = +0.40$ V

3. Relative Concentration of the Ions

If the concentrations of ions which could be discharged at an electrode are very different and their **electrode potentials ($E^{\ominus}$) are very close**, the ion present in **high concentration** *may* be preferentially discharged over other species.

E.g. In the electrolysis of brine (which contains **high concentrations of Na^{+} and Cl^{-} ions**)

Cathode: Na^{+} and H_2O migrate to the cathode.

$Na^{+} + e^{-} \rightleftharpoons Na$ $\quad E^{\ominus} = -2.71$ V
$2H_2O + 2e^{-} \rightleftharpoons H_2 + 2OH^{-}$ $\quad E^{\ominus} = -0.83$ V

H_2O is preferentially discharged (recall: factor 2).

$2H_2O + 2e^{-} \longrightarrow H_2 + 2OH^{-}$

Anode: Cl^{-} and H_2O migrate to the anode. Though H_2O has a less positive $E^{\ominus}$ (and expected to be preferentially discharged at the anode - recall factor 2), it is, however, **not** discharged.

$Cl_2 + 2e^{-} \rightleftharpoons 2Cl^{-}$ $\quad E^{\ominus} = +1.36$ V
$O_2 + 4H^{+} + 4e^{-} \rightleftharpoons 2H_2O$ $\quad E^{\ominus} = +1.23$ V

Cl^{-} is discharged instead.
$2Cl^{-} \longrightarrow Cl_2 + 2e^{-}$

Reason for the selective discharge of Cl^{-}:

Since $[Cl^{-}] >> 1$ mol dm^{-3} , the equilibrium position of $Cl_2 + 2e^{-} \rightleftharpoons 2Cl^{-}$ shifts to the left such that E becomes much lower than +1.36 V and hence **less positive** than +1.23 V ($E^{\ominus}$ (O_2/H_2O).

4. Nature of the Electrode

Unlike graphite (carbon) and platinum which are inert electrodes that do not affect the discharge of ions, **active electrodes** can participate in the oxidation or reduction half–reaction.

Example: Electrolysis of $CuSO_4$(aq) using graphite electrodes (inert electrodes)

At the cathode where reduction takes place:	At the anode where oxidation takes place:
$\mathbf{Cu^{2+}} + 2e^- \rightleftharpoons Cu$ $E^\ominus = +0.34$ V (✓) $\mathbf{2H_2O} + 2e^- \rightleftharpoons H_2 + 2OH^-$ $E^\ominus = -0.83$ V	$O_2 + 4H^+ + 4e^- \rightleftharpoons \mathbf{2H_2O}$ $E^\ominus = +1.23$ V (✓) $S_2O_8^{2-} + 2e^- \rightleftharpoons \mathbf{2SO_4^{2-}}$ $E^\ominus = +2.01$ V
Overall equation: $2Cu^{2+} + 2H_2O \longrightarrow 2Cu + O_2 + 4H^+$	

Note: The mass of cathode will increase as Cu(s) is deposited.
Concentration of Cu^{2+} will decrease, hence intensity of blue colour decreases with time.

Example: Electrolysis of $CuSO_4$(aq) using copper electrodes (active electrodes)

At the cathode where reduction takes place:	At the anode where oxidation takes place:
$\mathbf{Cu^{2+}} + 2e^- \rightleftharpoons Cu$ $E^\ominus = +0.34$ V (✓) $\mathbf{2H_2O} + 2e^- \rightleftharpoons H_2 + 2OH^-$ $E^\ominus = -0.83$ V	$O_2 + 4H^+ + 4e^- \rightleftharpoons \mathbf{2H_2O}$ $E^\ominus = +1.23$ V $S_2O_8^{2-} + 2e^- \rightleftharpoons \mathbf{2SO_4^{2-}}$ $E^\ominus = +2.01$ V $Cu^{2+} + 2e^- \rightleftharpoons \mathbf{Cu}$ $E^\ominus = +0.34$ V (✓)
Overall reaction: Cu metal is oxidised to Cu^{2+} at the anode, Cu^{2+} is reduced to Cu metal at the cathode.	

Note: Cu anode dissolves i.e. decreases in mass while Cu cathode increases in mass
Blue colour of electrolyte remains unchanged (no change in concentration of Cu^{2+})

Exercise 5: J99/1/3

Use relevant $E^\ominus$ data from the *Data Booklet* to suggest reasons for the following observations.

