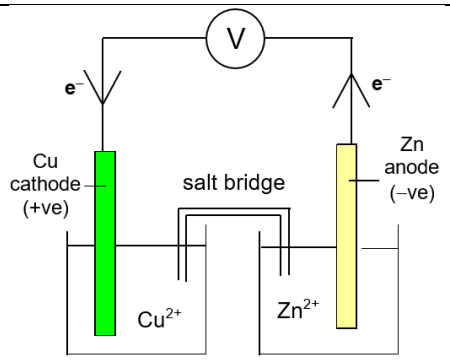
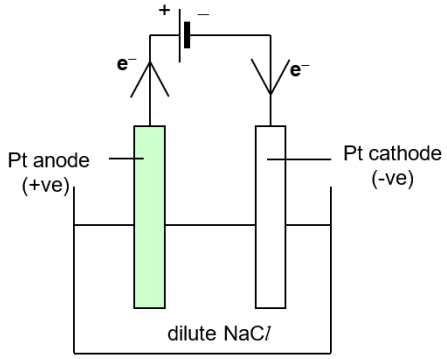
Electrochemistry

Electrochemistry is the study of the **inter-conversion of chemical and electrical energies**.
This inter-conversion of energies occurs in cells in which **redox reactions** (i.e. reactions involving the transfer of electrons from one chemical species to another) produce or utilise electrical energy.

Comparison of Electrochemical (Part 1) and Electrolytic cell (Part 2)

	ELECTROCHEMICAL CELL	**ELECTROLYTIC CELL**
		
Energy change	**chemical** energy → **electrical** energy	**electrical** energy → **chemical** energy
Cell Reaction	**Spontaneous** Chemical reaction takes place to generate electric current within celll (battery).	**Non-spontaneous** **External** electric current is applied to drive the reaction to occur.
Cathode (reduction)	**Positive (+) electrode**	**Negative (–) electrode**
Anode (oxidation)	**Negative (–) electrode**	**Positive (+) electrode**

Note:

1. In both electrochemical and electrolytic cells, **oxidation** always takes place at the **anode** while **reduction** always takes place at the **cathode**.

2. Polarity of electrode **always follow the polarity of the battery**.

   [ElectroCHEMICAL cell] The two half-cells form the battery.
   Anode is the negative terminal of the battery that releases electrons while cathode is the positive terminal of the battery that accepts electrons.

   [**ElectroLYTIC cell]** The ***polarities of the electrode are reversed***, as the electrodes follows the polarity of the battery terminal it is connected to.
   - **anode (+ve)** is connected to the +ve terminal of battery and **attracts anions** (−ve)
   - **cathode (−ve)** is connected to the –ve terminal of battery and **attracts cations** (+ve)

Electrochemical Cell (Part 1)

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, $E^{\ominus}$, and their uses
  (iii) batteries and fuel cells

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 (see also Section 13)
(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

References

- Chemistry; The Molecular Nature of Matter and Change, by Martin Silberberg, 2010, Publisher: McGraw Hill
- Chemistry for Advanced Level, by Peter Cann and Peter Hughes, 2002, Publisher: John Murray
- Chemguide: https://www.chemguide.co.uk/physical/redoxeqiamenu.html#top

Prerequisite to learn and understand this topic well

An understanding of *Redox* concepts, *Moles and Stoichiometry and Le Chatelier's principle are* imperative to do well for this chapter.

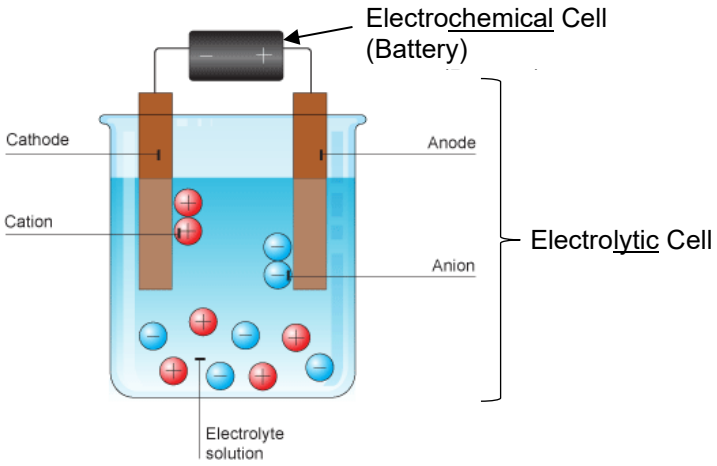
1 Introduction

Electrochemistry is the study of the **inter-conversion of chemical and electrical energies**.

Success Criteria

- I can differentiate between an electrochemical cell and electrolytic cell.

This inter-conversion of energies occurs in cells in which **redox reactions** (i.e. reactions involving the transfer of electrons from one chemical species to another) produce or utilise electrical energy.



There are two types of cells.

Electrochemical cell (also called galvanic cell or battery)	**Electrolytic cell**
Generation of Electricity	Use of Electricity for **Work**
Redox reaction is **spontaneous** ($\Delta G < 0$)	Redox reaction is **non-spontaneous** ($\Delta G > 0$)
Chemical → Electrical energy	**Electrical → Chemical energy**
Examples: dry cells, batteries, fuel cells 	*Examples*: extraction of aluminium metal from molten aluminium oxide, purification of copper, electroplating

1.1 About Redox Reactions

Success Criteria
- I know the difference between reduction and oxidation in terms of electron transfer and oxidation numbers

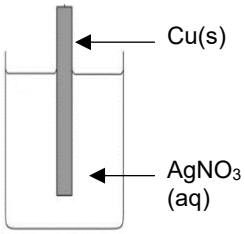
Oxidation: A process where a chemical species **loses electrons** (**increase in oxidation number**)

Reduction: A process where a chemical species **gains electrons** (**decrease in oxidation number**).

A **redox reaction** is a process involving electron transfer: **simultaneous** loss of electrons from the species undergoing oxidation and gain of electrons by the species undergoing reduction.

Worked Example 1

Video here:



(a) *Describe* and *explain* what is observed when a piece of copper metal is placed in a solution of silver nitrate.

Description:
- As the reaction proceeds, the **colourless** solution turns **blue** and the **pink** copper pipe is covered with **silver metal**, which falls off and collects under the pipe.

Explanation:
- Cu(s) **lose** electrons and get **oxidised** to $Cu^{2+}(aq)$ ions
- $Ag^{+}(aq)$ ions **gain** electrons and get **reduced** to Ag(s)
- A **redox** reaction has taken place.

(b) Write appropriate redox equations to describe the reactions taking place in the beaker.

[R]: $Ag^{+}(aq) + e^{-} \longrightarrow Ag(s)$ **[O]:** $Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^{-}$

Overall: $Cu(s) + 2Ag^{+}(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$

(c) What would you expect to observe if a piece of Ag metal is placed in a solution of Cu^{2+}?

Observations:
Since the reaction of $Ag^{+}(aq)$ and Cu(s) is spontaneous, the reverse reaction is expected to be **non-spontaneous**. Hence, the intensity of the blue $Cu^{2+}(aq)$ **remains the same** while Ag metal remains with nothing deposited on it.

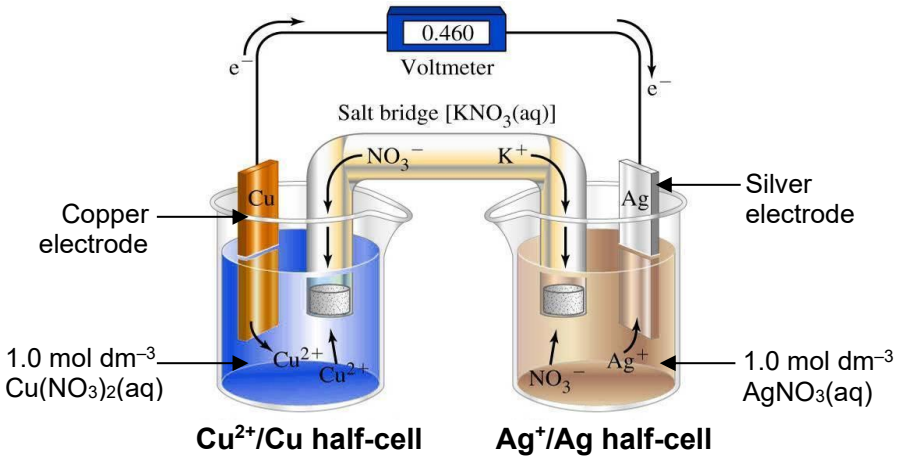
2 The Electrochemical Cell

Success Criteria:
- I can identify the polarity of the electrode based on the reaction occurring.
- I can predict the products formed at each electrode for the given example and understand how the observations occur for each half-cell.

In **Worked Example 1**, Cu(s) and $Ag^+(aq)$ are in **direct physical contact**, thus the electrons are transferred **directly** from Cu to Ag^+. The energy released from the reaction is given off as **heat**, and no usable energy is harnessed from this spontaneous redox reaction.

To capture this energy in the form of electrical energy, an **electrochemical cell** can be set up below by separating the two half-reactions above.

Worked Example 2



About the set-up
- A copper strip is dipped into a solution of Cu^{2+} ions in a beaker: **Cu^{2+}/Cu half-cell**
- A silver strip is dipped into a solution of Ag^+ ions in another beaker: **Ag^+/Ag half-cell**

- The two metal strips act as electrodes and are connected externally by an **electrical wire**.
- The **salt bridge** is an inverted U-tube containing a **gel** solution of **non–reacting ions**, in this case, **K^+ and NO_3^-**. It has porous plugs on the ends that allow ions to pass through while minimising the mixing of the electrolytes by diffusion. Each end is dipped into a half-cell. Other non-reacting ions include Na^+ and SO_4^{2-}.

Note:
A half-cell consists of **both** an electrode and an electrolyte(s). A half-cell contains 2 species of the same element with different oxidation state. E.g. Cu^{2+} and Cu & Ag^+ and Ag

Observations:
The voltmeter shows a **positive** voltage reading of 0.460 V.

After some time, in the Cu^{2+}/Cu half-cell, the Cu strip would **decrease in mass** due to loss of Cu into solution as $Cu^{2+}(aq)$ ions. In the Ag^+/Ag half-cell, the Ag strip would **increase in mass** due to Ag deposit formed from $Ag^+(aq)$ ions in solution.

