2023 JC2 H2 CHEMISTRY (9729)
EXTENSION TOPIC : ELECTROCHEMISTRY
(PART 1) – GALVANIC CELL
LECTURE NOTES

Learning Outcomes

Students should be able to:

(a) describe and explain redox processes in terms of electron transfer and/or of changes in oxidation number (oxidation state) Covered in JC1 Topic: Atoms, Moles and Stoichiometry

(b) define the terms:
- (i) standard electrode (reduction) potential
- (ii) standard cell potential

(c) describe the standard hydrogen electrode

(d) describe methods used to measure the standard electrode potentials of:
- (i) metals or non-metals in contact with their ions in aqueous solution
- (ii) ions of the same element in different oxidation states

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

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

(g) understand the limitations in the use of standard cell potentials to predict the 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 ions

(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

Content

1. Redox processes: electron transfer and changes in oxidation number (oxidation state)
2. Electrode potentials
   - (i) Standard electrode (redox) potentials, $E^{\ominus}$; the redox series
   - (ii) Standard cell potentials, $E^{\ominus}_{\text{cell}}$, and their uses
   - (iii) Batteries and fuel cells

References

1. Chemistry in Context by GC Hill & JS Holman
2. Chemistry the Central Science by TL Brown and HE Lemay

Lecture Contents

1 INTRODUCTION

Electrochemistry is the study of the **interconversion of electrical and chemical energy** via the movement of electrons from one chemical species to another, *i.e.* **redox reactions**.

There are two aspects of electrochemistry covered in this topic:

1. Galvanic cell
   - Conversion of **chemical** energy to **electrical** energy
   - Redox reaction is **spontaneous**.

2. Electrolytic cell (in electrolysis)
   - Conversion of **electrical** energy to **chemical** energy
   - Redox reaction is **non-spontaneous**.

2 THE GALVANIC CELL

2.1 Preliminary Investigation

When a clean strip of zinc is placed in copper(II) nitrate solution, the following are observed:

- Copper is deposited on the surface of the zinc strip.
- The blue colour of the $Cu(NO_3)_2$ solution fades with time.
- With time, the zinc strip erodes.

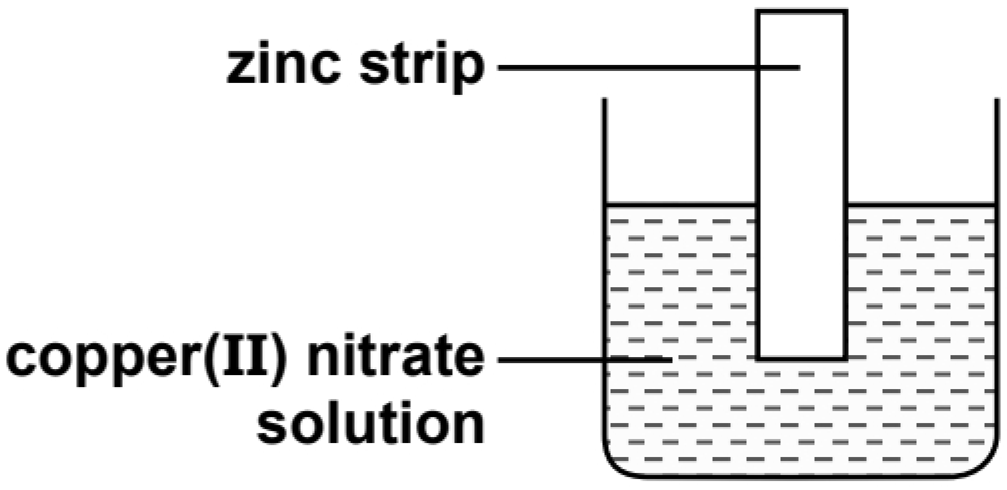


Figure 1 Spontaneous reaction between zinc and copper(II) ions

What was happening?

- The above set-up allows the following spontaneous redox reaction to occur:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

- As the two reactants, Zn(s) and $Cu^{2+}(aq)$, are in direct physical contact, the electrons are transferred directly from Zn(s) to $Cu^{2+}(aq)$.

- The chemical energy released in the spontaneous redox reaction can be converted into electrical energy. However, in this set-up, the reaction cannot be used to provide an electric current as electrons are transferred directly between the reactants, *i.e.* it cannot be used as a galvanic cell.

2.2 The Set-up of the Galvanic Cell

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

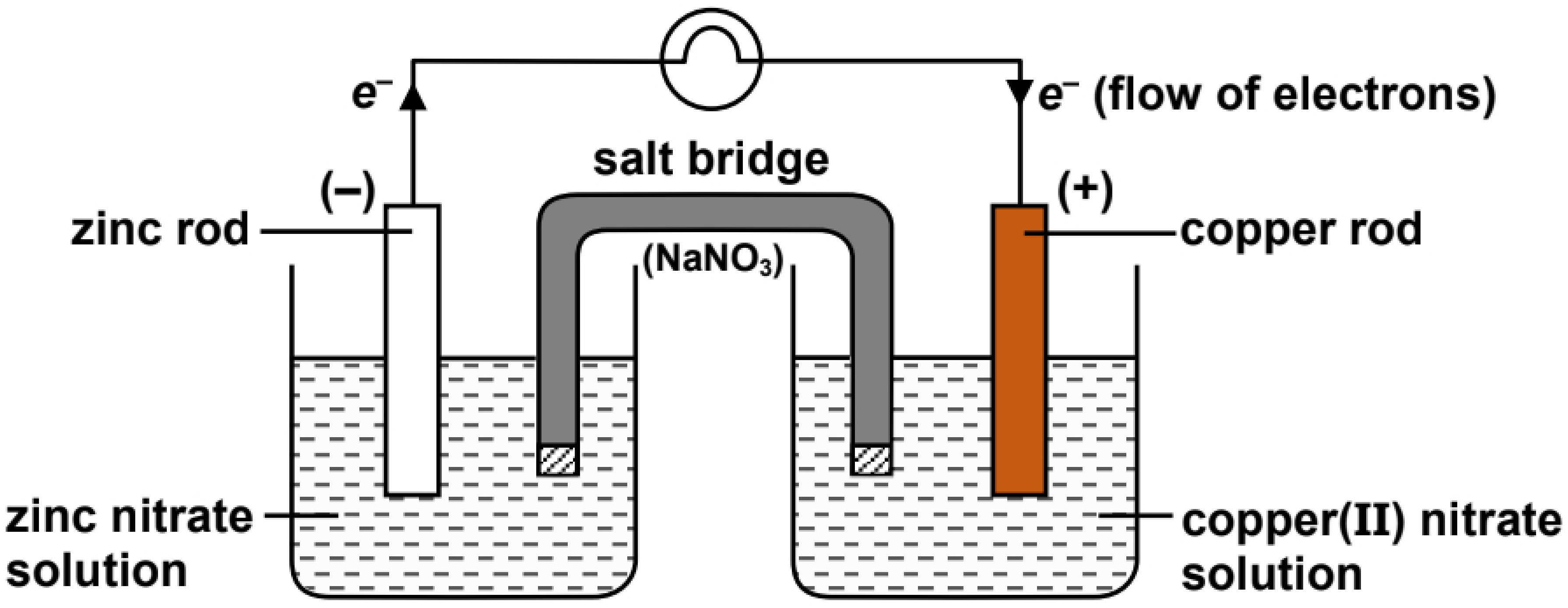


Figure 2
Set-up of Galvanic Cell made up of $Zn^{2+}(aq)|Zn(s)$ half-cell and $Cu^{2+}(aq)|Cu(s)$ half-cell

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

- The two reactants, $Zn(s)$ and $Cu^{2+}(aq)$, are not in direct physical contact this time.
- Each beaker forms a metal-metal ion half-cell.
- The zinc and copper strips act as electrodes. The electrodes are being connected by an electrical wire (via an external circuit).
- The salt bridge consists of an inverted U-tube containing a salt solution, e.g. $NaNO_3$, K_2SO_4. The salt chosen must not react with the ions in either half-cell. The ends of the salt bridge are stuffed with porous plugs to prevent direct mixing of the two solutions but allow the passage of ions through them.
  (The salt bridge can also be a piece of filter paper soaked in $NaNO_3(aq)$ or $K_2SO_4(aq)$.)

Observations:

- ➢ The light bulb glows.
- ➢ The blue colour of $Cu(NO_3)_2$ solution fades.
- ➢ The mass of the Cu electrode increases, while the mass of the Zn electrode decreases.

What was happening?

At the zinc electrode:

- Zinc atoms become zinc(II) ions and enter into solution.

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

- The zinc is the **anode** since ***oxidation*** occurs at this electrode.
  Electrons are produced at the anode during oxidation, resulting in a 'build-up' of electrons at the anode
  ➔ **anode of galvanic cell** is the **negative electrode**.

In the external circuit:

- The electrons leave the zinc electrode (*i.e.* anode) and make their way round to the $Cu^{2+}(aq)|Cu(s)$ half-cell via the wire and the current generate causes the bulb to light up.

At the copper electrode:

- The electrons from the zinc electrode use the copper electrode as a solid conductor to bring them in contact with the $Cu^{2+}(aq)$ ions. The $Cu^{2+}(aq)$ ions accept the electrons to become copper atoms, which are deposited on the surface of the electrode.

$$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$$

- The copper is the **cathode** as ***reduction*** occurs at this electrode.
  The cathode receives the electrons for the reduction reaction ➔ **cathode of galvanic cell** is the **positive electrode**.

In the salt bridge:

- The release of $Zn^{2+}(aq)$ cations into the $Zn(NO_3)_2$ solution causes a surplus of $Zn^{2+}(aq)$ cations, upsetting the electrical neutrality of the solution. Hence anions ($NO_3^{-}(aq)$) from the salt bridge would move into the $Zn(NO_3)_2$ solution (and some $Zn^{2+}(aq)$ ions move from the solution into the salt bridge) to balance the surplus of $Zn^{2+}(aq)$ cations.
- The removal of $Cu^{2+}(aq)$ ions from the $Cu(NO_3)_2$ solution creates a surplus of $NO_3^{-}(aq)$ anions. Hence cations ($Na^{+}(aq)$) from the salt bridge would move into the $Cu(NO_3)_2$ solution (and some $NO_3^{-}(aq)$ anions move from the solution into the salt bridge) to balance the surplus of $NO_3^{-}(aq)$ anions.
- Thus, the salt bridge has two functions:
  - Prevents direct mixing of $Zn(NO_3)_2$ and $Cu(NO_3)_2$ solutions but allows the passage of ions between the two half-cells to complete the electrical circuit.
  - Helps to maintain the electrical neutrality in each half-cell.

Thus, the overall reaction occurring in the cell is:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

2.3 Electromotive Force (e.m.f.) of a Galvanic Cell

When the light bulb in *Figure 2* is replaced with a high resistance voltmeter, a value of 1.10 V is recorded by the voltmeter under standard conditions. What does this value represent?

- The voltmeter measures the difference in electric potential between the 2 electrodes connected.
- The potential difference between two electrodes in a galvanic cell provides the "driving force" that pushes electrons through an external circuit. This potential difference is known as **electromotive force (e.m.f.)** or **cell potential**.
- The value of 1.10 V is the standard cell potential of the galvanic cell made up of the $Zn^{2+}(aq)|Zn(s)$ and $Cu^{2+}(aq)|Cu(s)$ half-cells under standard conditions.

The standard cell potential of a galvanic cell depends on the particular anode and cathode half-cells involved. If we can assign a standard potential to individual half-cells, we can then use these half-cell potentials to determine the standard cell potential for any anode/cathode combinations.