(i) The electrolysis of dilute NaC*l*(aq) produces mainly oxygen gas at the anode, whereas the electrolysis of concentrated NaC*l*(aq) produces mainly chlorine gas.

(ii) The electrolysis of either dilute or concentrated NaF(aq) produces only oxygen gas at the anode.

(i)

NaC*l*(aq)	conc. NaC*l*(aq)
$E^\ominus$ (Cl_2/Cl^-) = +1.36 V	$E^\ominus$ (Cl_2/Cl^-) = +1.36 V
$E^\ominus$ (O_2/H_2O) = +1.23 V	$E^\ominus$ (O_2/H_2O) = +1.23 V
→	→

$Cl_2 + 2e \rightleftharpoons 2Cl^-$
At high [Cl^-], position of equilibrium shifts to the _____ and E_{Cl2/Cl^-} becomes _____ than +1.23 V.

Hence, Cl^- is preferentially discharged and Cl_2 is evolved at the anode.

(ii)

NaF(aq)	conc. NaF(aq)
$E^\ominus$ (F_2/F^-) = +2.87 V	$E^\ominus$ (F_2/F^-) = +2.87 V
$E^\ominus$ (O_2/H_2O) = +1.23 V	$E^\ominus$ (O_2/H_2O) = +1.23 V
→	→

$F_2 + 2e \rightleftharpoons 2F^-$
At high [F^-], position of equilibrium shifts to the _____ and E_{F2/F^-} becomes _____ but still _____ than +1.23 V.

Hence, H_2O is still preferentially discharged and O_2 is evolved at the anode.

LEARNING POINTS for questions on ELECTROLYSIS

- Anions and water (applicable to **aqueous** solutions) migrate to the anode
- Cations and water (applicable to **aqueous** solutions) migrate to the cathode
- Decide which species will be discharged at each electrode based on the **electrode potential** values
    - **For anode: The species (find them on RHS of half–equations) with more negative electrode potential will be discharged**
    - **For cathode: The species (find them on LHS of half–equations) with more positive electrode potential will be discharged**
    - Exceptions:
        - If **active electrodes** are used, must consider the possibility of the metal being discharged (metal oxidised at anode)
        - **Concentration** of the solution can also affect the species being discharged
          ⇒ depends on what the question tells you (as seen in an earlier Exercise)

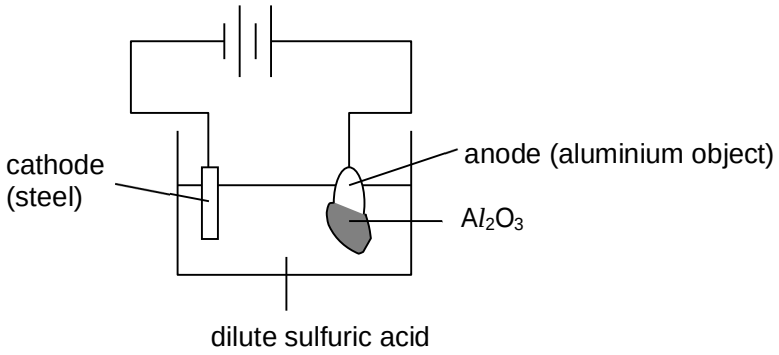
CHECKPOINT: *Determine the identities of substances liberated during electrolysis of the following electrolytes.*