In the half-cell:

Cu^{2+} / Cu half-cell	Ag^{+} / Ag half-cell
Cu atoms from Cu electrode are **oxidised** to Cu^{2+} ions and enter the solution. [O]: $Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^{-}$ **Polarity** of Cu electrode: **negative** This electrode loses electron to the external circuit, **negative terminal of battery**. The copper electrode is the **anode** since **oxidation** occurs here.	Ag^{+} ions are **reduced** to Ag atoms that deposit on the surface of Ag electrode. [R]: $Ag^{+}(aq) + e^{-} \longrightarrow Ag(s)$ **Polarity** of Ag electrode: **positive** This electrode gains electron from the external circuit, **positive terminal of battery** The silver electrode is the **cathode** as **reduction** occurs here.
Cu^{2+} is produced and goes into the solution. The solution becomes **positively charged**, with an excess of $Cu^{2+}(aq)$ ions. *Anions (NO_3^-) from the salt bridge migrate to the solution to balance excess $Cu^{2+}(aq)$ ions.*	Ag^{+} is removed from the solution. The solution becomes **negatively charged,** with an excess of $NO_3^-(aq)$ ions. *Cations (K^+) from the salt bridge migrate to the solution to balance excess $NO_3^-(aq)$ ions.*

Salt bridge

Without a salt bridge, this would give rise to a **charge imbalance in the cell and current flow will cease**. An electrochemical cell **cannot** operate without a salt bridge.

Function of salt bridge:
- **to complete the circuit**, and
- **maintain electrical neutrality** in each half-cell

Video on electrons flow in a electrochemical cell or galvanic cell:

In the external circuit

The electrons produced at the Cu^{2+}/Cu half-cell flow to the Ag^{+}/Ag half-cell via the electrical wire in the external circuit, i.e., **electrons flow from** the **negative** Cu anode **to** the **positive** Ag cathode.

Summary:

The overall reaction occurring in the electrochemical cell (separate half-cells) is the same as when Cu(s) and $Ag^{+}(aq)$ were mixed in a reaction vessel:

$$Cu(s) + 2Ag^{+}(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$$

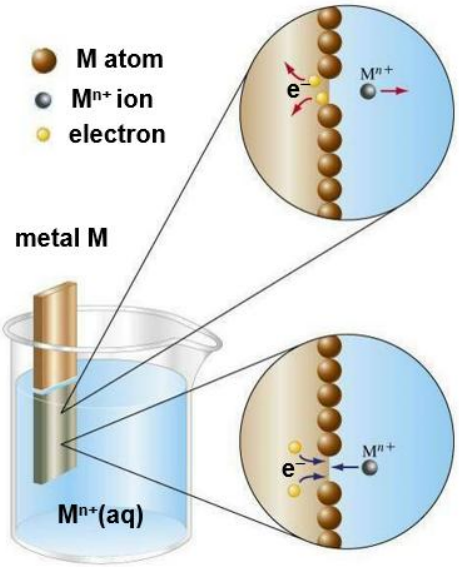
However, by separating the half-reactions into two different half-cells, the electrons must travel through the wire in the external circuit and this electrical energy can be harnessed to do work.

By separating the oxidation and reduction half-reactions, we can use spontaneous redox reactions ($\Delta G < 0$) to generate electrical energy!

3 Electrode Potential

Success Criteria
- I can appreciate how a potential difference is generated.

There are two possible situations when a strip of metal, M, is placed in a solution of its ions, M^{n+}.



Case 1:
Atoms from the metal lattice lose electrons to form the corresponding ions that enter the solution.

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

Case 2:
Some of the aqueous metal cations in the solution will reclaim their electrons to form the metal atoms.

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

Dynamic equilibrium is **established** where the rate of oxidation **equals** the rate of reduction.

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

Note:
By convention, half-reactions are written with reduction as the forward reaction.

Separation of charges between the electrons on the metal and its ions in solution results in a **potential difference** between the metal and the solution. This potential difference, $E(M^{n+}/M)$, is known as the **absolute electrode potential (reduction potential)**.

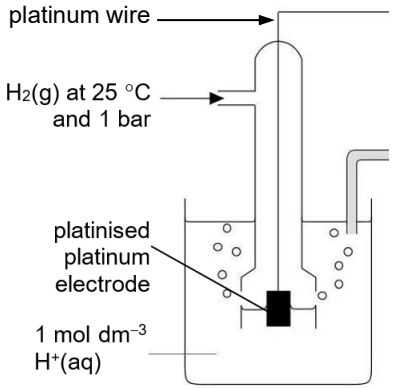
A more reactive metal gives a bigger magnitude of separation of charges, hence a greater magnitude of absolute electrode potential. However, **absolute electrode potential cannot be measured** since it is not possible to connect the voltmeter to the solution even though connection between voltmeter and metal can be done. Therefore, there is a need to measure potential difference between a particular half-cell with respect to a reference electrode.

4 Standard Hydrogen Electrode (S.H.E.)

Success Criteria
- I can identify the components of the standard hydrogen electrode.

In practice, the electrode potential of a half-cell is measured by connecting it to a standard reference electrode. A commonly used reference electrode is the **standard hydrogen electrode**, whose reduction potential is **assigned** to be **0.00 V**.

The standard hydrogen electrode consists of:
- a platinum wire and a piece of platinum foil covered with finely divided platinum (***platinised* platinum**) that serves as an inert electrode for redox reaction to take place.
- The electrode, encased in a glass tube, immersed in a solution of **1 mol dm^{-3} H$^+$** ions.
- **H_2 gas at a pressure of 1 bar at 298 K** is bubbled over the ***platinised* platinum** electrode.



On the surface of the platinum, equilibrium is established between hydrogen gas and hydrogen ions.

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g) \qquad E^\ominus(H^+/H_2) = 0.00\ V$$

Checkpoint 1

What should be the condition of the surface 1 mol dm^{-3} H$^+$(aq) electrode and the concentration of the sulfuric acid in a standard hydrogen electrode?

	Pt electrode	[H_2SO_4(aq)] / mol dm^{-3}
A	Platinised	0.5
B	Platinised	1.0
C	Polished	0.5
D	Polished	1.0

5 Standard Electrode Potential

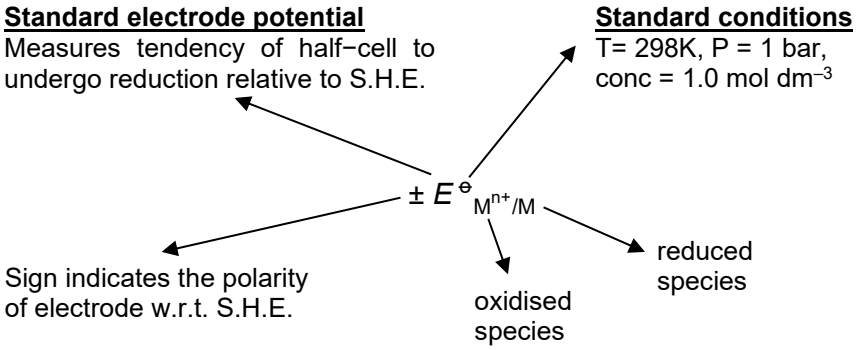
Success Criteria
- I know what the standard conditions are
- I know the representation of the notation for the standard electrode potential

Electrode potentials depend on conditions such as temperature, pressure and concentration. As such, electrode potential is commonly measured under a set of standard conditions.

Standard conditions for measuring electrode potential:
- temperature of **298 K**
- pressure of **1 bar (10^5 Pa)** for any gas
- concentration of **1 mol dm^{-3}** for any aqueous ions / species involved in redox

Definition of Standard Electrode Potential, $E^{\ominus}$

The ***standard electrode potential*** of a half-cell, $E^{\ominus}$, is the **potential difference between the half-cell and the standard hydrogen electrode (S.H.E)** measured at standard conditions (298 K, 1 bar for gases, and 1 mol dm^{-3} for aqueous ions)



The ***more +ve*** $E^{\ominus}$ $\Rightarrow$ Greater tendency for **reduction** to occur

The ***less +ve*** $E^{\ominus}$ $\Rightarrow$ Greater tendency for **oxidation** to occur

5.1 Measuring Standard Electrode Potentials

Success Criteria
- I can draw the 3 different types of half-cells listed below.

There are three types of half-cells that can be connected to the standard hydrogen electrode (**S.H.E**) to measure the standard electrode potential of a particular species. The types of half-cells are set up based on the states of the redox species involved.

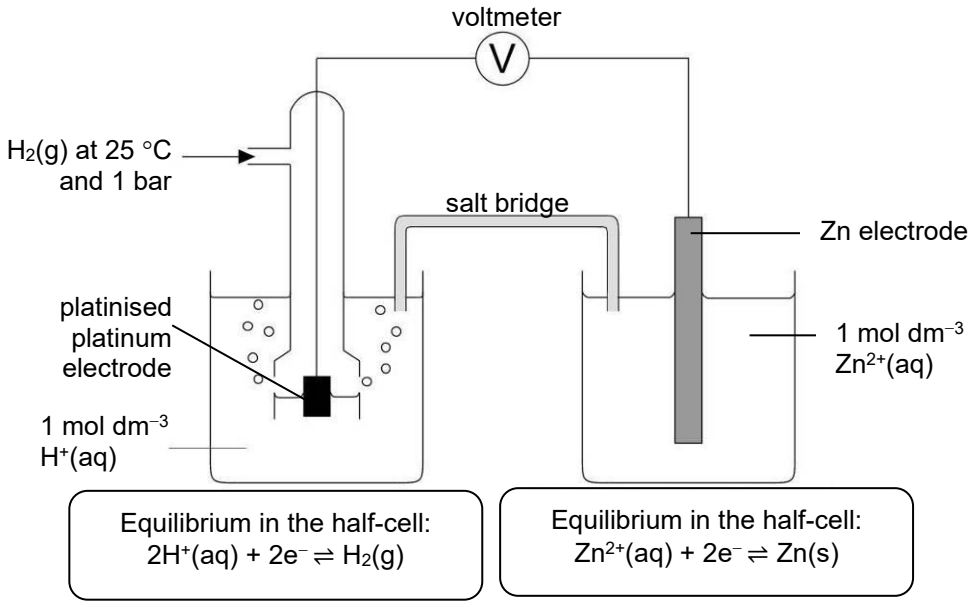
Half-Cell type	Redox Species 1	Redox Species 2	Example
1	Solid metal, M(s)	Aqueous metal ion, $M^{n+}(aq)$	$Zn^{2+}(aq)/Zn(s)$
2	Non-metal gas	Aqueous non-metal ion	$Cl_2(g)/Cl^-(aq)$
3	Aqueous ions of Oxidation State **A**	Aqueous ions of Oxidation State **B**	$Fe^{3+}(aq)/Fe^{2+}(aq)$