3 ELECTRODE POTENTIAL

3.1 Definition

- When a strip of metal (the electrode) is placed in a solution of its ions, some metal atoms will lose electrons and go into the solution as hydrated metal ions. The electrons will be left behind on the metal.

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

- Over time, there will be a build-up of negative charge on the metal surface. This will attract positive metal ions from the solution which may recombine with electrons to re-form metal atoms.

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

- A dynamic equilibrium is eventually established when the rates of the above two processes are equal (*Figure 3*):

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

At equilibrium (at a constant temperature), there will be a constant negative charge on the metal and a constant number of positive metal ions present in the solution around the metal. As a result of the separation of charge between the metal strip and the ions in solution, there is a potential difference between the metal and the solution. This potential difference is known as the *absolute electrode potential* and is written as $\boldsymbol{E}\left(\mathbf{M}^{n+}(\mathbf{aq})|\mathbf{M}(\mathbf{s})\right)$.

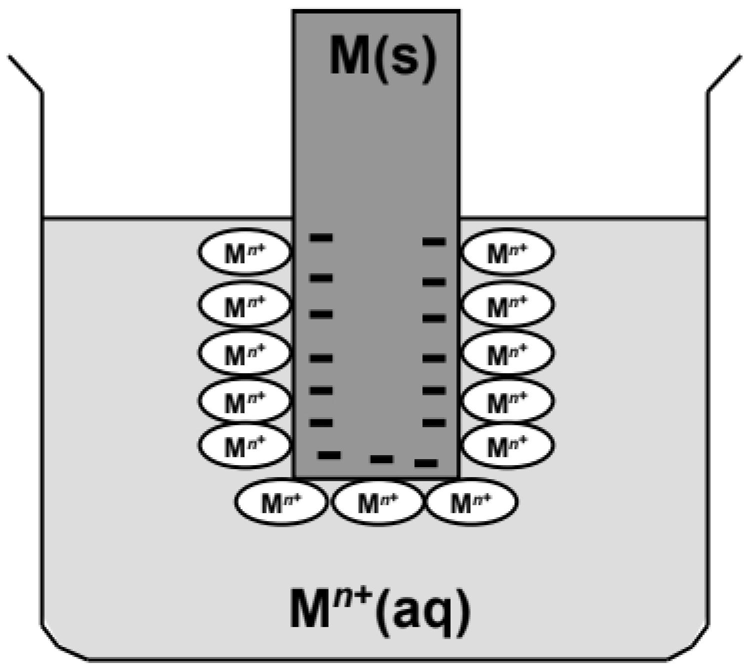


Figure 3
Dynamic equilibrium established by the metal in contact with its aqueous ions: ions are continually leaving and rejoining the metal surface

- By convention, the half-equation is written with ***reduction*** as the forward reaction:

$$M^{n+}(aq) + ne^- \rightleftharpoons M(s) \qquad E\left(M^{n+}(aq)|M(s)\right) \text{ [units: V]}$$

- The value of the electrode potential depends on the position of the above equilibrium.

Positive $\boldsymbol{E}\left(\mathbf{M}^{n+}(\mathbf{aq})|\mathbf{M}(\mathbf{s})\right)$ ⇒ equilibrium position lies more to the *right*
➔ **reduction** process favoured
Negative $\boldsymbol{E}\left(\mathbf{M}^{n+}(\mathbf{aq})|\mathbf{M}(\mathbf{s})\right)$ ⇒ equilibrium position lies more to the *left*
➔ **oxidation** process favoured

Factors which affect the position of the equilibrium would therefore affect the value of the electrode potential.

3.2 Factors Affecting Electrode Potential

1. *Nature of metal*

$$M^{n+}(aq) + ne^- \rightleftharpoons M(s) \qquad E\left(M^{n+}(aq)\middle|M(s)\right)$$

When a metal is highly electropositive, the metal atoms have a greater tendency to lose electrons and become positive ions. The position of equilibrium lies more to the left (*i.e.* oxidation reaction favoured) and the electrode potential therefore becomes more negative.

Example:

Half-reaction	**$E^\ominus$ / V**	
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34	$\downarrow$ Increasing tendency for metal to lose electrons and oxidation to occur
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	–0.76	
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	–2.71	

2. *Concentration of M^{n+} ions*

If the concentration of the hydrated metal ions is decreased in the equilibrium, the position of the equilibrium will shift to the left (*i.e.* oxidation reaction favoured) to replenish some of the metal ions removed. Thus the electrode potential becomes more negative.

Example: $Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$

At 298 K and 1 mol dm^{-3} $Pb^{2+}(aq)$, $E^\ominus\left(Pb^{2+}(aq)\middle|Pb(s)\right) = -0.13$ V

At 298 K and 0.001 mol dm^{-3} $Pb^{2+}(aq)$, $E\left(Pb^{2+}(aq)\middle|Pb(s)\right) = -0.22$ V

3. *Temperature*

If the temperature increases, there is an increasing tendency for the metal to dissolve in the solution and form hydrated metal ions. The position of equilibrium shifts to the left (*i.e.* oxidation reaction favoured) and the electrode potential becomes more negative.

4. *Pressure of gaseous species*

Example: $\mathrm{C}l_2(g) + 2e^- \rightleftharpoons 2\mathrm{C}l^-(aq)$ $\qquad E^\ominus\left(\mathrm{C}l_2(g)\middle|\mathrm{C}l^-(aq)\right) = +1.36$ V

What happens to the electrode potential when the pressure of chlorine gas is increased?

When the pressure of $\mathrm{C}l_2(g)$ is increased, the position of equilibrium shifts to the right (i.e. reduction reaction favoured) to reduce the number of gaseous molecules and hence the electrode potential becomes more positive.

4 STANDARD ELECTRODE POTENTIAL

4.1 Definition

- As electrode potentials depend on temperature, pressure and concentration, it is necessary to standardise these conditions if they are to be compared.
  Standard conditions are:
  ♦ 1 bar ♦ concentration of aqueous ions of 1 mol dm^{-3}
  The temperature in which the standard electrode potential is measured **should be stated**. Most measurements are made at 298 K (25 ºC).

- A metal placed in a solution of its ions is an example of a **half-cell**. It is not possible to measure the electrode potential for a single half-cell. Only the difference in the potentials of two electrodes in a complete circuit is measurable.

- To enable comparison of electrode potentials, it is useful to measure the electrode potential of all half-cells against a particular standard half-cell (known as a *reference electrode*), which is the **standard hydrogen electrode** (S.H.E.).

- *Definition of standard electrode potential:*

> **Standard electrode potential**, $E^\ominus$, of an electrode (also known as *standard reduction potential*) is the relative potential of this electrode under standard conditions compared with the standard hydrogen electrode whose electrode potential is assigned as 0 V (normally at 298 K).
>
> The standard hydrogen electrode consists of $H_2(g)$ at **1 bar** bubbling over **platinum electrode coated with finely divided platinum** which is dipped into **1 mol dm^{-3} $H^+(aq)$**.

4.2 Standard Hydrogen Electrode (S.H.E)

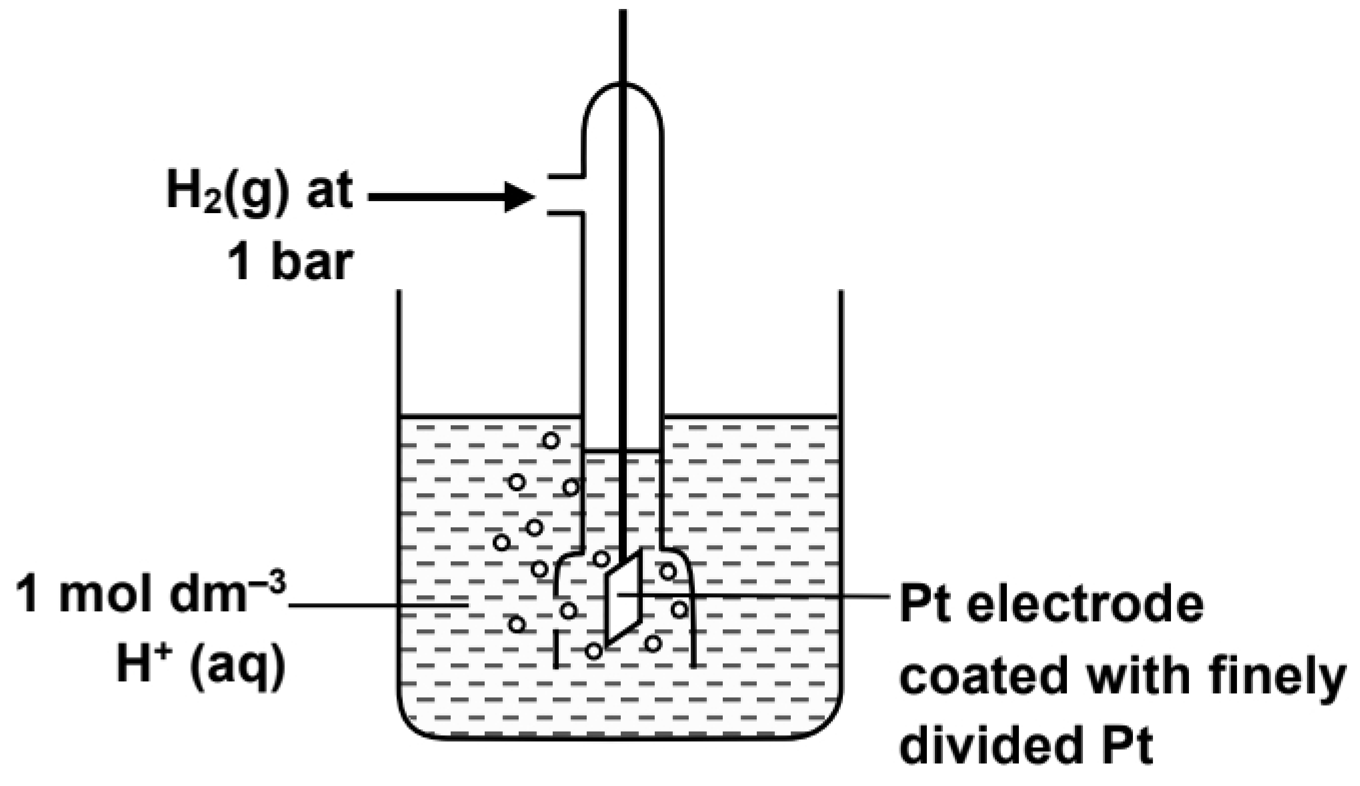


Figure 4 Standard Hydrogen Electrode

The S.H.E. consists of:

♦ $H_2(g)$ at 1 bar pressure bubbling around a Pt electrode coated with finely divided Pt (*so that equilibrium between $H_2(g)$ and $H^+(aq)$ can be established rapidly).*

♦ The electrode is immersed in a 1 mol dm^{-3} $H^+(aq)$.

Note: Pt is chosen for its inert property.

- By convention, the standard electrode potential for this reference hydrogen half-cell is taken to be 0 V.

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g) \qquad E^\ominus\left(H^+(aq)\middle|H_2(g)\right) = 0\ V$$

Note that if standard conditions are not achieved, $E\left(H^+(aq)\middle|H_2(g)\right)$ is not zero.

Other Reference Electrodes (Enrichment)

Although the S.H.E. is a useful reference electrode because $E^{\ominus}\left(H^{+}(aq)|H_2(g)\right) = 0\ V$, the cell itself is not very convenient to use. A cylinder of H_2 is needed and the pressure must be maintained at exactly 1 bar. A range of other reference electrodes is available, e.g. the $AgCl|Ag$ electrode (commonly used in pH meters) and the $Hg_2Cl_2|Hg$ electrode (commonly known as the calomel electrode).