Electrolyte	Electrode	At cathode (reduction – more positive $E^{\ominus}$)	At anode (oxidation – more negative $E^{\ominus}$)	Overall
NaOH(aq)	Pt	$E^{\ominus}(Na^+/Na)$ –2.71 V $E^{\ominus}(H_2O/H_2)$ –0.83 V ✓ **$4H_2O + 4e^- \longrightarrow 2H_2 + 4OH^-$**	$E^{\ominus}(O_2/OH^-)$ +0.40 V ✓ $E^{\ominus}(O_2/H_2O)$ +1.23 V **$4OH^- \longrightarrow O_2 + 2H_2O + 4e^-$**	$2H_2O \longrightarrow O_2 + 2H_2$
dil. H_2SO_4	Pt	$E^{\ominus}(H^+/H_2)$ 0.00 V $E^{\ominus}(H_2O/H_2)$ –0.83 V _____	$E^{\ominus}(S_2O_8^{2-}/SO_4^{2-})$ +2.01 V $E^{\ominus}(O_2/H_2O)$ +1.23 V _____	$2H_2O \longrightarrow O_2 + 2H_2$
Na_2SO_4(aq)	Pt	$E^{\ominus}(Na^+/Na)$ –2.71 V $E^{\ominus}(H_2O/H_2)$ –0.83 V _____	$E^{\ominus}(S_2O_8^{2-}/SO_4^{2-})$ +2.01 V $E^{\ominus}(O_2/H_2O)$ +1.23 V **$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$**	$2H_2O \longrightarrow O_2 + 2H_2$
dilute NaC*l*	Pt	$E^{\ominus}(Na^+/Na)$ –2.71 V $E^{\ominus}(H_2O/H_2)$ –0.83 V **$4H_2O + 4e^- \longrightarrow 2H_2 + 4OH^-$**	$E^{\ominus}$ (Cl_2/Cl^-) +1.36 V $E^{\ominus}(O_2/H_2O)$ +1.23 V **$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$**	$2H_2O \longrightarrow O_2 + 2H_2$
Conc NaC*l*	Pt	$E^{\ominus}(Na^+/Na)$ –2.71 V $E^{\ominus}(H_2O/H_2)$ –0.83 V **$4H_2O + 4e^- \longrightarrow 2H_2 + 4OH^-$**	***Selective discharge*** *of Cl^- at the anode due to high* [Cl^-] _____	**$4H_2O + 4Cl^- \longrightarrow 2H_2 + 4OH^- + 2Cl$**
$CuSO_4$ (aq)	Pt/C	$E^{\ominus}(Cu^{2+}/Cu)$ +0.34 V $E^{\ominus}(H_2O/H_2)$ –0.83 V _____	$E^{\ominus}(O_2/H_2O)$ +1.23 V $E^{\ominus}(S_2O_8^{2-}/SO_4^{2-})$ +2.01V **$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$**	**$2Cu^{2+} + 2H_2O \longrightarrow 2Cu + O_2 + 4H^+$**
$CuSO_4$ (aq)	Cu	$E^{\ominus}(Cu^{2+}/Cu)$ +0.34 V $E^{o}(H_2O/H_2)$ –0.83 V _____	$E^{\ominus}(Cu^{2+}/Cu)$ +0.34 V $E^{\ominus}(O_2/H_2O)$ +1.23 V _____	**Cu oxidised at the anode and Cu^{2+} reduced at the cathode**

(C) Industrial Processes involving electrolysis

1 Anodising of Aluminium

- Aluminium exposed to air acquires a protective layer of oxide.
- The protective layer can be enhanced by anodising.
- **Anodising** is the process of coating aluminium objects with aluminium oxide electrolytically.



Electrolyte: dilute H_2SO_4 or chromic(VI) acid

Anode: **aluminium** object

At the anode where oxidation takes place,
$E^{\ominus}(S_2O_8^{2-}/SO_4^{2-})$ +2.01 V
$E^{\ominus}(O_2/H_2O)$ +1.23 V (✓)

When a current is passed, H_2O is discharged and is oxidised to O_2 at the anode.

$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$ (1)

This is followed by oxidation of the A*l* object (anodising) where the O_2 liberated at the anode reacts with the A*l*, forming Al_2O_3 which is then deposited on the surface. The surface oxide layer is artificially thickened.

$4Al(s) + 3O_2(g) \longrightarrow 2Al_2O_3(s)$ (2)

Overall reaction at the ANODE (per mol of Al_2O_3 produced):

$2Al(s) + 3H_2O(g) \longrightarrow Al_2O_3(s) + 6H^+(aq) + 6e^-$ (3)

(*To obtain the overall equation (3), multiply **(1) by 3** before combining the 2 equations to get*
$4Al(s) + 6H_2O(g) \longrightarrow 2Al_2O_3(s) + 12H^+(aq) + 12e^-$

Then divide throughout by 2 to get the simplified final equation (3))

Advantages of anodising:

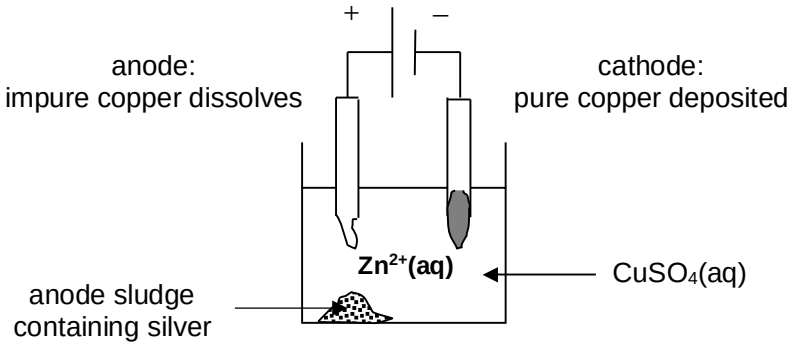
(i) Corrosion resistant
- allows aluminium utensils to be used in kitchens even for boiling acidic foods
- allows aeroplanes to survive flights through damp air
- protects overhead aluminium power lines, which are lighter and have higher conductivity than copper