Points to note for drawing setup to measure standard electrode potential

- ✓ Two half-cells each containing 2 species of an element with different oxidation state
- ✓ S.H.E. half-cell is used as a reference half-cell
- ✓ Label the standard conditions
- ✓ Salt bridge
- ✓ Voltmeter in external circuit

Type 1. A solid metal in contact with its aqueous ions

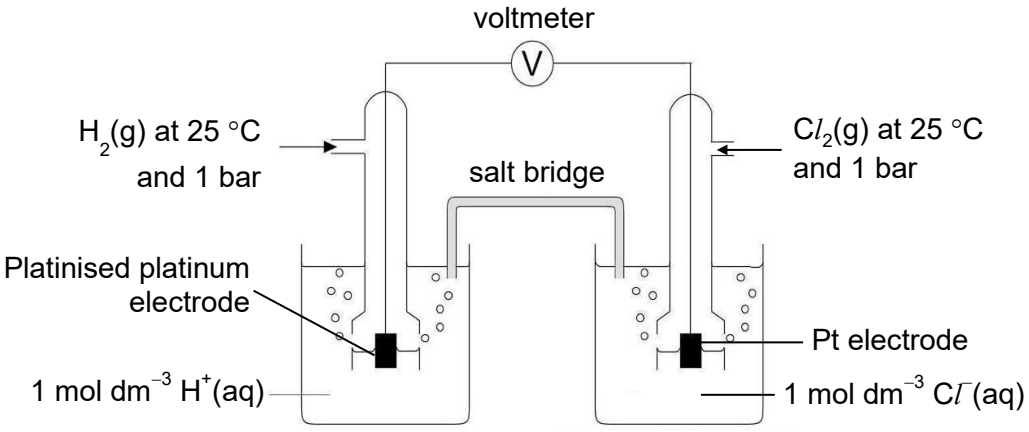
Example: $Zn^{2+}(aq)/Zn(s)$ half-cell



Note:
Inert Pt electrodes are required to provide an inert surface for redox reaction to take place in **(2)** and **(3),** Pt electrodes are not involved in the half-cell reactions.

Type 2. A <u>gaseous</u> non-metal in contact with its <u>aqueous</u> ions

Example: $Cl_2(g)/Cl^-(aq)$ half-cell



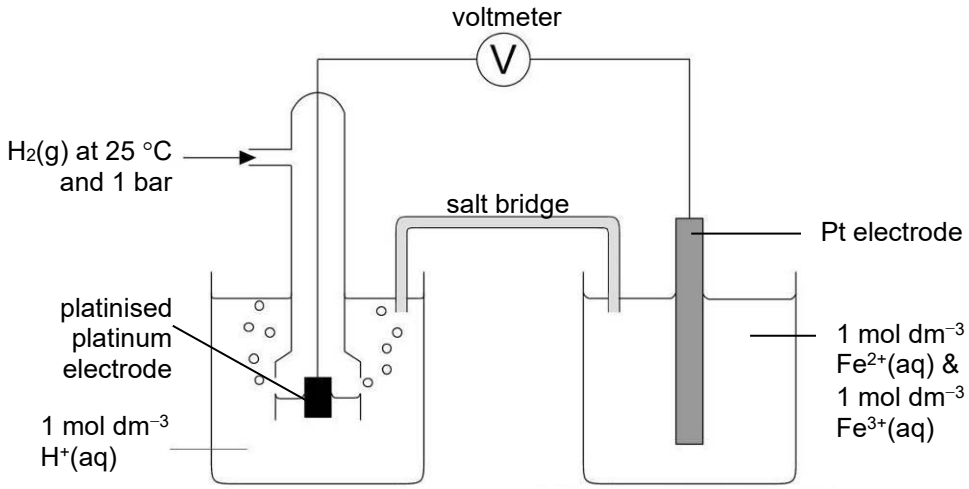
Equilibrium in the half-cell: $2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$

Equilibrium in the half-cell: $Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$

Type 3. A <u>aqueous</u> ions of <u>same element in different oxidation states</u>

Example: $Fe^{3+}(aq)/Fe^{2+}(aq)$ half-cell

Note:
Inert Pt electrodes are required to provide an inert surface for redox reaction to take place in **(2)** and **(3),** Pt electrodes are not involved in the half-cell reactions.



Equilibrium in the half-cell: $2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$

Equilibrium in the half-cell: $Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$

- The values of **standard electrode (reduction) potential,** $E^{\ominus}$, can be obtained from the *Data Booklet*. When $E^{\ominus}$ is being measured, **S.H.E** is always the **anode,** the negative electrode (oxidation) so that tendency of other half-cells to undergo reduction relative to **S.H.E** can be measured.

- Therefore, all the half-reactions in the *Data Booklet* are written as **reduction**.

  Oxidised species + ne^- $\rightleftharpoons$ Reduced species $\quad E^{\ominus} = \boldsymbol{x}$ V

- Half-reactions are written with an equilibrium arrow (⇌) because a half-reaction can either favour reduction or oxidation depending on the conditions and the $E^{\ominus}$ of the other half-reaction.

- When the half-reaction connected to **S.H.E** undergoes reduction, $E^{\ominus}$ will be a positive value. i.e. it has a greater tendency to be reduced compared to **S.H.E**. When the half-reaction connected to **S.H.E** undergoes oxidation, $E^{\ominus}$ will be a negative value as it has a lesser tendency to be reduced compared to **S.H.E**.

- The $E^{\ominus}$ value for a particular half-reaction is **independent of the number of electrons being transferred**.

  Example: $Ag^+(aq) + e^- \rightleftharpoons Ag(s) \quad E^{\ominus} = +0.80$ V
  $2Ag^+(aq) + 2e^- \rightleftharpoons 2Ag(s) \quad E^{\ominus} = +0.80$ V

6 Applications of Standard Electrode Potentials

6.1 Compare Oxidising and/or Reducing Strengths of Given Species

Success Criteria

- I know a more positive **$E^\ominus$ value** leads to an increasing tendency to be reduced and a more negative **$E^\ominus$ value** leads to an increasing tendency to be oxidised.

Oxidised species + ne^- $\rightleftharpoons$ Reduced species $\quad E^\ominus$ = **x** V

To determine the strength of O.A or R.A, compare the $E^\ominus$ value of the different species.

Note:
More positive (+) $E^\ominus$ value favours the forward reduction reaction.

Oxidising agent (**O.A**)	Reducing agent (**R.A**)
REDUCED when it oxidises others	**OXIDISED** when it reduces others
More positive/larger the $E^\ominus$ value • **forward reaction is more favourable** • leading to **greater tendency to reduce** • **stronger** the strength of **oxidising agent**	**Less positive (more negative)** the $E^\ominus$ value • **backward reaction** is **more favourable** • leading to **greater tendency to oxidise** • **stronger** the strength of **reducing agent**

Worked Example 3

1) Compare the strengths of oxidising agent (underlined species):

$\underline{Cl_2}(g) + 2e^- \rightleftharpoons 2Cl^-(aq) \quad E^\ominus(Cl_2/Cl^-) = +1.36$ V

$\underline{Br_2}(l) + 2e^- \rightleftharpoons 2Br^-(aq) \quad E^\ominus(Br_2/Br^-) = +1.07$ V

Since $E^\ominus(Cl_2/Cl^-)$ is **more positive** than $E^\ominus(Br_2/Br^-)$, Cl_2 has a **greater tendency to be reduced**. Cl_2 is thus a **stronger** oxidising agent than Br_2.

2) Compare the strengths of reducing agent (underlined species):

$Ca^{2+}(aq) + 2e^- \rightleftharpoons \underline{Ca}(s) \quad E^\ominus(Ca^{2+}/Ca) = -2.87$ V

$Mg^{2+}(aq) + 2e^- \rightleftharpoons \underline{Mg}(s) \quad E^\ominus(Mg^{2+}/Mg) = -2.38$ V

Since $E^\ominus(Ca^{2+}/Ca)$ is **less positive (more negative)** than $E^\ominus(Mg^{2+}/Mg)$, Ca has a **greater tendency to be oxidised**. Ca is thus a **stronger** reducing agent than Mg.

- The **electrochemical series** is a redox series arranged in order of increasing standard electrode potential values. The **metal reactivity series** is only part of the electrochemical series (see table below).

Making connections:
As metals undergo oxidation (i.e. act as reducing agents), the more negative the $E^{\ominus}$ value, the more reactive (greater tendency to get oxidised) they are. Hence, the $E^{\ominus}$ values of the metal reactivity series becomes more positive down the series.

Please	Potassium
Stop	Sodium
Calling	Calcium
Me	Magnesium
A	Aluminium
Careless	(Carbon)
Zebra	Zinc
Instead	Iron
Try	Tin
Learning	Lead
How	(Hydrogen)
Copper	Copper
Saves	Silver
Gold	Gold

increasing tendency to be reduced ∴ increasing oxidising strength

Gains electron

Half-equation	$E^{\ominus}$ / V
$Na^+ + e^- \rightleftharpoons Na$	–2.71
$Mg^{2+} + 2e^- \rightleftharpoons Mg$	–2.38
$Al^{3+} + 3e^- \rightleftharpoons Al$	–1.66
$Cr^{2+} + 2e^- \rightleftharpoons Cr$	–0.91
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	–0.76
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	–0.44
$Cr^{3+} + e^- \rightleftharpoons Cr^{2+}$	–0.41
$Co^{2+} + 2e^- \rightleftharpoons Co$	–0.28
$Ni^{2+} + 2e^- \rightleftharpoons Ni$	–0.25
$Sn^{2+} + 2e^- \rightleftharpoons Sn$	–0.14
$Pb^{2+} + 2e^- \rightleftharpoons Pb$	–0.13
$2H^+ + 2e^- \rightleftharpoons H_2$	0.00
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34
$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.54
$Ag^+ + e^- \rightleftharpoons Ag$	+0.80
$Br_2 + 2e^- \rightleftharpoons 2Br^-$	+1.07

Loses electron

increasing tendency to be oxidised ∴ increasing reducing strength

Checkpoint 2

Using the standard electrode potential in the *Data Booklet*, answer the following questions:

1(a) Decide if each statement is true (**T**) or false (**F**). Explain your answers.