4.3 Measuring Standard Electrode Potentials

- The following conditions must be used for measurement of standard electrode potentials:
  - All solutions have a concentration of **1 mol dm^{-3}** of the ions concerned.
  - Any gas involved has a pressure of **1 bar**.
  - **Platinum** is used as the electrode when the half-cell system does not include a metal.
  - The voltmeter must have high resistance so that negligible current flows and the maximum potential difference can be measured.

- Measurements are usually made at **298 K** (25 ºC). Temperature should be stated.

- The three most common types of half-cells involve:
  1. a metal in contact with its ions in aqueous solution (*e.g.* $Zn^{2+}(aq)|Zn(s)$ half-cell)
  2. a non-metal in contact with its ions in aqueous solution (*e.g.* $H^{+}(aq)|H_2(g)$ half-cell)
  3. ions of the same element in different oxidation states (*e.g.* $Fe^{3+}(aq)|Fe^{2+}(aq)$ half-cell)

(A) To determine $E^{\ominus}$ of a metal in contact with its ions in aqueous solution

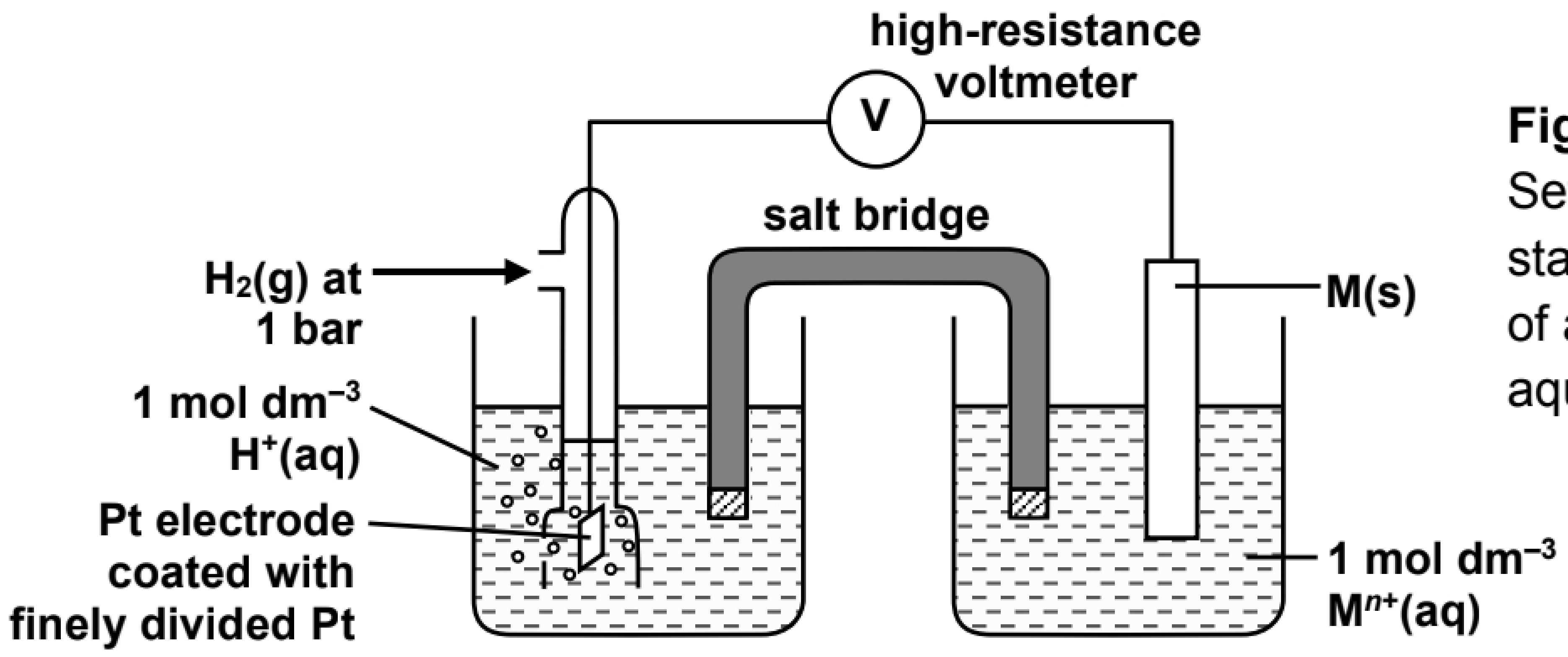


Figure 5
Set-up for measuring the standard electrode potential of a metal in contact with its aqueous ions

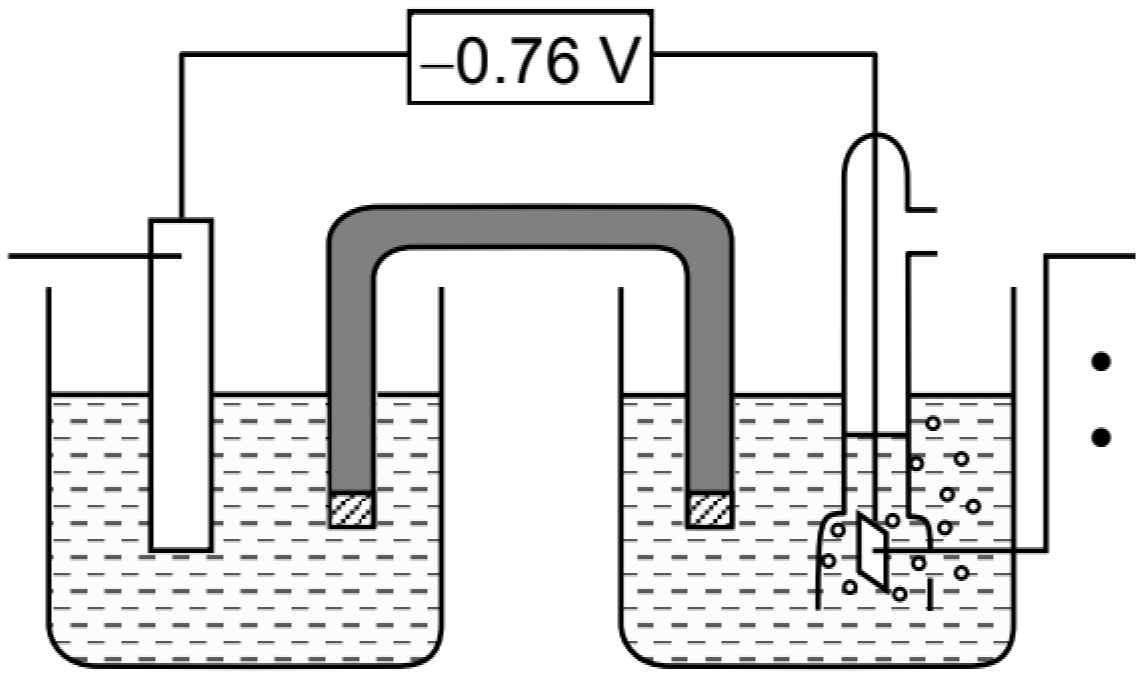
- The voltmeter measures the difference in the electrode potentials of the 2 electrodes connected.

- Since $E^{\ominus}\left(H^{+}(aq)|H_2(g)\right) = 0\ V$, the measured e.m.f. in the above setup gives the ***magnitude*** of the standard electrode potential of metal M.

Case 1: Electrons flow from metal electrode to S.H.E.

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

Observations: Zn electrode decreases in mass with time ⇒ *Zn(s) oxidised to give* $Zn^{2+}(aq)$;
Bubbles of $H_2(g)$ formed at surface of Pt electrode ⇒ $H^+(aq)$ *reduced to give* $H_2(g)$;
Voltmeter reads −0.76 V.



- $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
- ***Oxidation*** occurs
  ➔ Zn electrode is ***anode***.

- $2H^+(aq) + 2e^- \rightarrow H_2(g)$
- ***Reduction*** occurs
  ➔ Pt electrode of S.H.E. is ***cathode***.

Direction of e^- flow: From Zn electrode (anode) to Pt electrode of S.H.E. (cathode)

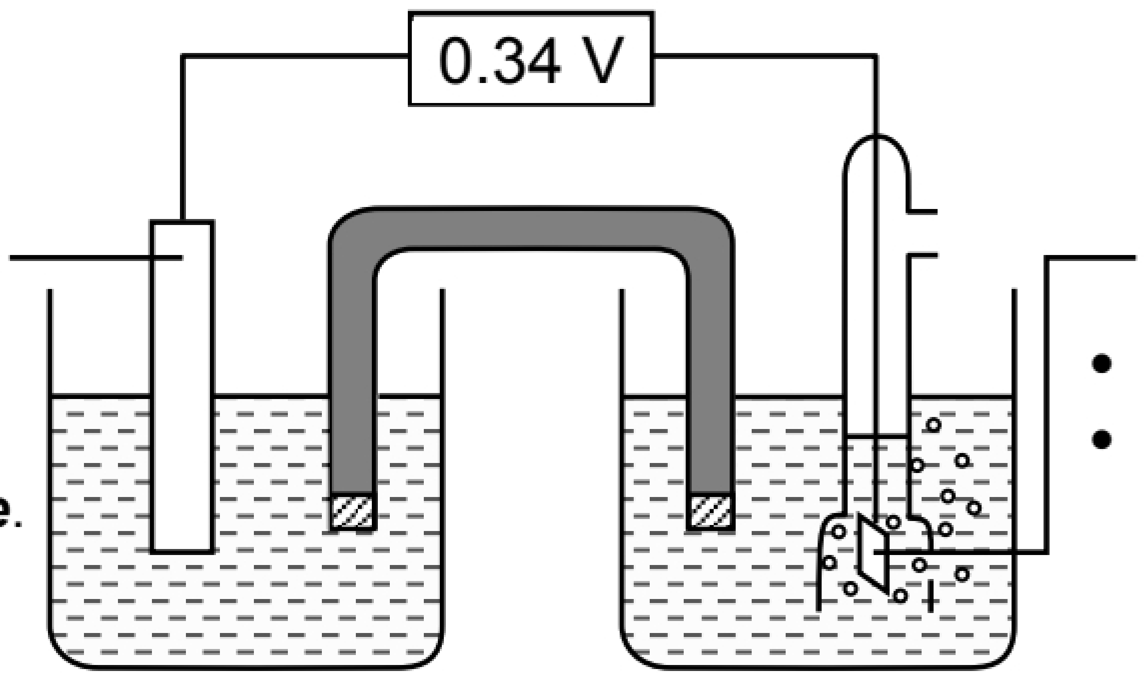
Polarity of electrode: Zn electrode (anode) is the **negative** electrode,
Pt electrode of S.H.E. (cathode) is the **positive** electrode.

$\therefore Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ $E^{\ominus}\left(Zn^{2+}(aq)\middle|Zn(s)\right) = -0.76 \text{ V}$

Case 2: Electrons flow from S.H.E. to metal electrode

Example: $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$

Observations: Cu electrode increases in mass with time and colour of $Cu^{2+}(aq)$ solution becomes paler with time ⇒ $Cu^{2+}(aq)$ *reduced to give Cu(s)*;
Voltmeter reads 0.34 V.



- $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
- ***Reduction*** occurs
  ➔ Cu electrode is ***cathode***.

- $H_2(g) \rightarrow 2H^+(aq) + 2e^-$
- ***Oxidation*** occurs
  ➔ Pt electrode of S.H.E. is ***anode***.

Direction of e^- flow: From Pt electrode of S.H.E. (anode) to Cu electrode (cathode)

Polarity of electrode: Pt electrode of S.H.E. (anode) is the **negative** electrode,
Cu electrode (cathode) is the **positive** electrode.