(ii) Decorative
- dyes can be added to electrolytic bath and are incorporated into the oxide

2 Electrolytic Purification of Copper

Common impurities found in impure copper are: iron, zinc, gold, silver and platinum.

Use $E^{\ominus}$ values to explain what happens to each of the metals (Cu, Zn and Ag) in the impure copper anode during the purification process.



Electrolyte: $CuSO_4(aq)$

$Ag^+ + e^- \rightleftharpoons Ag$ $\quad E^{\ominus} = +0.80$ V
$Cu^{2+} + 2e^- \rightleftharpoons Cu$ $\quad E^{\ominus} = +0.34$ V
$Zn^{2+} + 2e^- \rightleftharpoons Zn$ $\quad E^{\ominus} = -0.76$ V

Reactions at Anode (impure copper)

Copper dissolves: **$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$**
Zinc dissolves: **$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$**

The cell potential is adjusted such that Cu dissolves (oxidised to Cu^{2+}).

Impurities (e.g. **Zn**) with $E^{\ominus}$ values which are less positive than $E^{\ominus}_{Cu^{2+}/Cu}$ also dissolve (oxidised to ions).

Impurities (e.g. **Ag**) with $E^{\ominus}$ values which are more positive than $E^{\ominus}_{Cu^{2+}/Cu}$ remain undissolved (not oxidised). They separate out as anode sludge (from which valuable metals can be recovered).

Migration of cations

Cu^{2+} and Zn^{2+} ions migrate to the cathode.

Reactions at Cathode (pure copper)

Copper is deposited **$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$**

Zn^{2+} ions are less easily reduced (recall: $E^{\ominus}_{Zn^{2+}/Zn}$ is less positive).

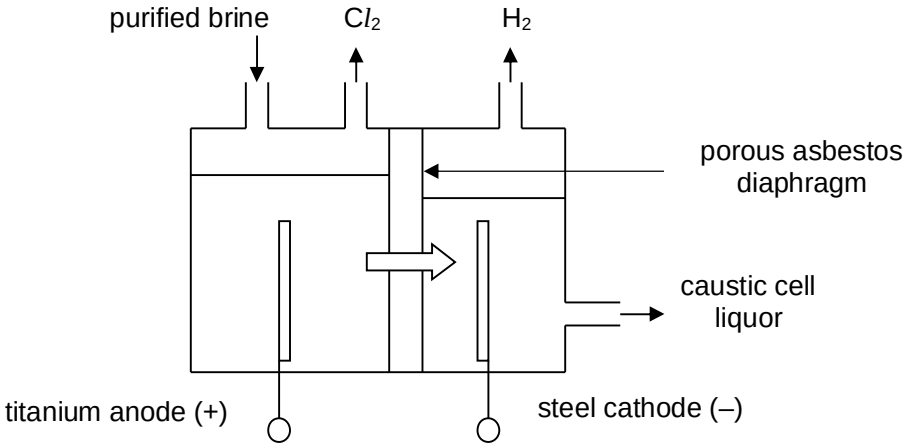
Hence, Zn^{2+} remains in solution while Cu^{2+} is preferentially reduced to Cu.

Overall reaction:

The net result is that copper from the impure copper anode is transferred to the pure copper cathode.

Purification produces copper of about 99.95 % purity.

3 Electrolysis of Brine using a Diaphragm Cell



Electrolyte: Purified brine (saturated/concentrated aqueous sodium chloride)
[Purification of brine is necessary to remove Ca^{2+} and Mg^{2+} which would precipitate as insoluble hydroxides and block the pores of the diaphragm.]

Anode: titanium (preferred due to corrosive nature of Cl_2 evolved)

Cl^- is discharged; Cl_2 liberated.
$2Cl^- \longrightarrow Cl_2 + 2e^-$

Recall that chloride is preferentially oxidised due to higher [Cl^-]
Remaining solution seeps through the asbestos diaphragm into cathode compartment.