- Fe^{2+} has a stronger oxidising power than Fe^{3+}. T / F

- Cr^{2+} is a stronger reducing agent than Fe^{2+}. T / F

(b) **(i)** the strongest oxidising agent is _____.
(ii) the strongest reducing agent is _____.

6.2 Standard Cell potential, $E^{\ominus}_{cell}$, of Electrochemical Cell

Success Criteria

- I can use the $E^{\ominus}$ **cell** equation to calculate the value of the potential difference between two half-cells

Note:
S.H.E. half-cell is NOT required when measuring standard cell potential.

S.H.E. half-cell is used as a reference when measuring standard **electrode** potential not the full cell.

Definition of Standard Cell Potential, $E^{\ominus}_{cell}$

*The **standard cell potential**, $E^{\ominus}_{cell}$,* is the **potential difference between the two half-cells** measured at standard conditions (298 K, 1 bar for gases, and 1 mol dm^{-3} for aqueous ions).

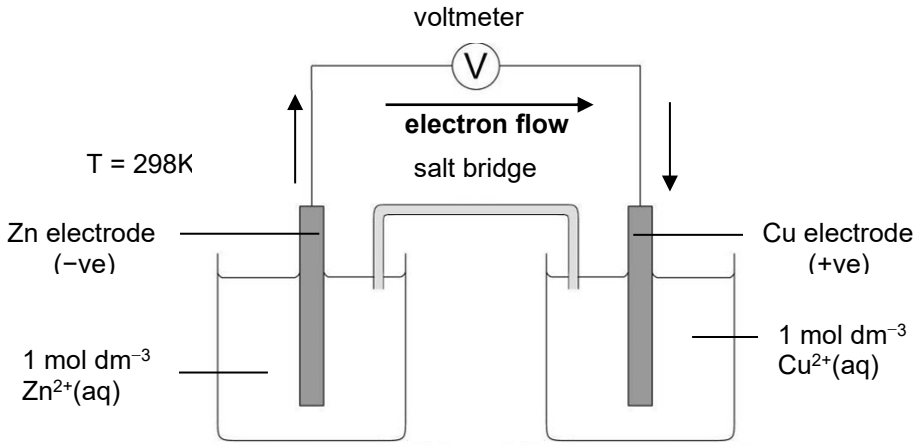
- The $E^{\ominus}_{cell}$ for a cell is calculated from the **difference between the standard reduction potentials** of the two half-reactions:

$$E^{\ominus}_{cell} = E^{\ominus}_{[R]} - E^{\ominus}_{[O]}$$

Example: An electrochemical cell consisting of a Zn^{2+}/Zn half-cell and a Cu^{2+}/Cu half-cell.

Points to note for drawing setup to measure standard cell potential

- ✓ Two half-cells each containing 2 species of an element with different oxidation state
- ✓ Label polarity of electrode
- ✓ Indicate direction of electron flow
- ✓ Label the standard conditions
- ✓ Salt bridge
- ✓ Voltmeter in external circuit



- The voltmeter will measure the potential difference between the two half-cells, i.e. $E^{\ominus}_{cell}$, also known as the electromotive force, or **e.m.f.** of the cell.

Using the *Data Booklet*;

Note:
In Step 1, reversible arrow is usually used as we are unsure of the direction of the half-reactions. Upon predicting the direction of feasible (or spontaneous) reaction using $E^\ominus$ values in steps 1, the equations of the half-reactions and the overall cell reaction are written with the single arrow symbol (⟶)

1) Identify the half-equations that represent the equilibrium in each half-cell and compare their $E^\ominus$ values .

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

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

2) The half–reaction with the more positive $E^\ominus$ value undergoes reduction.

Since $E^\ominus (Cu^{2+}/Cu)$ is **more positive** than $E^\ominus (Zn^{2+}/Zn)$, **reduction** occurs in the Cu^{2+}/Cu half-cell.

[R]: $Cu^{2+} + 2e^- \longrightarrow Cu$

3) For the half-equation with a less positive (more negative) $E^\ominus$ value, flip the ionic equation over. This half-cell undergo oxidation.

Oxidation then occurs in the Zn^{2+}/Zn half-cell.

[O]: $Zn \longrightarrow Zn^{2+} + 2e^-$

4) Combining the two half-equations gives the overall cell reaction.

Overall: $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$

5) Calculate $E^\ominus_{cell}$ of the reaction.

$E^\ominus_{cell} = E^\ominus_{[R]} - E^\ominus_{[O]}$
$= E^\ominus (Cu^{2+}/Cu) - E^\ominus (Zn^{2+}/Zn)$
$= \mathbf{+0.34 - (-0.76) = +1.10\ V}$

More positive $E^\ominus$
⇒ Greater tendency for species to be reduced
⇒ Species is a **stronger oxidising agent**

Less positive $E^\ominus$
⇒ Greater tendency for species to be oxidised
⇒ Species is a **stronger reducing agent**

Checkpoint 3

An electrochemical cell is set up by connecting Cr^{3+}/Cr half-cell with Fe^{2+}/Fe half-cell.

Which statements are true for this cell?

1	Chromium is reduced, while Fe is oxidised.	T	/	F
2	The e.m.f. of the cell is +0.30 V.	T	/	F
3	Iron will be deposited at one of the electrodes.	T	/	F

6.2.1 Direction of Electron Flow

Success Criteria
- I can determine the direction of the flow of electrons based on the redox half equation that is occurring at the half-cell.

- Electrode in the **oxidation** half-cell is known as the **anode**.
  Anode loses electrons to the external circuit during **oxidation.**

- Electrode in the **reduction** half-cell is known as the **cathode**.
  Cathode gains electrons from the external circuit during **reduction.**

  In the electrochemical cell consisting of a Zn^{2+}/Zn half-cell and a Cu^{2+}/Cu half-cell.

  [R]: $Cu^{2+} + 2e^- \longrightarrow Cu(s)$
  [O]: $Zn(s) \longrightarrow Zn^{2+} + 2e^-$

  - Hence, electrons flow from the **Zn electrode to the Cu electrode** via the wire in the external circuit.

6.2.2 Polarity of Electrodes

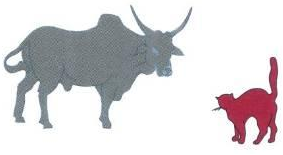
Success Criteria
- I can determine the polarity of the electrode based on the direction of electron flow.

- The two half-cells form a complete cell. Electrons flow from the negative terminal of the battery through the external circuit to the positive terminal of the battery.

- In the cell in Section **6.2**, the Zn electrode is the negative electrode (Negative terminal of the battery) and Cu electrode is the positive electrode**.** (Positive terminal of the battery)

Summary: For Electrochemical Cell

Useful aid: (**An Ox, Red Cat**)



electrode	cathode	anode
Type of process	reduction	oxidation
Electron transfer	accepts electron	releases electron
Polarity of electrode	positive	negative
Direction of electron flow	from anode to cathode	

6.3 Effects of Changing Conditions on Standard Electrode Potential and Cell Potential

Success Criteria

- I can predict qualitatively how the value of an electrode potential and cell potential varies with the concentration of the aqueous ion.

Recall: Standard conditions for measuring electrode potential:

- temperature of **298 K**
- pressure of **1 bar (10^5 Pa)** for any gas
- concentration of **1 mol dm^{-3}** for any aqueous ions / species involved in redox

Under **non-standard conditions**, the position of equilibrium would be shifted and the electrode potential would deviate from the standard electrode potential given in the *D*ata *B*ooklet.

Considering the following half-cell:

$$Cu^{2+} + 2e^- \rightleftharpoons Cu \qquad E^\ominus(Cu^{2+}/Cu) = +0.34\ V$$

When $[Cu^{2+}]$ increases, e.g. from 1.0 to 2.0 mol dm^{-3}, the position of equilibrium would shift to the **right**, with a **greater tendency for reduction** of Cu^{2+}, $E(Cu^{2+}/Cu)$ **increases** (e.g. from +0.34 V to +0.35 V).

When $[Cu^{2+}]$ decreases, e.g. from 1.0 to 0.1 mol dm^{-3}, the position of equilibrium would shift to the **left**, with a **lower tendency for reduction** of Cu^{2+}, $E(Cu^{2+}/Cu)$ **decreases** (e.g. from +0.34 V to +0.31 V).

For the electrochemical cell containing Zn^{2+}/Zn and Cu^{2+}/Cu half-cells.

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

$$E^\ominus_{cell} = E^\ominus_{[R]} - E^\ominus_{[O]}$$
$$= E^\ominus(Cu^{2+}/Cu) - E^\ominus(Zn^{2+}/Zn)$$
$$= +0.34 - (-0.76)) = +1.10\ V$$

Scenario 1: When $[Cu^{2+}]$ is changed to 0.1 mol dm^{-3},
position of Cu^{2+}/Cu equilibrium shifts to the left, $E(Cu^{2+}/Cu)$ decreases

- E_{cell} decreases [$E_{cell} = E(Cu^{2+}/Cu) - E^\ominus(Zn^{2+}/Zn)$]

Scenario 2: When $[Zn^{2+}]$ is changed to 0.1 mol dm^{-3},
position of Zn^{2+}/Zn equilibrium shifts to the left, $E(Zn^{2+}/Zn)$ decreases

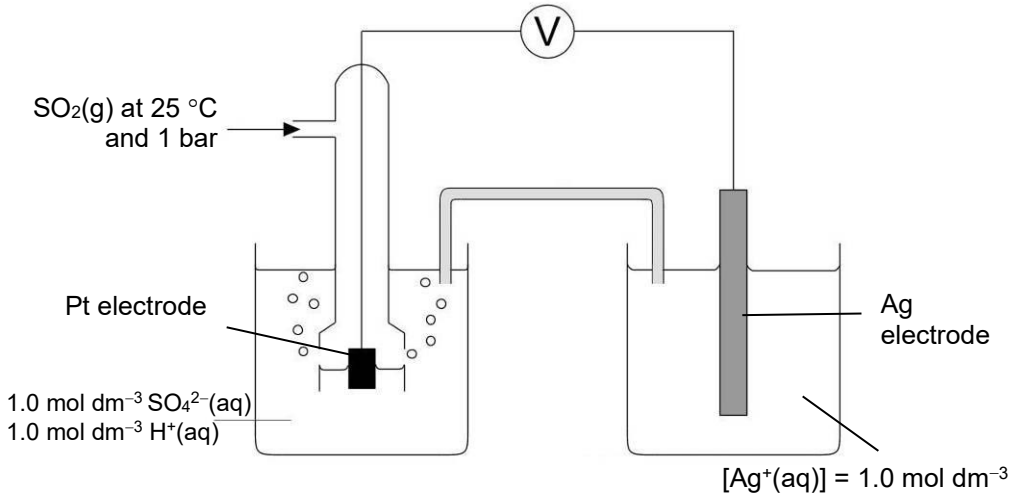
- E_{cell} increases [$E_{cell} = E^\ominus(Cu^{2+}/Cu) - E(Zn^{2+}/Zn)$]

Checkpoint 4

(a) Calculate the $E^{\ominus}_{cell}$ for the electrochemical cell shown below.