$\therefore Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ $E^{\ominus}\left(Cu^{2+}(aq)\middle|Cu(s)\right) = +0.34 \text{ V}$

(B) To determine $E^\ominus$ of a non-metal in contact with its ions in aqueous solution

Example: $Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$

Observations: No bubbles formed at surface of both electrodes ⇒ *$Cl_2(g)$ reduced to give $Cl^-(aq)$;*
$H_2(g)$ oxidised to give $H^+(aq)$;

Voltmeter reads 1.36 V.

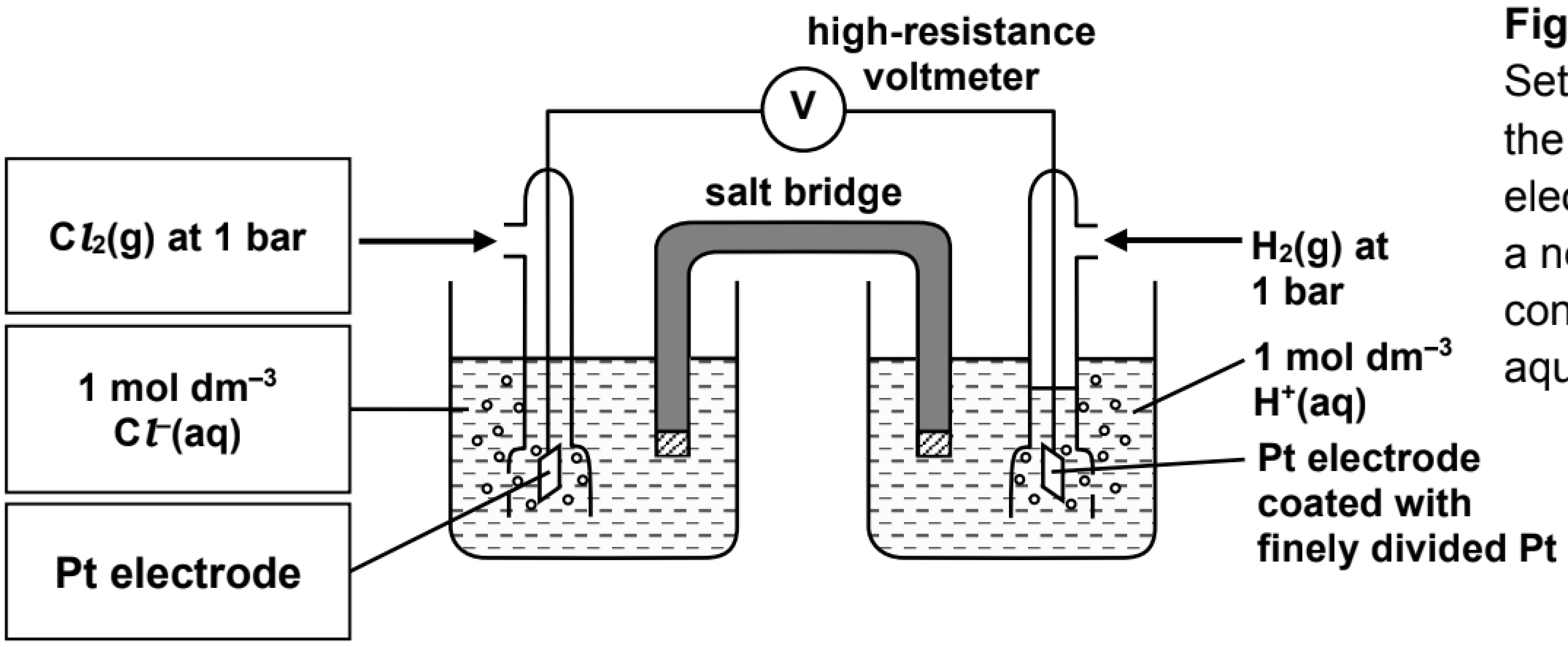


Figure 6
Set-up for measuring the standard electrode potential of a non-metal in contact with its aqueous ions

Equations:

$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$ *{reduction at cathode}*

$H_2(g) \rightarrow 2H^+(aq) + 2e^-$ *{oxidation at anode}*

Direction of e^- flow: From Pt electrode of S.H.E. (anode) to Pt electrode of $Cl_2(g)|Cl^-(aq)$ half-cell (cathode)

Polarity of electrode: Pt electrode of S.H.E. (anode) is the **negative** electrode,
Pt electrode of $Cl_2|Cl^-$ half-cell (cathode) is the **positive** electrode.

$\therefore Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$ $E^\ominus(Cl_2(g)|Cl^-(aq)) = +1.36$ V

(C) To determine $E^{\ominus}$ of ions of the same element in different oxidation states

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

Observations: Solution in $Fe^{3+}(aq)|Fe^{2+}(aq)$ half-cell becomes paler in colour ⇒ *$Fe^{3+}(aq)$ reduced to $Fe^{2+}(aq)$*;
Voltmeter reads 0.77 V.

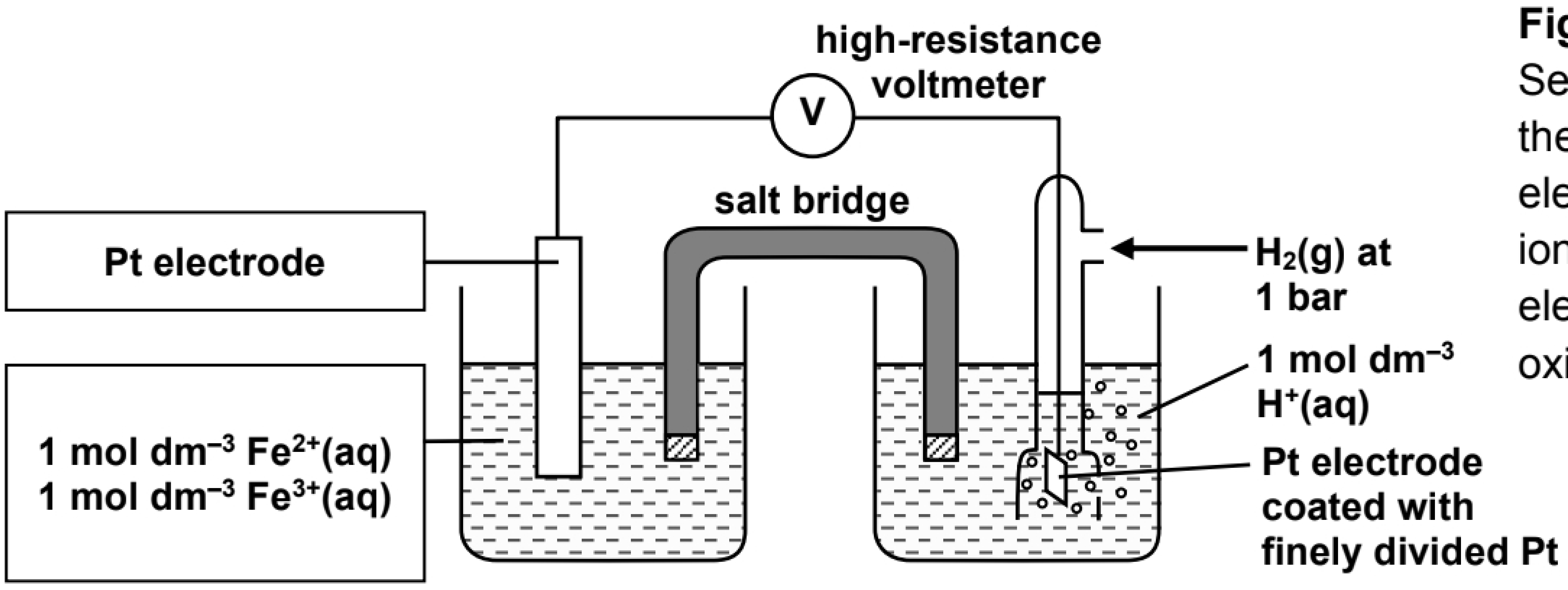


Figure 7
Set-up for measuring the standard electrode potential of ions of the same element in different oxidation states

Equations :

$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$		*{reduction at cathode}*
$\frac{1}{2}H_2(g) \rightarrow H^+(aq) + e^-$		*{oxidation at anode}*

Direction of e^- flow: From Pt electrode of S.H.E. (anode) to Pt electrode of $Fe^{3+}(aq)|Fe^{2+}(aq)$ half-cell (cathode)

Polarity of electrode: Pt electrode of S.H.E. (anode) is the **negative** electrode,
Pt electrode of $Fe^{3+}|Fe^{2+}$ half-cell (cathode) is the **positive** electrode.

$$\therefore Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq) \qquad E^{\ominus}\left(Fe^{3+}(aq)|Fe^{2+}(aq)\right) = +0.77 \text{ V}$$

Example 4A

State the electrolyte and electrode that would be used in the half-cell to measure the standard electrode potential of the following:

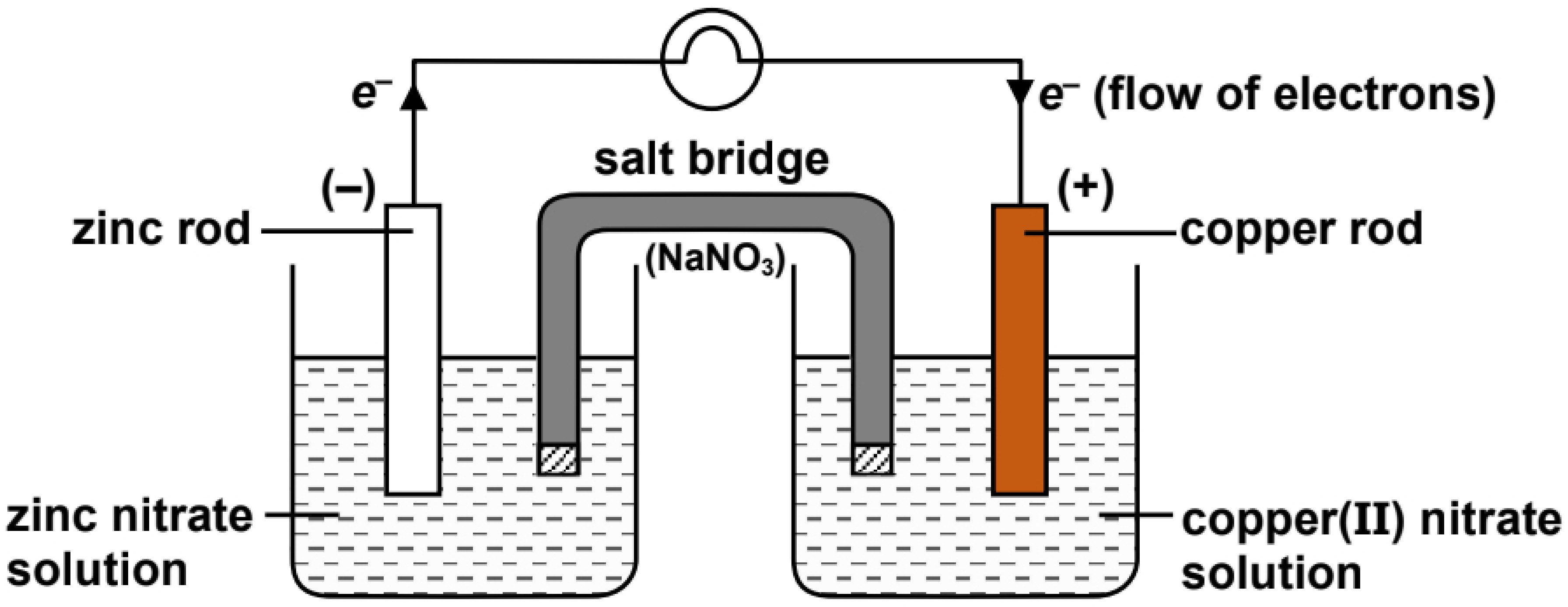
Half-equations	Electrolyte	Electrode
(a) $Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$		
(b) $Cr^{3+}(aq) + e^- \rightleftharpoons Cr^{2+}(aq)$		
(c) $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$		

5 CELL NOTATIONS / CELL DIAGRAMS

- An electrochemical cell (*i.e.* two half-cells connected together) can be represented by a cell diagram or cell notation. The notations used are as follow:

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

For example,



the cell diagram for the cell above is:

$$\underbrace{\mathrm{Zn(s)} \mid \mathrm{Zn^{2+}(aq)}}_{\substack{\text{anode half-cell}\\ \text{(oxidation)}}} \parallel \underbrace{\mathrm{Cu^{2+}(aq)} \mid \mathrm{Cu(s)}}_{\substack{\text{cathode half-cell}\\ \text{(reduction)}}}$$

- By convention, the half-cell with the **anode** (the **negative electrode** at which **oxidation** takes place) is placed on the **Left**.
  The half-cell with the **cathode** (the **positive electrode** at which **reduction** takes place) is placed on the **Right**.