Cathode: steel

H_2O is discharged; H_2 liberated.
$2H_2O + 2e^- \longrightarrow 2OH^- + H_2$

Overall reaction:

Cl_2, H_2 and NaOH are produced in the mole ratio 1 : 1 : 2.

$2NaCl(aq) + 2H_2O(l) \longrightarrow Cl_2(g) + H_2(g) + 2NaOH(aq)$

Cell liquor: contains a mixture of NaOH(aq) and NaCl(aq) (not all Cl^- is discharged at the anode)
On concentrating (by evaporation), NaCl crystallises out, and a concentrated solution of fairly pure NaOH remains.

Porous asbestos diaphragm

The diaphragm prevents the mixing of NaOH (formed at the cathode) and Cl_2 (at the anode), to prevent the disproportionation of Cl_2 to Cl^- and ClO^-.

It also serves to prevent the highly reactive H_2 (formed at the cathode) and Cl_2 (at the anode) from coming into contact and they can be sold separately as useful chemicals.

(D) Faraday's Laws of Electrolysis

Faraday's First Law:
The **mass** of a substance produced at an electrode during electrolysis is **directly proportional** to the **quantity of electricity** passed.

$$m \propto Q$$

where $$\mathbf{Q = I \times t}$$

Q = quantity of electricity in coulombs (units: **C**)
I = current in ampere (units: **A**)
t = time in seconds, (units: **s**)
m = mass deposited in grams, (units: **g**)

The charge of a single electron is 1.602×10^{-19} C (**e**)
The number of electrons in 1 mol is 6.023×10^{23} electrons (**L**),

Hence, the **charge on 1 mol of electrons = charge of one electron x no. of electrons in 1 mol**
$= 1.602 \times 10^{-19}$ C $\times 6.023 \times 10^{23} = 96\,500$ C
This amount of charge is referred to as 1 Faraday (**F**).

Hence the relationship: **F = Le**

⇨ the total amount of charge (**Q**) required to discharge 1 mol of M^{n+} ion to form 1 mol of M(s) is $\mathbf{n_e \times F}$. (where n_e = no. of moles of electrons involved)

This leads us to:

Faraday's Second Law:
The **number of Faradays** required to discharge one mole of an ion at an electrode is **equal to the charge** of the ion.

Example:

To discharge **1 mole** of	It implies that
Pb^{2+} requires **2F** (or 2 x 96500 C) of electricity	$Pb^{2+} + 2e^- \longrightarrow Pb$ it requires 193 000 C to deposit 207 g Pb
Br^- requires **1F** (or 96500 C) of electricity	$Br^- \longrightarrow \frac{1}{2}Br_2 + e^-$ it requires 96 500 C to produce 79.9 g Br_2
Al^{3+} requires **3F** (or 3 x 96500 C) of electricity	$Al^{3+} + 3e^- \longrightarrow Al$ it requires 289500 C to deposit 27.0 g Al

Combining both Faraday's First and Second Law,

$$\mathbf{Q = It} \quad \text{and} \quad \mathbf{Q = n_eF}$$
(where n_e = no. of moles of electrons involved)

$$\mathbf{n_eF = It}$$

Hence, the number of moles of electrons (and eventually mass of a substance produced) during electrolysis depends on:

1. magnitude of **current** passed (**I**)
2. **time** for which the current is passed (**t**)

} 1st Law

The mass of substance produced does **NOT** depend on the concentration of the ions and $E^{\ominus}$ values.

Exercise 6

1. A metal of relative atomic mass 27 is deposited by electrolysis. If 0.176 g of the metal is deposited on the cathode when 0.15 A of electric current flows for 3½ h, what is the charge on the cation of this metal?

Let M^{n+} be the cation.

$M^{n+} + ne^- \longrightarrow M$

$\mathbf{n_e \times F = I \times t}$

$\mathbf{n_e} \times$ =

No. of mole of e $\mathbf{(n_e)}$ = [0.15 x (3.5 x 60 x 60)] ÷ 96500 = 0.0196 mol

No. of mole of metal = 0.176 ÷ 27 = 0.00652 mol

$\frac{n(e)}{n(M)} = \frac{x}{1}$

$\frac{x}{1} = \frac{0.0196}{0.00652}$

$x \approx \mathbf{3}$

charge on cation = **3+**

2. A direct current of 10.0 mA flows for 4.00 h through 3 cells in series. They contain inert electrodes and solutions of silver nitrate, copper(II) sulfate and dilute sulfuric acid respectively.