(b) Indicate on the diagram the
(i) type of electrode (cathode or anode)
(ii) polarity of the electrodes and
(iii) direction of electron flow.

Note:
The value of $E^{\ominus}$ is unaffected when the half–equation is multiplied by any factor. The tendency to undergo oxidation or reduction does not depend on how many moles of substance are involved.



(c) Suggest how E_{cell} value would be affected when
(i) a few drops of NaOH(aq) is added to the SO_4^{2-}/SO_2 half-cell

(ii) a few drops of NaCl(aq) is added to the Ag^+/Ag half-cell

7 To Predict the Feasibility of a Redox Reaction

Success Criteria
- I know the having a positive sign of the $E^{\ominus}_{cell}$ value means the reaction is spontaneous and vice versa.

To predict if a redox reaction would occur when two chemical species are mixed,
1. **Select appropriate reduction half-reactions** where each species appear (**either as reactant or product**) from the *Data Booklet* and write them down together with their $E^{\ominus}$ values. The **two species must be on opposite sides** of the half-equations, the reacting species on the **left** will be **reduced** and the reacting species on the **right** will be **oxidised**. A redox reaction is possible.
2. Write the reduction and oxidation half-equations using full arrows "⟶".
3. Calculate the $E^{\ominus}_{cell}$ of the redox reaction using: $E^{\ominus}_{cell} = E^{\ominus}_{[R]} - E^{\ominus}_{[O]}$

- If $E^{\ominus}_{cell}$ **is positive (> 0)**, reaction is **spontaneous**
  - **(thermodynamically feasible)** under standard conditions.
- If $E^{\ominus}_{cell}$ **is negative (< 0)**, reaction is **not spontaneous (thermodynamically not feasible)** under standard conditions.
- If $E^{\ominus}_{cell}$ **= 0**, **equilibrium** is attained.

Note:
Once the half−equations are identified, select the combination of reduction and oxidation half−equations that produces the most positive $E^{\ominus}_{cell}$. This is achieved by selecting:

1) [R] half−eqn with most positive $E^{\ominus}$, (highest tendency to undergo [R])

   and

2) [O] half−eqn with most negative $E^{\ominus}$, (highest tendency to undergo [O]).

3)

Worked Example 4

Using the standard electrode potentials given, predict if each of the following pairs of reagents are likely to react when mixed.
Calculate the $E^{\ominus}_{cell}$ and write a balanced equation for any reaction taking place.

(a) I_2(aq) and Cr^{3+}(aq)

	Half-equation	$E^{\ominus}$ / V
Equations where reactants are reduced	$\underline{I_2}$ + $2e^-$ ⇌ $2I^-$	+0.54
	$\underline{Cr^{3+}}$ + $3e^-$ ⇌ Cr	−0.74
	$\underline{Cr^{3+}}$ + e^- ⇌ Cr^{2+}	−0.41
Equations where reactants are oxidised	$Cr_2O_7^{2-}$ + $14H^+$ + $6e^-$ ⇌ $2\underline{Cr^{3+}}$ + $7H_2O$	+1.33

[R] $\underline{I_2}$ + $2e^-$ ⟶ $2I^-$
[O] $2\underline{Cr^{3+}}$ + $7H_2O$ ⟶ $Cr_2O_7^{2-}$ + $14H^+$ + $6e^-$

$E^{\ominus}_{cell} = E^{\ominus}_{[R]} - E^{\ominus}_{[O]} = \underline{+0.54 - (+1.33)} = \underline{-0.79\ V\ (< 0)}$
∴ Reaction is <u>not spontaneous</u> ⇒ reaction <u>cannot</u> occur.

Overall equation for reaction: <u>not applicable</u>

Note:
In acidic condition, MnO_4^- is reduced to Mn^{2+}.

Reduction of MnO_4^- to MnO_2 is not applicable in acidic medium as MnO_2 will undergo further reduction to give Mn^{2+}

$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$

(b) $MnO_4^-(aq)$ and $Fe^{2+}(aq)$ in **acidic medium**

	Half-equation	$E^\ominus$ / V
Equations where reactants are reduced	~~$MnO_4^- + 4H^+ + 3e^- \rightleftharpoons MnO_2 + 2H_2O$~~	~~+1.67~~
	$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	+1.52
	$Fe^{2+} + 2e^- \rightleftharpoons Fe$	−0.44
Equations where reactants are oxidised	$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.77

[R] $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$
[O] $Fe^{2+} \longrightarrow Fe^{3+} + e^-$

$E^\ominus_{cell} = E^\ominus_{[R]} - E^\ominus_{[O]} = +1.52 - (+0.77) = +0.75$ V (> 0)
∴ Reaction is spontaneous ⇒ reaction can occur.

Overall equation:
$5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq) \longrightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)$

(c) $F_2(g)$ and $Cr_2O_7^{2-}(aq)$ in **acidic medium**

	Half-equation	$E^\ominus$ / V
Equations where reactants are reduced	$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	+1.33
	$F_2 + 2e^- \rightleftharpoons 2F^-$	+2.87
Equations where reactants are oxidised	No equation.	

Reaction cannot occur as both $Cr_2O_7^{2-}$ and F_2 undergo reduction.

(d) $V^{3+}(aq)$ and $Cu^{2+}(aq)$

	Half-equation	$E^\ominus$ / V
Equations where reactants are reduced	$V^{3+} + e^- \rightleftharpoons V^{2+}$	−0.26
	$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34
	$Cu^{2+} + e^- \rightleftharpoons Cu^+$	+0.15
Equations where reactants are oxidised	$VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O$	+0.34

[R] $Cu^{2+} + 2e^- \longrightarrow Cu$
[O] $V^{3+} + H_2O \longrightarrow VO^{2+} + 2H^+ + e^-$

$E^\ominus_{cell} = E^\ominus_{[R]} - E^\ominus_{[O]} = +0.34 - (+0.34) = 0.00$ V

⇒ *equilibrium* is achieved.

Overall equation:
$Cu^{2+}(aq) + 2V^{3+}(aq) + 2H_2O(l) \rightleftharpoons Cu(s) + 2VO^{2+}(aq) + 4H^+(aq)$

Checkpoint 5

Use standard electrode potentials from the *Data Booklet* to predict whether any reaction occurs between $Sn^{2+}(aq)$ and acidified solution of $H_2O_2(aq)$.

	Half-equation	$E^{\ominus}$ / V
Equations where reactants are reduced		
Equations where reactants are oxidised		

8 Relationship between Standard Cell Potential and Standard Gibbs Free Energy

Success Criteria

- I can know that the negative sign of $\Delta G^{\ominus}$ means that the reaction is feasible and vice versa
- I can use the $\Delta G^{\ominus} = -\mathbf{n}FE^{\ominus}_{cell}$ to determine the values of $\Delta G^{\ominus}$, $E^{\ominus}_{cell}$ and no. of electrons transferred.

For a reaction to be feasible or spontaneous, $\Delta G^{\ominus} < 0$ and $\Delta G^{\ominus}$ is related to $E^{\ominus}_{cell}$ by the thermodynamic equation:

$$\Delta G^{\ominus} = -\mathbf{n}FE^{\ominus}_{cell}$$

Note:
n is always an integer

where $\Delta G^{\ominus}$ is the standard free energy change in J mol^{-1},
n is the stoichiometric ratio of the electrons transferred during the redox reaction per mole of written equation (**n** is a whole number)
F is the Faraday's constant ($F = 9.65 \times 10^4$ C mol^{-1})

Worked Example 5

With reference to the Data Booklet, calculate the $E^{\ominus}_{cell}$ and hence the $\Delta G^{\ominus}$ of the following reaction:

$$Pb(s) + 2Ag^{+}(aq) \longrightarrow Pb^{2+}(aq) + 2Ag(s)$$

From the *Data Booklet,*

	Half-equation	$E^{\ominus}$ / V
Equations where reactants are reduced	**Ag^{+}** + e^{-} $\rightleftharpoons$ Ag	+0.80
Equations where reactants are oxidised	Pb^{2+} + $2e^{-}$ $\rightleftharpoons$ **Pb**	–0.13

[R] $Ag^{+} + e^{-} \rightarrow Ag$ [O] $Pb \rightarrow Pb^{2+} + 2e^{-}$

Note:
There are **2 mol of electrons** transferred per mol of this reaction, hence n = 2.

$E^{\ominus}_{cell} = E^{\ominus}_{[R]} - E^{\ominus}_{[O]} = +0.80 - (-0.13) = +0.93V$

Apply the formula $\Delta G^{\ominus} = -nFE^{\ominus}_{cell}$
$\Delta G^{\ominus} = -(2)(9.65 \times 10^{4})(+0.93) = -1.79 \times 10^{5}$ J mol^{-1} = –179 kJ mol^{-1}

Checkpoint 6

Consider the following redox reaction between ethanedioic acid and potassium manganate(VII) in acidic medium

$$5H_2C_2O_4 + 2MnO_4^{-} + 6H^{+} \longrightarrow 10CO_2 + 2Mn^{2+} + 8H_2O \qquad \Delta G^{\ominus} = -1940 kJ\ mol^{-1}$$

By applying the relationship $\Delta G^{\ominus} = -nFE^{\ominus}_{cell}$ and making reference to the *Data Booklet*, calculate the standard redox potential, $E^{\ominus}$, for the reduction of carbon dioxide to ethanedioic acid: $2H^{+} + 2CO_2 + 2e^{-} \rightleftharpoons H_2C_2O_4$

Note:
Ions such as K^{+}, Na^{+} and SO_4^{2-} are usually not involved in redox reactions. They are usually spectator ions.