- Thus,

  $\mathrm{Zn(s)} \mid \mathrm{Zn^{2+}(aq)}$ represents $\mathrm{Zn(s)} \rightarrow \mathrm{Zn^{2+}(aq)} + 2e^-$ *Oxidation*

  $\mathrm{Cu^{2+}(aq)} \mid \mathrm{Cu(s)}$ represents $\mathrm{Cu^{2+}(aq)} + 2e^- \rightarrow \mathrm{Cu(s)}$ *Reduction*

- Remember that an inert electrode such as Pt must be used for the following half-cells:
  - For a non-metal in contact with its ions in aqueous solution
    e.g. $\mathrm{Pt(s)} \mid \mathrm{H_2(g)} \mid \mathrm{H^+(aq)} \parallel$ … …
  - For ions of the same element in different oxidation states
    e.g. … … $\parallel \mathrm{Fe^{3+}(aq), Fe^{2+}(aq)} \mid \mathrm{Pt(s)}$

6 APPLICATIONS OF STANDARD ELECTRODE POTENTIALS

6.1 The Redox Series

- When electrode potentials are determined experimentally, they are compiled and arranged in decreasing order to give the Redox Series.

Electrode reaction	$E^{\ominus}$ / V
$F_2 + 2e^- \rightleftharpoons 2F^-$	+2.87
$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$	+2.01
$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	+1.77
$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	+1.52
$PbO_2 + 4H^+ + 2e^- \rightleftharpoons Pb^{2+} + 2H_2O$	+1.47
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	+1.33
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23
$Br_2 + 2e^- \rightleftharpoons 2Br^-$	+1.07
$NO_3^- + 10H^+ + 8e^- \rightleftharpoons NH_4^+ + 3H_2O$	+0.87
$ClO^- + H_2O + 2e^- \rightleftharpoons Cl^- + 2OH^-$	+0.81
$NO_3^- + 2H^+ + e^- \rightleftharpoons NO_2 + H_2O$	+0.81
$Ag^+ + e^- \rightleftharpoons Ag$	+0.80
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.77
$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.54
$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$	+0.40
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34
$SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons SO_2 + 2H_2O$	+0.17
$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$	+0.15
$S_4O_6^{2-} + 2e^- \rightleftharpoons 2S_2O_3^{2-}$	+0.09
$2H^+ + 2e^- \rightleftharpoons H_2$	0.00
$Pb^{2+} + 2e^- \rightleftharpoons Pb$	–0.13
$Sn^{2+} + 2e^- \rightleftharpoons Sn$	–0.14
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	–0.44
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	–0.76
$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$	–0.83
$V^{2+} + 2e^- \rightleftharpoons V$	–1.20
$Mg^{2+} + 2e^- \rightleftharpoons Mg$	–2.38
$Ca^{2+} + 2e^- \rightleftharpoons Ca$	–2.87
$K^+ + e^- \rightleftharpoons K$	–2.92

- Note that the electrode potential is independent of the number of electrons being transferred.

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

  $3Cu^{2+}(aq) + 6e^- \rightarrow 3Cu(s)$ $E^{\ominus} = +0.34$ V

- **Oxidising agent** is always itself reduced. ⇒ *species on LHS of electrode reaction are oxidising agents.*

  More positive $E^{\ominus}$ ➔ greater tendency for the species on the LHS to be reduced ➔ stronger oxidising agent

- **Reducing agent** is always itself oxidised. ⇒ *species on RHS of electrode reaction are reducing agents.*
  More negative $E^{\ominus}$ ➔ greater tendency for the species on the RHS to be oxidised ➔ stronger reducing agent

Example: Based on the Redox Series above,
(a) which is the strongest reducing agent in this set of reagents? K
(b) which is the strongest oxidising agent in this set of reagents? F_2

Example 6A

Arrange the following oxidising agents in increasing order of oxidising power under standard conditions.

$Br_2(l)$ acidified $Cr_2O_7^{2-}(aq)$ $Fe^{3+}(aq)$ acidified $H_2O_2(aq)$

Example 6B

Arrange the following reducing agents in increasing order of reducing power under standard conditions.

$Al(s)$ $Cu(s)$ $Fe^{2+}(aq)$ $H_2(g)$ $I^-(aq)$

6.2 Predicting Relative Stabilities of Metallic Ions in Different Oxidation States

How can we prevent the oxidation of $Fe^{2+}(aq)$ to $Fe^{3+}(aq)$?

In acidic medium: $Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$ $E^{\ominus} = +0.77$ V

In alkaline medium: $Fe(OH)_3(s) + e^- \rightleftharpoons Fe(OH)_2(s) + OH^-(aq)$ $E^{\ominus} = -0.56$ V

Since $E^\ominus\left(\mathrm{Fe^{3+}(aq)|Fe^{2+}(aq)}\right)$ is more positive than $E^\ominus\left(\mathrm{Fe(OH)_3(s)|Fe(OH)_2(s)}\right)$, Fe(II) is more stable with respect to Fe(III) in acidic medium than in alkaline medium. Hence a solution of Fe^{2+} can be stabilised against oxidation by addition of a small amount of acid.

6.3 Determine Standard Cell Potential

- *Definition of standard cell potential:*

> **Standard cell potential**, $E^\ominus_{\text{cell}}$, is the e.m.f. of a galvanic cell which consists of two half-cells connected under standard conditions. The $E^\ominus_{\text{cell}}$ value is the difference between the two standard electrode potentials.

- The following equation is used to calculate $E^\ominus_{\text{cell}}$:

$$\boxed{\boldsymbol{E^\ominus_{\text{cell}} = E^\ominus_{\text{red}}(\text{reduction}) - E^\ominus_{\text{red}}(\text{oxidation})}}$$

where $\boldsymbol{E^\ominus_{\text{red}}(\text{reduction})}$: standard reduction potential of the half-cell at which reduction occurs
$\boldsymbol{E^\ominus_{\text{red}}(\text{oxidation})}$: standard reduction potential of the half-cell at which oxidation occurs

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

$$\mathrm{Cu^{2+}(aq)|Cu(s)} \text{ and } \mathrm{Mg^{2+}(aq)|Mg(s)}$$

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

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

Since $\underline{E^\ominus\left(\mathrm{Cu^{2+}(aq)|Cu(s)}\right)}$ is more positive than $\underline{E^\ominus\left(\mathrm{Mg^{2+}(aq)|Mg(s)}\right)}$, reduction takes place in the $\mathrm{Cu^{2+}(aq)|Cu(s)}$ half-cell while oxidation takes place in the $\mathrm{Mg^{2+}(aq)|Mg(s)}$ half-cell.

$$\begin{aligned}\therefore E^\ominus_{\text{cell}} &= E^\ominus_{\text{red}}(\text{reduction}) - E^\ominus_{\text{red}}(\text{oxidation}) = E^\ominus\left(\mathrm{Cu^{2+}(aq)|Cu(s)}\right) - E^\ominus\left(\mathrm{Mg^{2+}(aq)|Mg(s)}\right)\\ &= +0.34 - (-2.38)\\ &= +2.72\ \mathrm{V}\end{aligned}$$

Example 6C

For the following combination of half-cells, determine the (a) cell reaction; (b) cell e.m.f.; (c) anode/ cathode; (d) direction of electron flow.

$Fe^{2+}(aq)|Fe(s)$ half-cell and $Ni^{2+}(aq)|Ni(s)$ half-cell

Self-Check 6A

In the orange juice clock experiment, the cell was made up of a magnesium strip and a copper strip immersed in a cup of orange juice. Predict the reactions occurring at each electrode and hence the e.m.f. of the cell (assuming standard conditions).

Possible reactants present:

$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$ (most favourable oxidation)

$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ (most favourable reduction but not possible since no Cu^{2+} present)

$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$ (more favourable reduction)

At Mg(s) anode:
At Cu(s) cathode:
Overall:

6.4 Predict Feasibility of Redox Reactions

To predict whether a redox reaction occurs, $E^{\ominus}_{\text{cell}}$ is calculated.

- If $\boldsymbol{E^{\ominus}_{\text{cell}} > 0}$ **V**, the forward reaction is **energetically feasible**, *i.e.* reaction is expected to be spontaneous under standard conditions.
- If $\boldsymbol{E^{\ominus}_{\text{cell}} < 0}$ **V**, the forward reaction is **NOT energetically feasible**. However, the reverse reaction is expected to be spontaneous under standard conditions if the required reactants are available.
- If $\boldsymbol{E^{\ominus}_{\text{cell}} = 0}$ **V**, an **equilibrium** is established.

  {Note: In the case where $E^{\ominus}_{\text{cell}}$ = 0 V in a galvanic cell, there is no flow of electrons since there is no potential difference between the two half-cells, i.e. no current flows.}

Example: Use relevant data in the *Data Booklet* to decide which of these reactions will proceed spontaneously under standard conditions.

(a) $I_2(aq) + 2Fe^{2+}(aq) \rightarrow 2I^-(aq) + 2Fe^{3+}(aq)$

$I_2(aq) + 2e^- \rightleftharpoons 2I^-(aq)$ $\quad E^{\ominus} = +0.54$ V

$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$ $\quad E^{\ominus} = +0.77$ V

$$E^{\ominus}_{\text{cell}} = +0.54 - (+0.77) = -0.23 \text{ V}$$

Since $\underline{E^{\ominus}_{\text{cell}} < 0}$, the reaction is not spontaneous.

(b) $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6I^-(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 3I_2(aq)$

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons Cr^{3+}(aq) + 7H_2O(l)$ $\quad E^{\ominus} = +1.33$ V

$I_2(aq) + 2e^- \rightleftharpoons 2I^-(aq)$ $\quad E^{\ominus} = +0.54$ V

$$E^{\ominus}_{\text{cell}} = +1.33 - (+0.54) = +0.79 \text{ V}$$

Since $E^{\ominus}_{\text{cell}} > 0$, the reaction is spontaneous.

(c) $2Fe^{3+}(aq) + Br_2(aq) \rightarrow 2Fe^{2+}(aq) + 2Br^-(aq)$

$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$ $\quad E^{\ominus} = +0.77$ V

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

No reaction because Fe^{3+} and Br_2 cannot both be reduced at the same time.

Example 6D

State and explain, with the aid of the *Data Booklet*, what happens when H_2O_2 is added to acidified KI(aq).