Calculate the mass of metal and volume of gas produced at the cathode of each cell at room temperature and pressure.

[**F** = 96500 C mol^{-1}; A_r of Ag = 108; Cu = 63.5; H = 1.0; O = 16.0; molar volume at r.t.p. is 24.0 dm^3]

(Note: "*connected in series*" ⇒ current is the same for all 3 cells)

Since the cells are in series, the _____ quantity of electricity passes through them.

$\mathbf{n_e \times F = I \times t}$

$n_e \times 96500 =$

No. of moles of electrons (n_e) = _____ **mol**

for **$AgNO_3$(aq)**, at the cathode:

Ag^+/Ag +0.80 V
H_2O/H_2 –0.83 V

_____ is preferentially discharged.
_____ → _____

n(__) = n(e) =

Mass of ____ =
= **0.161 g**

for **$CuSO_4$(aq)**, at the cathode:

Cu^{2+}/Cu +0.34 V
H_2O/H_2 –0.83 V

____ is preferentially discharged.
_____ → _____

n(___) = ½ x n(e) = ½ x 0.00149
Mass of ____ = = **0.0473 g**

for **dil. H_2SO_4**, at the cathode:

H^+/H_2 0.00 V
H_2O/H_2 –0.83 V

H^+ is preferentially discharged.
_____ → _____

$n(H_2)$ = ½ x n(e) = ½ x 0.00149

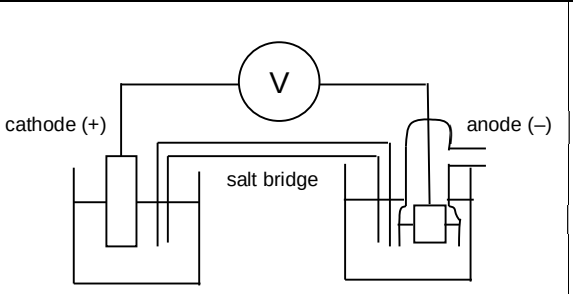
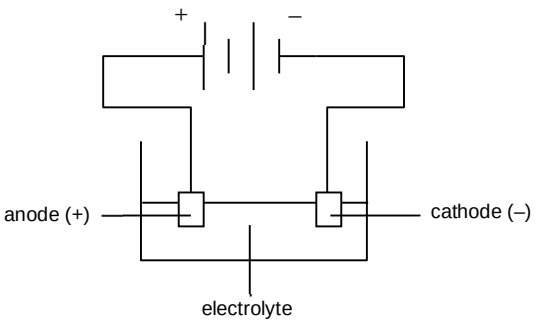
Volume of H_2 = ½ x 0.00149 x 24 dm^3
= **0.0179 dm^3**

(IV) SUMMARY

1. Redox reaction involves **red**uction and **ox**idation occurring simultaneously.

2. Reduction involves the gain of electron(s) with a decrease in oxidation number while oxidation involves the loss of electron(s) with an increase in oxidation number.

3. Comparison of electrochemical cell and electrolytic cell:

electrochemical cell	**electrolytic cell**
	
chemical energy ⟶ electrical energy	electrical energy ⟶ chemical energy
Cathode (+): **R**edu**C**tion **A**node (–): **O**xid**A**tion	**C**athode (–): **R**edu**C**tion **A**node (+): **O**xid**A**tion

4. For electrochemical cell,

   (a) Steps involved in determining flow of electrons:

      (i) identify the species that must (or can only) be reduced / oxidised
      It will be very obvious, look out for common oxidising agents (MnO_4^-, $Cr_2O_7^{2-}$, elements existing in their maximum O.N. – e.g. Ag^+, Cu^{2+}) or reducing agents (metals, halides).

      (ii) the other will then undergo oxidation / reduction

      (iii) write out the half–equation with the electrode potential for both the reduction and oxidation reactions as it appears in the *Data Booklet* (**NO NEED** to reverse direction). After writing them down, check that the reactants given appear on OPPOSITE side of their respective equations

   (b) Steps involved in determining if a reaction between 2 given compounds is spontaneous:

      (i) calculate the $\boldsymbol{E^{\ominus}_{cell} = E^{\ominus}_{reduction} - E^{\ominus}_{oxidation}}$
      (use the electrode potentials as given in the *Data Booklet*)

      (ii) if $\boldsymbol{E^{\ominus}_{cell} > 0\ V}$, then $\boldsymbol{\Delta G^{\ominus} < 0}$. Hence, reaction is spontaneous (thermodynamically feasible)

      (iii) write the reduction and oxidation half–equations and balance the no. of electrons on both equations before adding them together to get the balanced equation for the reaction

5. For electrolytic cell,

   (a) Terms used in electrolysis:

      (i) **discharged**: refer to the ions/H_2O

      (ii) **deposited**: refer to solid product formed (usually metal)

      (iii) **evolved**: refer to gaseous product formed

(b) Steps involved in determining the ions to be discharged:

(i) cations migrate to cathode and anions migrate to anode.