Consider the mols of e^{-} transferred per mol of this reaction in order to determine the value of n.

In the formula, $\Delta G^{\ominus} = -nFE^{\ominus}_{cell}$ units of ΔG is $Jmol^{-1}$

9 Limitations of Using Standard Cell Potentials to Predict Spontaneity

9.1 Spontaneity (Thermodynamic Feasibility) vs Kinetic Feasibility

$E^{\ominus}$ values **cannot predict the rate of a redox reaction**. It only tells us whether a reaction is **spontaneous**. No information is given about the kinetic feasibility, which is related to activation energy.

For example, $E^{\ominus}$ values predict that $Cu^{2+}(aq)$ should oxidise $H_2(g)$ to $H^+(aq)$.

$Cu^{2+}(aq) + H_2(g) \longrightarrow Cu(s) + 2H^+(aq)$ $\quad E^{\ominus}_{cell} = +0.34\ V\ (> 0)$

However, in practice, no reaction occurs when hydrogen gas is bubbled into copper(II) sulfate solution because the reaction rate is effectively zero due to a high activation energy.

9.2 Non-Standard Conditions

$E^{\ominus}$ values relate only to **standard conditions**. Changes in concentration, temperature and pressure will affect the values of electrode potential, E. (Recall Le Chatelier's Principle, see section 6.3)

The Nernst Equation (For Your Information)

Electrode potentials under non-standard conditions may be determined using the Nernst equation.

For a reaction: $aA + bB \rightleftharpoons cC + dD$, let $Q = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$

Nernst equation is: $E = E^{\ominus} - \dfrac{RT}{zF} \ln Q$

where R is the gas constant, T is the temperature in K, z is the number of electrons transferred when the oxidised species changes into the reduced species and F is the Faraday's constant, 96 500 C mol^{-1}.

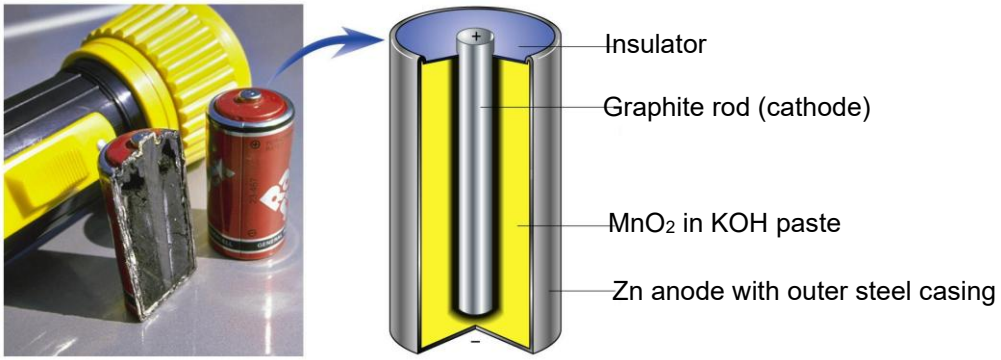
10 Applications of Electrochemical Cells

Batteries and fuel cells are two common examples of electrochemical cells that provide a portable and convenient way of obtaining energy from chemical reactions.

10.1 Conventional Batteries (FYI, no longer in syllabus)

Although the operation of a battery is similar in principle to that of the electrochemical cells described in Section 2, a battery has the advantage of being completely self-contained and required no auxiliary components such as salt bridges.

(i) Non-rechargeable alkaline battery used in toys and flashlights



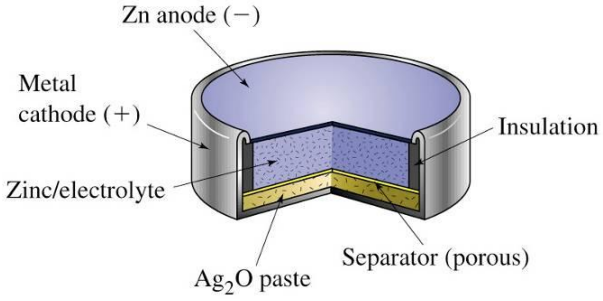
Anode (–) [O]: $Zn(s) + 2OH^-(aq) \longrightarrow ZnO(s) + H_2O(l) + 2e^-$

Cathode (+) [R]: $MnO_2(s) + 2H_2O(l) + 2e^- \longrightarrow Mn(OH)_2(s) + 2OH^-(aq)$

Overall cell reaction:

$Zn(s) + MnO_2(s) + H_2O(l) \longrightarrow ZnO(s) + Mn(OH)_2(s)$ $E_{cell} = +1.5$ V

(ii) Non-rechargeable silver button battery used in watches, cameras, heart pacemakers and hearing aids



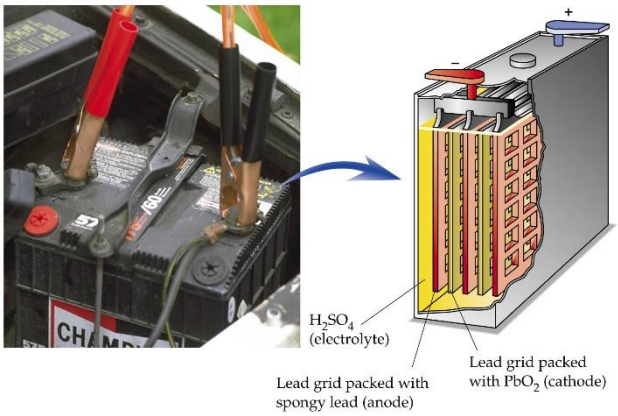
Anode (–) [O]: $Zn(s) + 2OH^-(aq) \longrightarrow ZnO(s) + H_2O(l) + 2e^-$

Cathode (+) [R]: $Ag_2O(s) + H_2O(l) + 2e^- \longrightarrow 2Ag(s) + 2OH^-(aq)$

Overall cell reaction:

$Zn(s) + Ag_2O(s) \longrightarrow ZnO(s) + 2Ag(s)$ $E_{cell} = +1.6$ V

(iii) Rechargeable lead-acid battery used to power the starter motor in a car



Anode (–) [O]: $Pb(s) + H_2SO_4(aq) \longrightarrow PbSO_4(s) + 2H^+(aq) + 2e^-$

Cathode (+) [R]: $PbO_2(s) + H_2SO_4(aq) + 2H^+(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)$

Overall cell reaction (*during discharge*):

$PbO_2(s) + Pb(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l)$ E_{cell} = +2.1 V

When the cell is ***recharged***, it uses electrical energy as an electrolytic ce (electrolysis) and the half-reactions and overall reaction are reversed.

Overall cell reaction (*during recharge*):

$2PbSO_4(s) + 2H_2O(l) \longrightarrow PbO_2(s) + Pb(s) + 2H_2SO_4(aq)$

10.2 Fuel Cells (In syllabus)

Success Criteria

- When given a diagram of fuel cell, I can recognise the half equations that lead to the overall chemical reaction in the cells

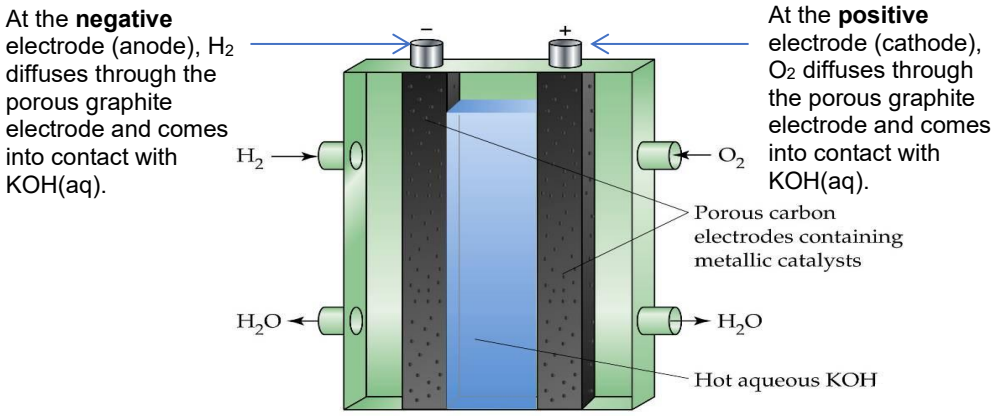
When a fuel is burnt in a power station, the heat is usually used to produce steam to drive a piston or to turn the blades of a turbine. The overall efficiency is always low no matter how well the plant is designed.

To achieve higher efficiencies, efforts have been made to convert the chemical energy of a fuel ***directly*** into electrical energy by means of a **fuel cell**. The fuel (hydrogen, hydrocarbons and alcohols) and an oxidant (usually oxygen) enter the fuel cell, and the products leave, generating electricity through the controlled oxidation of the fuel. The fuel *does not burn* because, as in other batteries, the half-reactions are separated, and the electrons are transferred through an external circuit.

The **main differences** between fuel cells and ordinary batteries are the **constant supply of reactants and removal of products in fuel cells**, and fuel cells work indefinitely as long as there is a supply of reactants.

10.2.1 Hydrogen Fuel Cells (Case study)

The most common fuel cell is the **hydrogen-oxygen fuel cell**.



Half-equations to consider for **alkaline** medium:

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

$\underline{\mathbf{O_2}} + H_2O + 2e^- \rightleftharpoons HO_2^- + OH^-$ $E^\ominus = -0.08$ V

$2H_2O + 2e^- \rightleftharpoons \underline{\mathbf{H_2}} + 2OH^-$ $E^\ominus = -0.83$ V

Anode (–) : [O] $H_2(g) + 2OH^-(aq) \longrightarrow 2H_2O(l) + 2e^-$

Cathode (+) : [R] $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$

Overall cell reaction:

$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

$E^\ominus_{cell} = E^\ominus_{[R]} - E^\ominus_{[O]}$

$= +0.40 - (-0.83) =$ **+1.23 V**

Hydrogen-oxygen fuel cells have been used for years to provide electricity and pure water during space flights. In the future, similar ones may be used to supply electric power for transportation, residential and commercial needs.

Advantages of hydrogen-oxygen fuel cells

- The product is H_2O (non-polluting) as compared to production of CO_2 in typical hydrocarbon combustion
- High efficiency and good energy-to-mass ratio
  They convert about 75% of the chemical energy of the fuel into useable power as compared to 40% for a coal-fired power plant and 20-25% for a gasoline-powered car engine.