Species present: $H_2O_2(aq)$, $K^+(aq)$, $I^-(aq)$

<u>Possible reduction</u>

$\mathbf{H_2O_2(aq)} + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(\ell)$ (only possible reduction)

(Note: $K^+(aq) + e^- \rightleftharpoons K(s)$ $\left(E^\ominus = -2.92\text{ V}\right)$ is much less favourable so not considered)

<u>Possible oxidation</u>

$O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons \mathbf{H_2O_2(aq)}$

$I_2(aq) + 2e^- \rightleftharpoons 2I^-(aq)$ (more favourable oxidation)

Example 6E

Predict the reaction, if any, when the following pairs of solutions are mixed. If a reaction occurs, write a balanced equation and calculate the $E^\ominus_{\text{cell}}$.

(a) $\text{SnC}\ell_2(aq)$ and $Br_2(aq)$

Species present:

<u>Possible reduction</u>

$\mathbf{Sn^{2+}(aq)} + 2e^- \rightleftharpoons Sn(s)$ $E^\ominus = -0.14\text{ V}$

$\mathbf{Br_2(aq)} + 2e^- \rightleftharpoons 2Br^-(aq)$ $E^\ominus = +1.07\text{ V}$
(more favourable)

<u>Possible oxidation</u>

$Sn^{4+}(aq) + 2e^- \rightleftharpoons \mathbf{Sn^{2+}(aq)}$ $E^\ominus = +0.15\text{ V}$
(more favourable)

$\text{C}\ell_2(g) + 2e^- \rightleftharpoons \mathbf{2C\ell^-(aq)}$ $E^\ominus = +1.36\text{ V}$

$E^\ominus_{\text{cell}} =$

$Br_2(aq) + 2e^- \rightarrow 2Br^-(aq)$
$Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2e^-$

(b) acidified $K_2Cr_2O_7(aq)$ and $\text{HC}\ell(aq)$

Species present:

<u>Possible reduction</u>

$\mathbf{Cr_2O_7^{2-}(aq)} + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(\ell)$
$E^\ominus = +1.33\text{ V}$
(more favourable)

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

<u>Possible oxidation</u>

$\text{C}\ell_2(g) + 2e^- \rightleftharpoons \mathbf{2C\ell^-(aq)}$ $E^\ominus = +1.36\text{ V}$

$E^\ominus_{\text{cell}} =$

7 LIMITATIONS OF STANDARD ELECTRODE POTENTIALS

- $E^\ominus$ values tell us whether a reaction is possible (*i.e.* ***energetic stability***), but not the rate of the reaction (*i.e.* ***kinetic stability***).

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

  $$Cu^{2+}(aq) + H_2(g) \rightarrow Cu(s) + 2H^+(aq) \qquad E^\ominus_{cell} = +0.34\ V$$

  However no reaction occurs when hydrogen is bubbled into copper(II) sulfate solution because the reaction rate is effectively zero due to the **high activation energy**. The reaction is said to be *energetically feasible* but *kinetically not feasible*.

- $E^\ominus$ values relate only to **standard conditions**. Changes in temperature, pressure and concentration will affect the values of electrode potentials.

.

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

  (*i.e.* conditions of 1.0 mol dm^{-3} Cu^{2+}(aq) at 298 K and 1 atm)

  But when 0.1 mol dm^{-3} Cu^{2+}(aq) is used at 298 K and 1 atm, the electrode potential becomes +0.31 V.

Example 7A

Example 6D(b), it is predicted that acidified $Cr_2O_7^{2-}$ ions cannot oxidise Cl^- ions to give Cl_2 gas. However, when acidified $K_2Cr_2O_7$ solution is added to concentrated HC*l*, Cl_2 gas is readily formed. Explain.

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

[Cl^-(aq)] in conc. HCl is greater than 1 mol dm^{-3} and hence the equilibrium position of (*) shifts to the ________________, giving rise to a ______________________________ $E\left(Cl_2(g)|Cl^-(aq)\right)$.

As a result, $E_{cell}\left(=E\left(Cr_2O_7^{2-}(aq)|Cr^{3+}(aq)\right)-E\left(Cl_2(g)|Cl^-(aq)\right)\right)$ becomes ________________

and the reaction is ____.

Example 7B

Consider the galvanic cell made up of the following half-cells:

$Cu^{2+}(aq) + 2e^{-} \rightleftharpoons Cu(s)$ $E_1^{\ominus} = +0.34$ V

$Fe^{3+}(aq) + e^{-} \rightleftharpoons Fe^{2+}(aq)$ $E_2^{\ominus} = +0.77$ V

(a) Calculate $E_{\text{cell}}^{\ominus}$.

(b) The above galvanic cell is initially set up under standard conditions. The following changes are made to the galvanic cell. Consider the effect of each change on E_1 or E_2 and hence predict whether the new E_{cell} is higher or lower than $E_{\text{cell}}^{\ominus}$.

Change	Effect on E_1 or E_2	Effect on $E_{\text{cell}} = E_2 - E_1$
(i) Adding water to $Cu^{2+}\|Cu$ half-cell *$[Cu^{2+}]$ decreases $\Rightarrow$ equilibrium position of $Cu^{2+}\|Cu$ half-equation shifts left*		
(ii) Adding NaOH(aq) to $Cu^{2+}\|Cu$ half-cell *$Cu^{2+}(aq)$ precipitated out as $Cu(OH)_2(s)$, hence $[Cu^{2+}]$ decreases $\Rightarrow$ equilibrium position of $Cu^{2+}\|Cu$ half-equation shifts left*		
(iii) Using a smaller piece of Cu in $Cu^{2+}\|Cu$ half-cell *No change in $[Cu^{2+}]$ $\Rightarrow$ no effect on equilibrium position of $Cu^{2+}\|Cu$ half-equation*		
(iv) Adding water to $Fe^{3+}\|Fe^{2+}$ half-cell *Both $[Fe^{3+}]$ and $[Fe^{2+}]$ decreases by the same extent $\Rightarrow$ no effect on equilibrium position of $Fe^{3+}\|Fe^{2+}$ half-equation*		
(v) Adding some $FeCl_2(s)$ to $Fe^{3+}\|Fe^{2+}$ half-cell *$FeCl_2(s)$ dissolves to give $Fe^{2+}(aq)$, hence $[Fe^{2+}]$ increases $\Rightarrow$ equilibrium position of $Fe^{3+}\|Fe^{2+}$ half-equation shifts left*		

8 Relationship between the Gibbs free energy and electrode potential

Redox reactions can be used to generate electricity in electrochemical cells. The change in the Gibbs free energy accompanying the reaction, ΔG^θ, can be converted into electrical energy. If the cell is operated so that the current flows infinitely slowly, i.e. under reversible conditions, we have

$\Delta G^\ominus = -nFE^\ominus_{\text{cell}}$ where n is the number of electrons per mole reaction,
and F is the Faraday constant (9.65×10^4 C mol^{-1})

Similarly, the change in the Gibbs free energy for a half-reaction is related to the reduction

potential, E: $\Delta G^\ominus = -nFE^\ominus$

Hence, a spontaneous redox reaction $(\Delta G < 0)$ would mean that $\boldsymbol{E_{\text{cell}} > 0}$. In other words, the extent of a redox reaction is governed by the sign and magnitude of $E^\ominus_{\text{cell}}$, like in the case of $\Delta G^\ominus$.

Since $E^\ominus_{\text{cell}}$ is dependent on both temperature and concentration (Nernst equation), a non-spontaneous reaction under standard conditions can be made feasible under non-standard conditions (e.g***. increasing temperature or concentration***).

Similar to the use of $\Delta G^\ominus$ to predict the feasibility of a reaction, $E^\ominus_{\text{cell}}$ only gives an indication of the *thermodynamic* feasibility (spontaneity), *i.e.* based on energy consideration.

The other important aspect, the *kinetic* feasibility (looking at the activation energy, E_a) must also be considered in order to understand fully whether a reaction is likely to proceed on its own.

9 DEVELOPMENT OF IMPROVED BATTERIES

- Galvanic cells and batteries provide a useful and economic way of obtaining energy from chemical reactions.

- Trend in developing improved batteries is to look for battery with
  - smaller size,
  - lower mass,
  - higher voltage, and
  - be produced at a low cost with a long shelf-life.

9.1 Zinc-Carbon Dry Cell

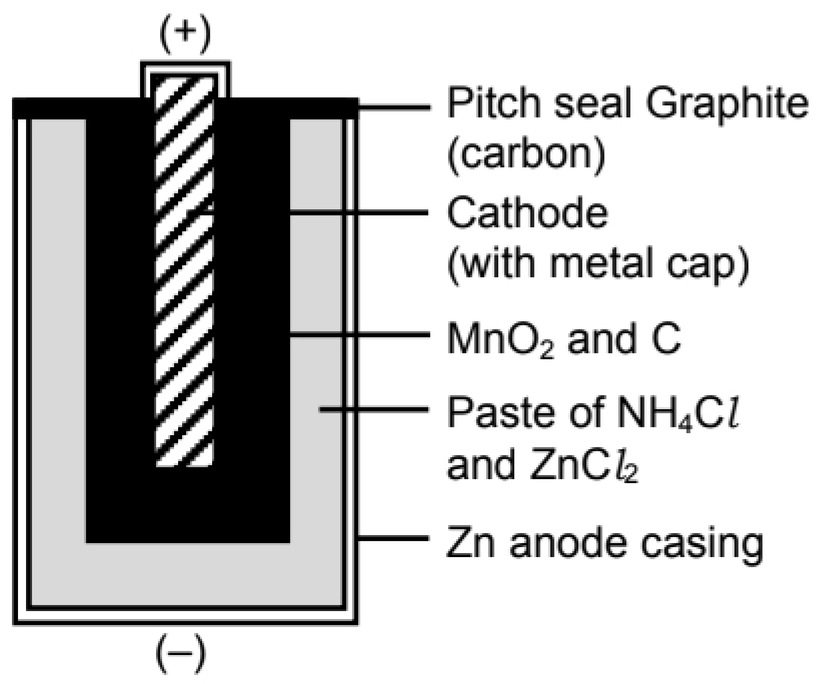


Figure 8
Cross-section of a dry cell

- Primary cell (non-rechargeable) used in portable radios, clocks, electric bells and torches.

- Convenient portable source of electricity because all its components are solids or pastes which are tightly sealed from the environment.

- The electrolyte of the dry cell consists of a paste made up of zinc chloride, ammonium chloride and water. It is necessary to use a paste because dry ammonium chloride would not conduct electricity.

- At the zinc anode (negative electrode), which is the casing of the dry cell:
  - Oxidation takes place: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

- At the graphite cathode (positive electrode):
  - Reduction takes place:

    $$2NH_4^+(aq) + 2MnO_2(s) + 2e^- \rightarrow 2NH_3(g) + Mn_2O_3(s) + H_2O(l)$$

  - The cathode is surrounded by a layer of manganese(IV) oxide and carbon. This helps to increase the surface area of the cathode, thus enabling a larger current to flow.

- The overall reaction is

  $$Zn(s) + 2NH_4^+(aq) + 2MnO_2(s) \rightarrow Zn^{2+}(aq) + 2NH_3(g) + Mn_2O_3(s) + H_2O(l)$$

  E.m.f. of cell = 1.5 V

- Advantages:
  1) Cheap and portable source of electricity.
  2) Supplies a reliable voltage.

- Disadvantages:
  1) Poor shelf-life as zinc casing disintegrates (due to reaction with acidic ammonium chloride) and the paste oozes through the outer casing.
  2) It provides a low voltage.
  3) It cannot be recharged (discarded once completely discharged).

9.2 Alkaline Dry Cell

- Similar to Zinc-Carbon dry cell except that KOH is used in place of NH_4Cl.