(ii) identify all ions (include H_2O if aqueous) present at cathode and anode respectively.

(iii) use the electrode potential given in the *Data Booklet* (or in question). Always use the electrode potential value as given. For **oxidised** form, it will appear on the **LHS** of equation while for **reduced** form, on the **RHS**.

(iv) among those present at cathode (reduction): choose the most positive electrode potential and that will be the species discharged at the cathode.

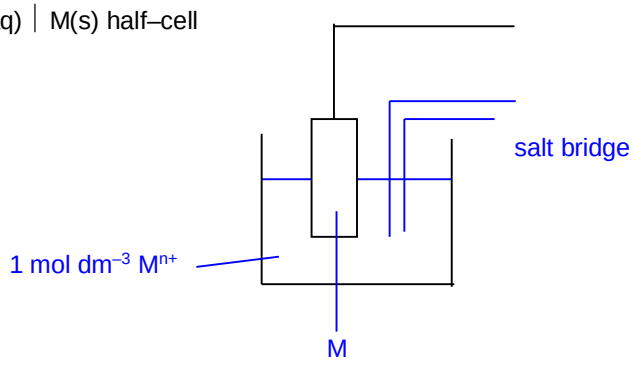
(v) among those present at anode (oxidation): choose the most negative electrode potential and that will be the species discharged at the anode.

(vi) sometimes *concentration* and the *nature of electrode* affect the species discharged.

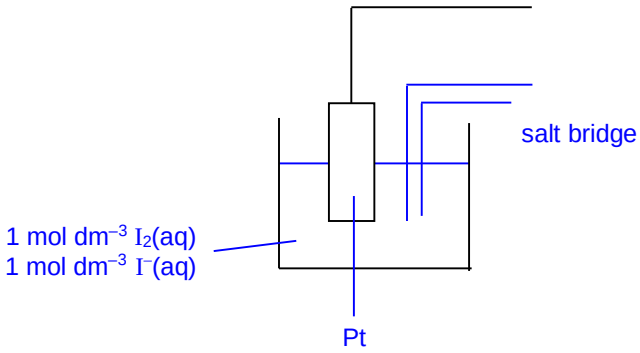
Determining electrode potential of a half–cell

3 types of diagrams that you will need to know how to draw:

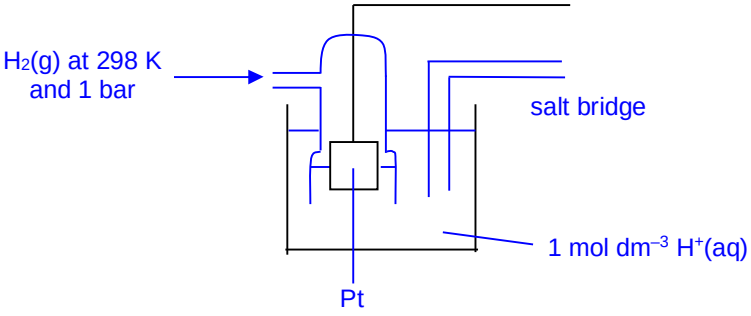
(i) $M^{n+}(aq) \mid M(s)$ half–cell



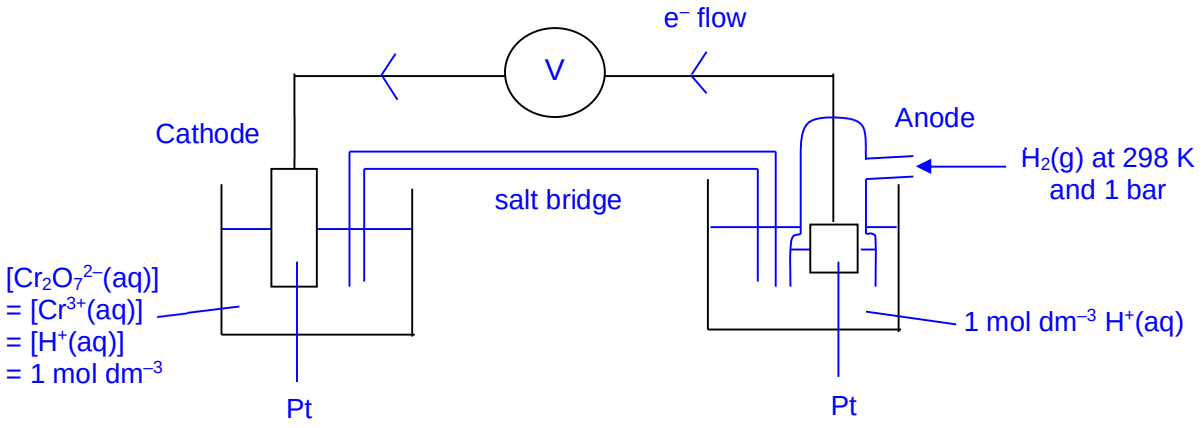
(ii) $I_2(aq)$, $I^-(aq)$ or $Fe^{3+}(aq)$, $Fe^{2+}(aq)$ half–cell



(iii) $H^+(aq) \mid H_2(g)$ or $Cl_2(g) \mid Cl^-(aq)$ half–cell



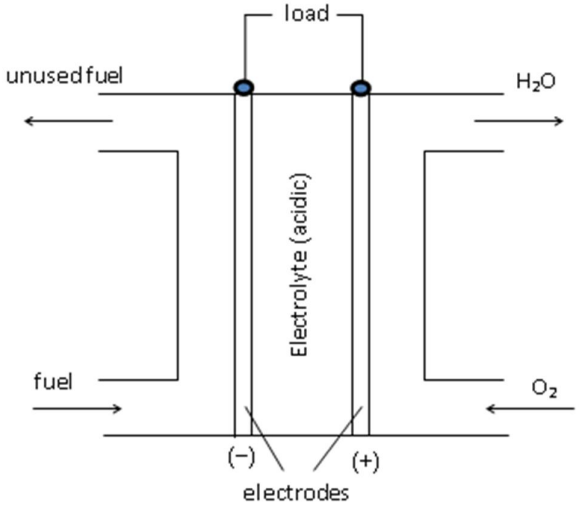
How to determine the standard electrode potential of a half–cell against S.H.E.
E.g. determining the standard electrode potential for the $Cr_2O_7^{2-}(aq)\,|\,Cr^{3+}(aq)$ half–cell



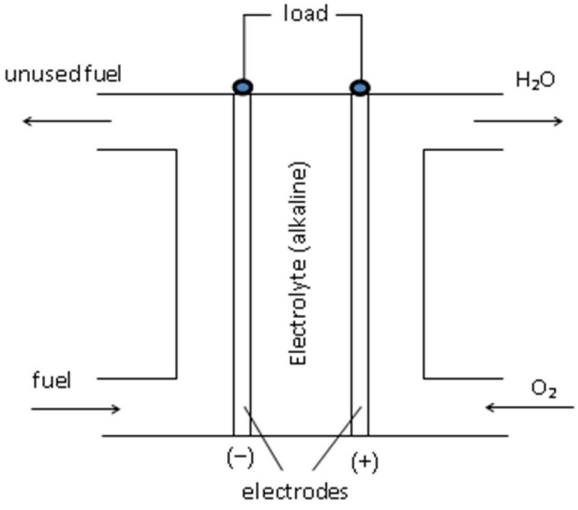
The potential difference shown on the high–resistance voltmeter gives the standard electrode potential for the $Cr_2O_7^{2-}(aq)\,|\,Cr^{3+}(aq)$ half–cell.

Fuel Cell Diagrams (commonly seen in Prelim papers)

Acidic electrolyte



Alkaline electrolyte



Anode:
$H_2 \longrightarrow 2H^+ + 2e^-$

Cathode:
$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$

Anode:
$H_2 + 2OH^- \longrightarrow 2H_2O + 2e^-$

Cathode:
$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$

If fuel used contains carbon (e.g. methanol, ethanol), CO_2 will be produced at the anode.

Important equations from Faraday's Laws of Electrolysis

(i)	**F = Le**	F = 96500 C mol^{-1}; L = 6.02 x 10^{23}; e = 1.60 x 10^{-19} C (from *Data Booklet*)
(ii)	**$Q = n_eF$**	Q = quantity of charge (C); n_e = no. of moles of e^- involved
(iii)	**Q = It**	I = size of current (A); t = time (s)