Disadvantages of hydrogen-oxygen fuel cells

- Expensive due to the use of Pt catalyst at the graphite electrodes.
- Hydrogen is potentially explosive

Despite steady progress, the focus of current fuel cell research remains on lowering costs by improving membrane conductivity and developing more efficient catalysts.

Checkpoint 7

Write the equations for the half-reactions that occur if an acid is used as the electrolyte in the hydrogen-oxygen fuel cell. Hence, calculate the standard cell e.m.f. for the reaction.

Half-equations to consider for **acidic** medium:

$\underline{\mathbf{O_2}} + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ $E^\ominus = +1.23$ V

$\underline{\mathbf{O_2}} + 2H^+ + 2e^- \rightleftharpoons H_2O_2$ $E^\ominus = +0.68$ V

$2H^+ + 2e^- \rightleftharpoons \underline{\mathbf{H_2}}$ $E^\ominus = 0.00$ V

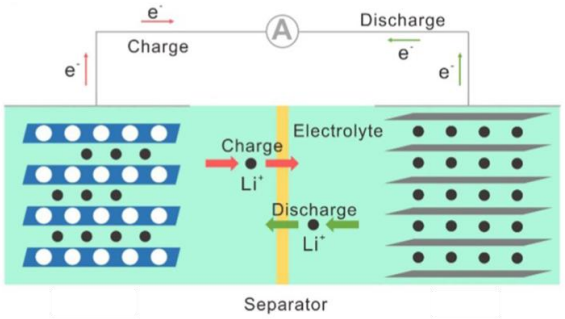
Overall cell reaction:

10.3 Development of Other Types of Cells

The development of improved cells aims to have smaller size, lower mass, higher voltage, longer life, greater reliability, quicker recharging e.g. for electric vehicles, mobile phones, portable PCs, watches etc.

10.3.1 Lithium-ion Batteries

The lithium–ion battery has a mass about half that of a Ni–Cd battery providing similar energy. Extremely high energy/mass ratio, and avoids the toxicity of cadmium in Ni-Cd battery.



10.3.2 Solid-state Batteries

Solid-state batteries promise higher energy density, faster charging times, and improved safety due to their lack of liquid electrolytes that can pose a fire risk.

10.3.3 Graphene-based Batteries

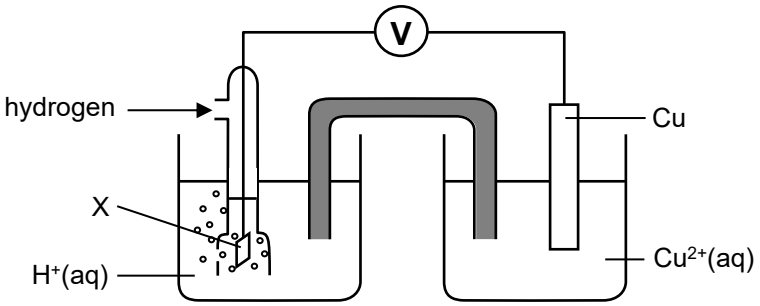
Though still in the early developmental stage, graphene-based batteries offer significant improvements in conductivity and charge rates, we could see batteries that charge in minutes rather than hours.

ELECTROCHEMICAL CELL TUTORIAL

Standard Electrode Potential

1 N13/1/33

The diagram shows apparatus that can be used to measure the standard electrode potential of copper, $E^{\ominus}$.



What factors are essential for an accurate $E^{\ominus}$ to be measured?

1 The hydrogen must be dry.

2 The $Cu^{2+}(aq)$ should be at a concentration of 1.0 mol dm^{-3}.

3 The electrode X should be made of platinum.

A **1, 2** and **3** are correct

B **1** and **2** are correct

C **2** and **3** are correct

D **1 only** is correct

Application of Standard Electrode Potential

2 Two electrode potentials are given:

$V^{2+} + 2e^- \rightleftharpoons V$	$E^{\ominus} = -1.20$ V
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	$E^{\ominus} = -0.76$ V

Which species is the strongest reducing agent?

A Zn^{2+} **B** V^{2+} **C** V **D** Zn

Standard Cell Potential of an Electrochemical Cell

3 [modified N92/1/]

(a) Define "*standard electrode potential"* and "*standard cell potential".*

(b) Chlorine dioxide acts as a powerful oxidising agent in acidic solution:

$$ClO_2(aq) + 4H^+(aq) + 5e^- \rightleftharpoons Cl^-(aq) + 2H_2O(l) \qquad E^\ominus = +1.50\ V$$

Draw labelled diagrams to show how you could measure the standard electrode potential of each of the following electrode systems:

(i) $Co^{2+}(aq)/Co(s)$

(ii) $ClO_2(aq), H^+(aq)/ Cl^-(aq)$

(c) A cell is constructed by connecting the $Co^{2+}(aq)/Co(s)$ half-cell to the ClO_2 (aq)/ $Cl^-(aq)$ half-cell.

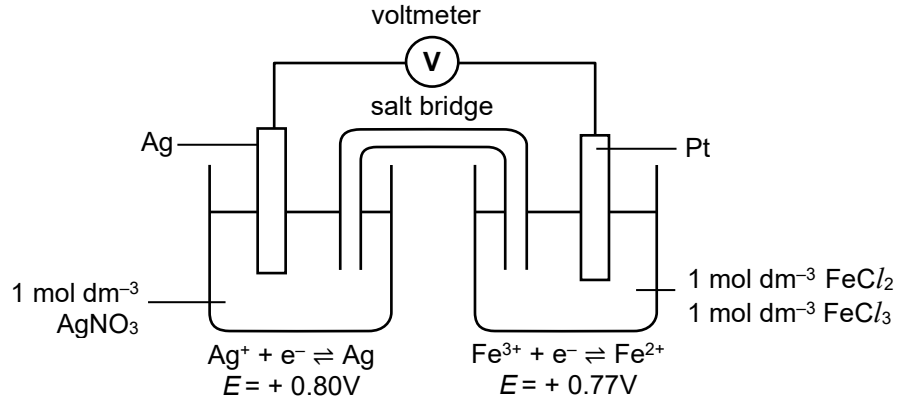
(i) Write an equation for the reaction occurring in each half-cell, and hence write a balanced equation for the overall reaction which takes place.

(ii) Use the *Data Booklet* to calculate the value of $E^\ominus_{cell}$ and hence $\Delta G^\ominus$ for the reaction.

(iii) State the direction of electron flow and the polarity of each electrode.

4 [N16/1/11]

The following electrochemical cell was set up.



Which change to the half-cells could result in a cell potential of 0.00 V?

A increase $[AgNO_3]$ **B** increase $[FeCl_2]$

C increase $[FeCl_3]$ **D** increase the surface area of Ag electrode

Predicting the Feasibility of a Redox Reaction

5 *The use of the Data Booklet is relevant to this question.*

Many laboratory spatulas are made of nickel.

Which aqueous solution might react with a nickel spatula?

A $Cu^{2+}(aq)$ **B** $Co^{2+}(aq)$ **C** $Mn^{2+}(aq)$ **D** $Fe^{2+}(aq)$

6 The standard cell potentials for the redox equilibria of aqueous vanadium–containing ions and the colours of these ions are given below.

$VO_2^+ + 2H^+ + e^- \rightleftharpoons H_2O + VO^{2+}$ $E^\ominus = +1.00$ V
yellow blue

$VO^{2+} + 2H^+ + e^- \rightleftharpoons H_2O + V^{3+}$ $E^\ominus = +0.34$ V
blue green

$V^{3+} + e^- \rightleftharpoons V^{2+}$ $E^\ominus = -0.26$ V
green purple

What is likely to be the final colour when excess metallic tin is added to a solution containing VO^{2+}?

A yellow **B** blue **C** green **D** purple

Answer key for MCQ:
1) C 2) C 4) C 5) A 6) C

7 **(a)** Construct a balanced equation for the reaction between manganate(VII) and iron(II) ions in acidic medium.

(b) Explain why the titration with manganate(VII) must take place in the presence of sulfuric acid, not hydrochloric acid.

(c) The standard redox potential of chlorate(V) ions is given below.

$$ClO_3^- + 6H^+ + 6e^- \rightleftharpoons Cl^- + 3H_2O \qquad E^\ominus = +1.45 \text{ V}$$

Predict what you would expect to observe when acidified potassium chlorate(V) is added separately to each of the following reagents given that ClO_3^- is colourless.

Write a balanced equation for any reaction that occurs.

(i) aqueous iron(II) sulfate

(ii) acidified potassium manganate(VII)

(d) When a few drops of acidified hydrogen peroxide are added to an excess of aqueous potassium iodide, the solution turns brown without effervescence. Account for this observation with suitable calculations.

8 **(a)** Use $E^{\ominus}$ values from the *Data Booklet* to show that the reaction between aqueous copper(II) sulfate and potassium iodide is unlikely to occur.

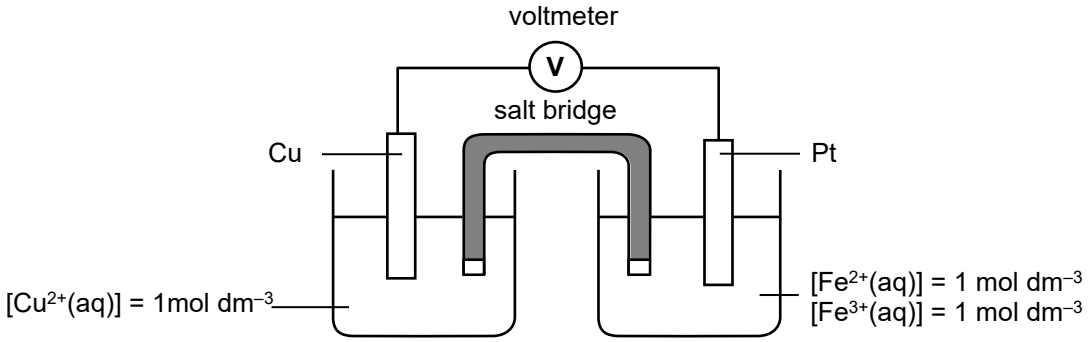
(b) When dilute copper(II) sulfate is added to acidified aqueous potassium iodide, reaction occurred and a cream precipitate of the following mass composition is formed: Cu: 33.3%; I: 66.7%

Determine the formula of the cream precipitate and explain the apparent contradiction.