- At the anode: $Zn(s) + 2OH^-(aq) \rightarrow ZnO(s) + H_2O(l) + 2e^-$
  At the cathode: $2MnO_2(s) + H_2O(l) + 2e^- \rightarrow Mn_2O_3(s) + 2OH^-(aq)$
  The overall reaction: $Zn(s) + 2MnO_2(s) \rightarrow ZnO(s) + Mn_2O_3(s)$

- Similar advantages and disadvantages as the Zinc-Carbon dry cell except that it is more expensive but lasts longer as the zinc anode corrodes more slowly under alkaline conditions.

9.3 Nickel-Cadmium Rechargeable Cell

- Secondary cell (rechargeable) used in mobile phones, laptops, etc.

- The electrolyte is aqueous potassium hydroxide.

- At the anode (cadmium): $Cd(s) + 2OH^-(aq) \rightarrow Cd(OH)_2(s) + 2e^-$
  At the cathode (nickel hydroxide): $2NiO(OH)(s) + 2H_2O(l) + 2e^- \rightarrow 2Ni(OH)_2(s) + 2OH^-(aq)$
  The overall reaction: $Cd(s) + 2NiO(OH)(s) + 2H_2O(l) \rightarrow Cd(OH)_2(s) + 2Ni(OH)_2(s)$
  E.m.f. of cell = 1.2 V

- The reaction can be readily reversed because the products, $Ni(OH)_2$ and $Cd(OH)_2$, adhere to the electrode surfaces.

- Advantages:
  1) Rechargeable.
  2) Portable source of electricity.
  3) Typically lasts longer, in terms of number of charge/discharge cycles, than other rechargeable batteries.

- Disadvantages:
  1) Higher cost (due to the use of nickel and cadmium).
  2) It provides a low voltage.
  3) Prone to damage by overcharging.
  4) Memory effect – drop in discharge capacity after multiple recharging of battery.
  5) Cadmium, being a heavy metal, can cause pollution during its disposal.

9.4 Lead-Acid Accumulator

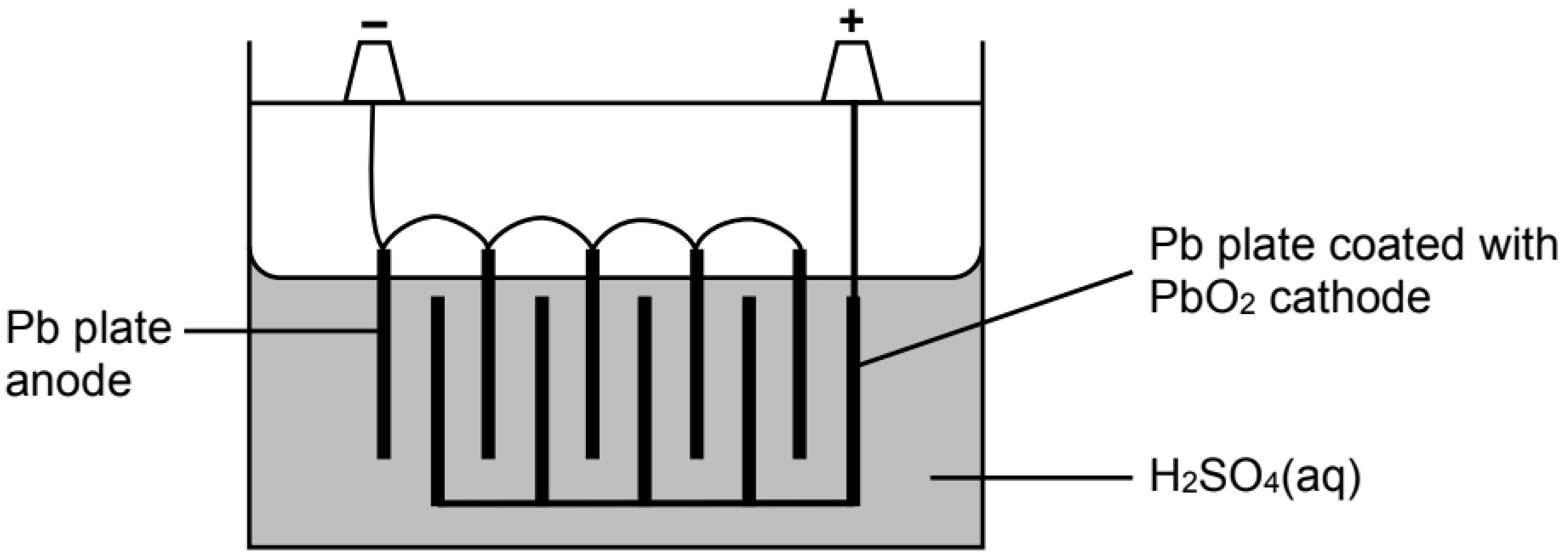


Figure 9
Schematic cross section of a lead-acid battery

- The lead-acid accumulator is sometimes known as the lead-acid storage battery. It is a secondary cell (rechargeable) as the half-reactions at the electrodes are readily reversible.

- The electrolyte is dilute sulfuric acid.

- During **DISCHARGING** (*i.e.* cell is providing current):
  - At the lead anode:

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

  - At the cathode, which is lead(IV) oxide coated on lead:

    $$PbO_2(s) + 4H^+(aq) + 2e^- \rightarrow Pb^{2+}(aq) + 2H_2O(l)$$

  - The overall reaction is

    $$Pb(s) + PbO_2(s) + 4H^+(aq) \rightarrow 2Pb^{2+}(aq) + 2H_2O(l)$$

    $$\text{E.m.f. of cell} = E^{\ominus}_{\text{red}}\left(PbO_2 \middle| Pb^{2+}\right) - E^{\ominus}_{\text{red}}\left(Pb^{2+} \middle| Pb\right)$$

    $$= +1.47 - (-0.13) = +1.60 \text{ V (theoretical value)}$$

    But actual e.m.f. = +2.0 V, so that the voltage of car battery = 6 × 2.0 = 12.0 V.

  - **Why is the actual e.m.f. of a cell in the car battery 2.0 V and not 1.60 V?**
    In practice, $Pb^{2+}(aq)$ is removed as it precipitates out as $PbSO_4(s)$. As a result, $E_{\text{red}}\left(PbO_2 \middle| Pb^{2+}\right)$ is more positive than +1.47 V *{as equilibrium in $PbO_2 + 4H^+ + 2e^- \rightleftharpoons Pb^2 + 2H_2O$ shifts to RHS}* and $E_{\text{red}}\left(Pb^{2+} \middle| Pb\right)$ is more negative than –0.13 V *{as equilibrium in $Pb^2 + 2e^- \rightleftharpoons Pb$ shifts to LHS}*.

  - During discharging, a film of white lead(II) sulfate forms at both electrodes, thus reducing the concentration and relative density of sulfuric acid. The relative density of sulfuric acid thus indicates the state of charge in the battery.
    [When the cell is fully charged, the sulfuric acid has a relative density of about 1.275.]

- During **CHARGING**, an external current is applied to reverse the electrode reactions.

  $$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \underset{\text{charging}}{\overset{\text{discharging}}{\rightleftharpoons}} 2PbSO_4(s) + 2H_2O(l)$$

- Advantage: Provide a high initial current, which is required to start a car engine.

- Disadvantages:
  1) Rather large and heavy due to the lead, hence produces low power for its mass.
  2) $PbSO_4$ deposits on the electrodes in a finely divided form during discharging. If a discharged battery stands for a long time, the small grains of $PbSO_4$ may grow into large crystals that fall from the electrodes. If too much $PbSO_4$ is lost, the cell cannot be recharged and results in loss of capacity

9.5 Fuel Cells

- Fuel cells differ from normal electrochemical cells in having a steady supply of reactants to produce an electric current. Hence fuel cells are not energy storage cells.

- Reactants (fuels) are continuously replaced as they are consumed and the products are continuously removed as they are formed.

- Fuel cells use a wide variety of fuels including hydrogen, hydrocarbons and alcohols.

- The hydrogen-oxygen fuel cell is an example of a fuel cell.

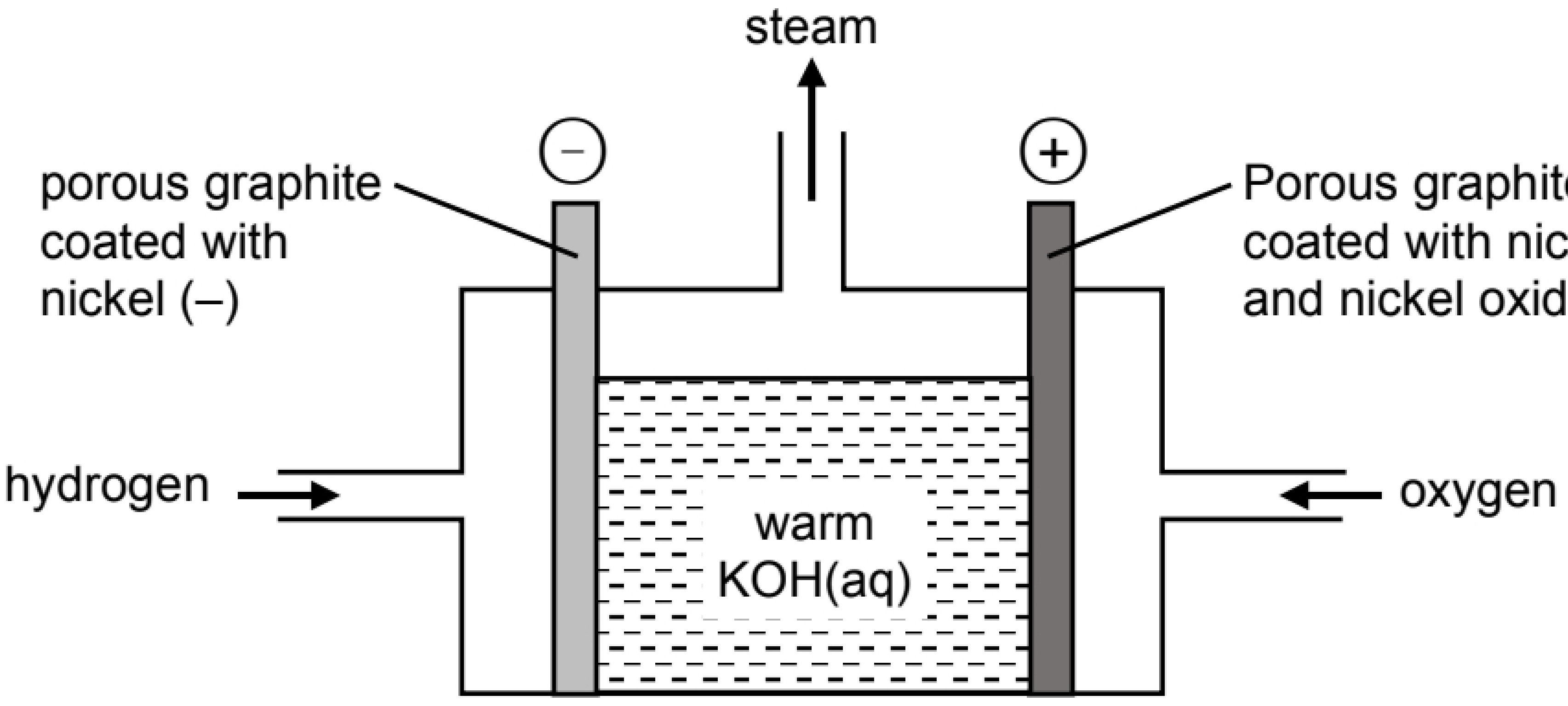


Figure 10
A hydrogen-oxygen fuel cell using an alkaline electrolyte, KOH(aq)

- ♦ The porous graphite electrodes are coated with Ni and NiO which act as catalysts on the surface of the terminals. (Note that other metal catalysts such as Pt and Pd can also be used.)