[*N06/2/2(e) (modified)*]

Application Questions

9 A cell consisting of a $Cu^{2+}(aq)|Cu(s)$ half-cell and a $Fe^{3+}(aq), Fe^{2+}(aq)|Pt(s)$ half-cell is shown below



(a) Calculate the standard potential, $E^{\ominus}$, of this cell. Write the equation for the reaction taking place and calculate the $\Delta G^{\ominus}$ for the reaction.

(b) Discuss the effect of the following changes on the electrode potential of the $Cu^{2+}(aq)|Cu(s)$ system and hence the cell potential of the above cell:

(i) adding water to the Cu^{2+}/Cu half-cell.

(ii) using a larger copper electrode.

(iii) adding sodium hydroxide into the Cu^{2+}/Cu half-cell.

(c) Suggest a replacement half-cell for the $Cu^{2+}(aq)|Cu(s)$ system which would reverse the direction of electron flow in the $Fe^{3+}(aq), Fe^{2+}(aq)|Pt(s)$ half-cell.

State the electrode and the reagents in the new half-cell.

10 A simple rechargeable cell may be constructed by dipping two lead electrodes into aqueous acidified lead(II) nitrate and passing a current for a few minutes. During the process, lead(IV) oxide is deposited on one of the electrodes.

When the power source is disconnected and a bulb is connected across the two electrodes, the bulb lights for some time as the cell discharges.

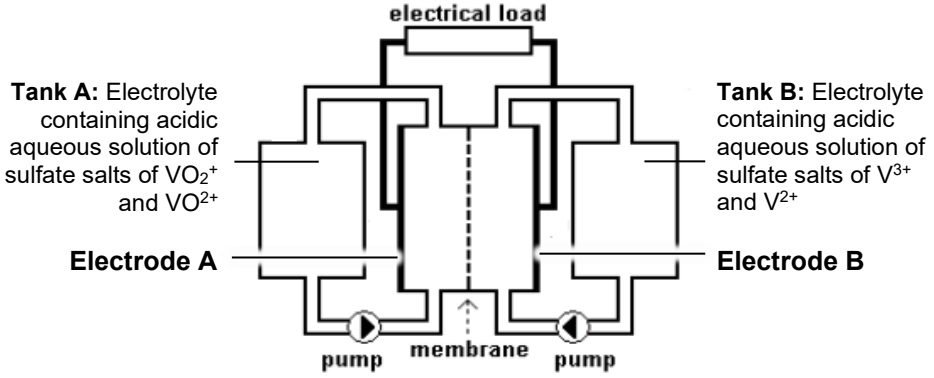
(a) With reference to the *Data Booklet*, choose two half-equations to construct the full equation for the reaction that occurs during discharge. Calculate the value of $E^{\ominus}_{cell}$ for this cell reaction.

(Hint: Consider what are the half-cells present in the set up.)

(b) In a lead-acid car battery, similar reactions take place but the electrolyte of dilute sulfuric acid causes the lead(II) ions to be precipitated as $PbSO_4(s)$, which coats the electrode. The e.m.f. of this cell is 2.0 V.

*E*xplain the difference between this e.m.f. and the $E^{\ominus}_{cell}$ calculated in **(a)**.

11 A new type of rechargeable battery which uses vanadium salts is hailed as a possible battery for electric car. The battery is a flow battery in which the electrolytes are stored in tanks and pumped through the cell during discharge. A diagram of the battery is shown below:



The two electrolytes are separated in the cells by an extremely thin membrane that only allows selected ions to flow through. Also in the cells are very stable porous carbon electrodes, where reduction and oxidation reactions take place.

(a) Write equations for the reactions taking place at electrodes **A** and **B** and calculate the standard cell potential.

(b) State if electrode **A** is the positive or negative electrode. Give a reason for your answer.

(c) Suggest why must the carbon electrodes used be porous.

(d) The membrane serves to keep the two electrolytes separated. Explain why it needs to allow selected ions to flow through.

(e) Name an advantage that a flow battery has over a conventional battery in which the reactive materials are stored within the cell.

12 In an experiment to study the reaction between nickel and the metal ion, $M^{2+}(aq)$, an electrochemical cell was set up using the Ni^{2+}/Ni and M^{2+}/M half-cells at 298 K.

During the experiment, the concentration of Ni^{2+} ions in the Ni^{2+}/Ni half-cell was kept at 1.0 mol dm^{-3} but the concentration of M^{2+} ions in the M^{2+}/M half-cell was changed. The e.m.f. of the cell was measured with each change of solution in the M^{2+}/M half-cell, and the results obtained are tabulated below.

$[M^{2+}]$ / mol dm^{-3}	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}
e.m.f. / V	0.091	0.061	0.032	0.002	–0.028	–0.057
lg $[M^{2+}]$	–1.0	–2.0	–3.0	–4.0	–5.0	–6.0

(a) Plot a graph of e.m.f. against lg $[M^{2+}]$.

(b) Using the graph plotted, suggest whether M^{2+}/M half-cell undergoes oxidation or reduction.

(c) With the aid of the graph plotted and relevant data from the *Data Booklet*, determine the standard electrode potential of the M^{2+}/M half-cell.

(d) The above electrochemical cell is 'dead' when the overall cell reaction reaches equilibrium. With the aid of the graph plotted, calculate the equilibrium constant, K_c, for the cell reaction shown below at 298 K.

$$Ni(s) + M^{2+}(aq) \rightleftharpoons Ni^{2+}(aq) + M(s)$$

(e) Using your answer from **(c)** and relevant data from the *Data Booklet*, predict what might be observed when a rod of metal M is dipped into an aqueous copper(II) nitrate solution.

4 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, i.e. a redox series.

4(a) $E^{\ominus}$ in alphabetical order

Electrode reaction	$E^{\ominus}$ / V
$Ag^+ + e^- \rightleftharpoons Ag$	+0.80
$Al^{3+} + 3e^- \rightleftharpoons Al$	–1.66
$Ba^{2+} + 2e^- \rightleftharpoons Ba$	–2.90
$Br_2 + 2e^- \rightleftharpoons 2Br^-$	+1.07
$Ca^{2+} + 2e^- \rightleftharpoons Ca$	–2.87
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36
$2HOCl + 2H^+ + 2e^- \rightleftharpoons Cl_2 + 2H_2O$	+1.64
$ClO^- + H_2O + 2e^- \rightleftharpoons Cl^- + 2OH^-$	+0.81
$Co^{2+} + 2e^- \rightleftharpoons Co$	–0.28
$Co^{3+} + e^- \rightleftharpoons Co^{2+}$	+1.89
$[Co(NH_3)_6]^{2+} + 2e^- \rightleftharpoons Co + 6NH_3$	–0.43
$Cr^{2+} + 2e^- \rightleftharpoons Cr$	–0.91
$Cr^{3+} + 3e^- \rightleftharpoons Cr$	–0.74
$Cr^{3+} + e^- \rightleftharpoons Cr^{2+}$	–0.41
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	+1.33
$Cu^+ + e^- \rightleftharpoons Cu$	+0.52
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34
$Cu^{2+} + e^- \rightleftharpoons Cu^+$	+0.15
$[Cu(NH_3)_4]^{2+} + 2e^- \rightleftharpoons Cu + 4NH_3$	–0.05
$F_2 + 2e^- \rightleftharpoons 2F^-$	+2.87
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	–0.44
$Fe^{3+} + 3e^- \rightleftharpoons Fe$	–0.04

Electrode reaction	$E^{\ominus}$ / V
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.77
$[Fe(CN)_6]^{3-} + e^- \rightleftharpoons [Fe(CN)_6]^{4-}$	+0.36
$Fe(OH)_3 + e^- \rightleftharpoons Fe(OH)_2 + OH^-$	–0.56
$2H^+ + 2e^- \rightleftharpoons H_2$	0.00
$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.54
$K^+ + e^- \rightleftharpoons K$	–2.92
$Li^+ + e^- \rightleftharpoons Li$	–3.04
$Mg^{2+} + 2e^- \rightleftharpoons Mg$	–2.38
$Mn^{2+} + 2e^- \rightleftharpoons Mn$	–1.18
$Mn^{3+} + e^- \rightleftharpoons Mn^{2+}$	+1.54
$MnO_2 + 4H^+ + 2e^- \rightleftharpoons Mn^{2+} + 2H_2O$	+1.23
$MnO_4^- + e^- \rightleftharpoons MnO_4^{2-}$	+0.56
$MnO_4^- + 4H^+ + 3e^- \rightleftharpoons MnO_2 + 2H_2O$	+1.67
$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	+1.52
$NO_3^- + 2H^+ + e^- \rightleftharpoons NO_2 + H_2O$	+0.81
$NO_3^- + 3H^+ + 2e^- \rightleftharpoons HNO_2 + H_2O$	+0.94
$NO_3^- + 10H^+ + 8e^- \rightleftharpoons NH_4^+ + 3H_2O$	+0.87
$Na^+ + e^- \rightleftharpoons Na$	–2.71
$Ni^{2+} + 2e^- \rightleftharpoons Ni$	–0.25
$[Ni(NH_3)_6]^{2+} + 2e^- \rightleftharpoons Ni + 6NH_3$	–0.51
$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	+1.77
$HO_2^- + H_2O + 2e^- \rightleftharpoons 3OH^-$	+0.88
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23
$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$	+0.40
$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2$	+0.68

Electrode reaction	$E^{\ominus}$ / V
$O_2 + H_2O + 2e^- \rightleftharpoons HO_2^- + OH^-$	–0.08
$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$	–0.83
$Pb^{2+} + 2e^- \rightleftharpoons Pb$	–0.13
$Pb^{4+} + 2e^- \rightleftharpoons Pb^{2+}$	+1.69
$PbO_2 + 4H^+ + 2e^- \rightleftharpoons Pb^{2+} + 2H_2O$	+1.47
$SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons SO_2 + 2H_2O$	+0.17
$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$	+2.01
$S_4O_6^{2-} + 2e^- \rightleftharpoons 2S_2O_3^{2-}$	+0.09
$Sn^{2+} + 2e^- \rightleftharpoons Sn$	–0.14
$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$	+0.15
$V^{2+} + 2e^- \rightleftharpoons V$	–1.20
$V^{3+} + e^- \rightleftharpoons V^{2+}$	–0.26
$VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O$	+0.34
$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$	+1.00
$VO_3^- + 4H^+ + e^- \rightleftharpoons VO^{2+} + 2H_2O$	+1.00
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	–0.76

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