- ♦ The electrolyte is warm aqueous potassium hydroxide (alkaline conditions).

- ♦ At the anode (negative terminal): $H_2(g) + 2\mathbf{OH^-}(aq) \rightarrow 2H_2O(l) + 2e^-$
  At the cathode (positive terminal): $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4\mathbf{OH^-}(aq)$

- ♦ The overall reaction: $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

$$E^{\ominus}_{\text{cell}} = E^{\ominus}\left(O_2(g)\middle|OH^-(aq)\right) - E^{\ominus}\left(H_2O(l)\middle|H_2(g)\right)$$
$$= +0.40 - (-0.83)$$
$$= +1.23\text{ V}$$

Note that different pairs of reduction-oxidation equations are chosen depending on the pH of the electrolyte. However, $E^{\ominus}_{\text{cell}}$ for both cases is the same.

- When an acidic electrolyte (e.g. HC*l*) is used, the reactions are as follows:
  At the anode: $2H_2(g) \rightarrow 4\mathbf{H^+}(aq) + 4e^-$
  At the cathode: $O_2(g) + 4\mathbf{H^+}(aq) + 4e^- \rightarrow 2H_2O(l)$
  Overall: $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

$$E^{\ominus}_{\text{cell}} = E^{\ominus}\left(O_2(g)\middle|H_2O(l)\right) - E^{\ominus}\left(H^+(aq)\middle|H_2(g)\right)$$
$$= +1.23 - (0.00)$$
$$= +1.23\text{ V}$$

- Fuel cells are very efficient, with 70% or more of the chemical energy being converted into electricity. They are used in spacecraft to provide not only energy but also water for the astronauts.

- Advantages:
  1) Pollution-free (only water produced).
  2) High power to mass ratio.
  3) Highly efficient, with 70% or more of the chemical energy being converted into electricity.

  ⇒ consequently, fuel cells are used in spacecraft to provide not only energy but also water for the astronauts

- Disadvantages:
  1) Expensive due to large amounts of nickel and platinum metals required as catalysts for the electrode reactions.
  2) The catalysts are easily poisoned by impurities in the fuel and oxygen and thus are less able to function efficiently for long periods of time without contamination.
  3) Most fuels require a high temperature to react in the fuel cell.

Example 9A

Complete the following table of the two fuel cells using ethane but different electrolytes.

Fuel cell	**1**	**2**
Fuel used	ethane, C_2H_6	ethane, C_2H_6
Oxidising agent	air	air
Electrolyte	$H_2SO_4(aq)$	$NaOH(aq)$
Reaction at anode		
Reaction at cathode		
Overall reaction		

Answer to Self Check 6A

Possible reactants present: $Mg(s)$, $Cu(s)$, $H^+(aq)$ (from orange juice)

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

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

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

At Mg(s) anode: $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$

At Cu(s) cathode: $2H^+(aq) + 2e^- \rightarrow H_2(g)$

Overall: $Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$

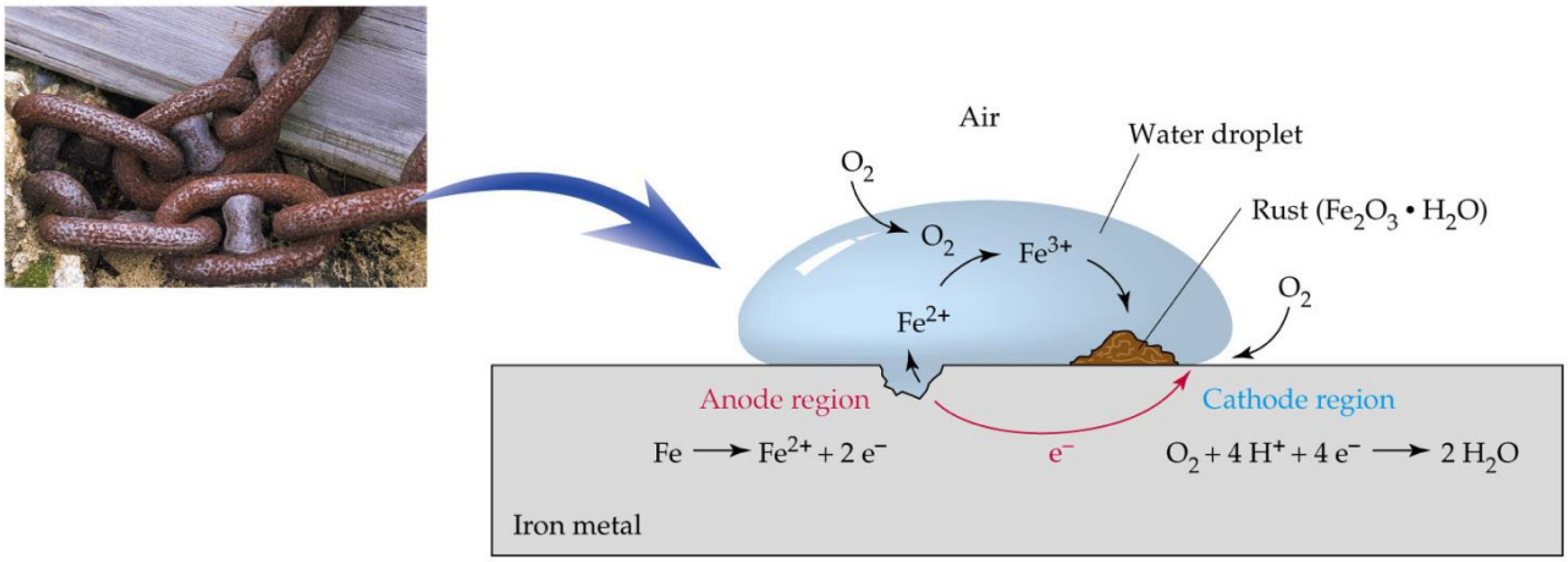
$E^\ominus_{cell} = 0.00 - (-2.38) = +2.38\ V$

Annex A: Extract from A-Level Data Booklet

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
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+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
$O_2 + H_2O + 2e^- \rightleftharpoons HO_2^- + OH^-$	–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.

Annex B: Corrosion of Iron (Enrichment)



The corrosion of iron (rusting) requires both oxygen and water. Other factors – such as the pH of the solution, the presence of salts, contact with metals that are more difficult to oxidise than iron, and stress on the iron – can accelerate rusting.

The corrosion of iron is electrochemical in nature. Not only does the corrosion process involve oxidation and reduction, the metal itself conducts electricity. Thus, electrons can move through the metal from a region where oxidation occurs to another region where reduction occurs, as in voltaic cells.

Because the standard reduction potential for the reduction of Fe^{2+}(aq) is less positive than that for the reduction of O_2(g), Fe(s) is oxidised.

Anode: $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$

The anodic region is the portion of the iron at which the oxidation of Fe(s) to Fe^{2+}(aq) occurs. Once the Fe atoms are oxidised, a pit forms where the iron is lost.

The electrons produced migrate through the metal to another portion of the surface with relatively high O_2(g) concentration near the surface of a surrounding water droplet, which serves as the cathode. At the cathodic region, the electrons released from the Fe atoms reduce O_2 molecules.

Cathode: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$

The reduction of O_2(g) requires H^+(aq), so lowering the concentration of H^+(aq) (*i.e.* increasing the pH) makes the reduction of O_2(g) less favourable.

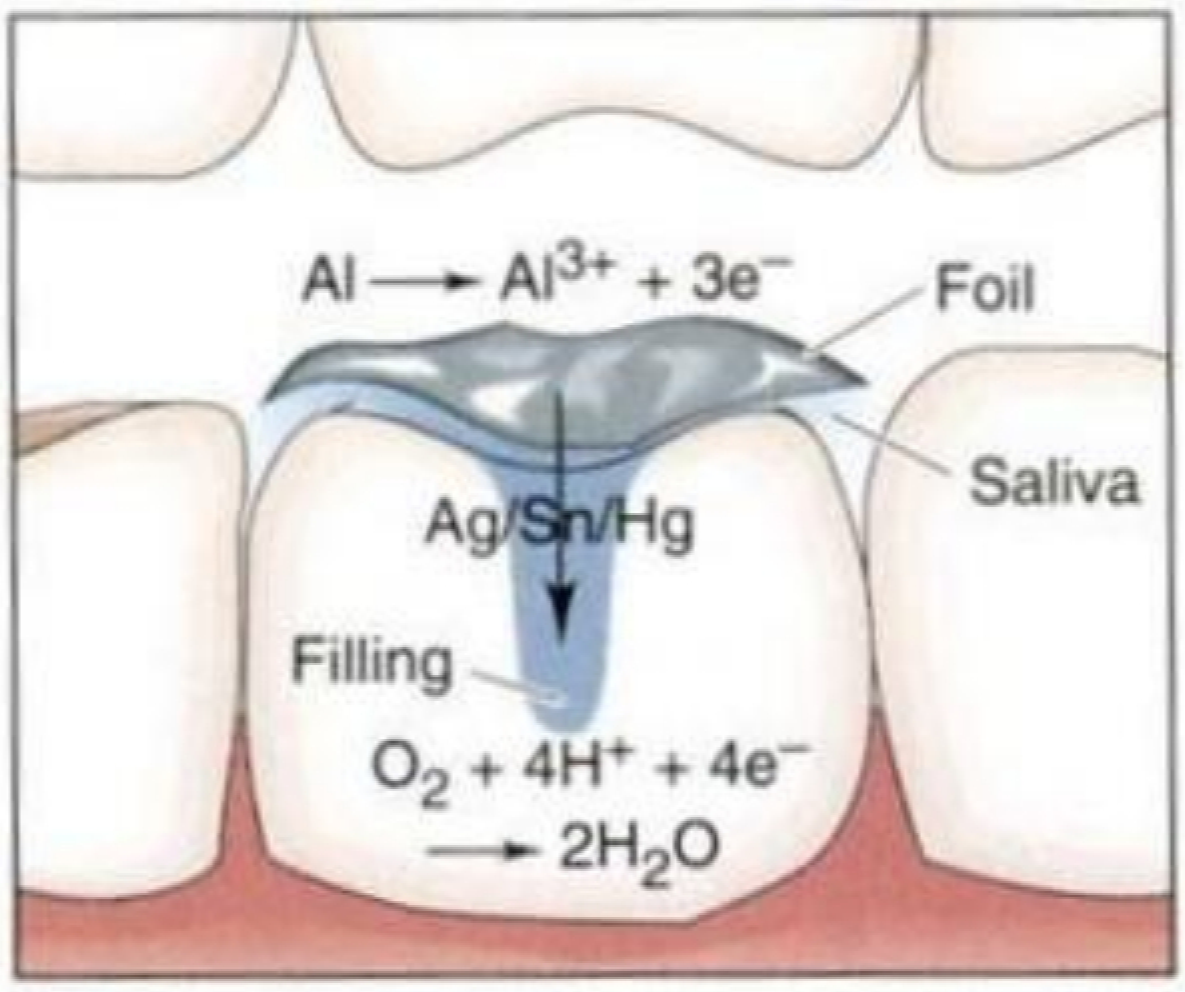
Rust forms through another redox reaction in which the reactants contact each other directly. The Fe^{2+}(aq) ions formed originally at the anodic region disperse through the surrounding water and react with O_2(g), often at some distance from the pit. The overall reaction for this step is

$$2Fe^{2+}(aq) + \tfrac{1}{2}O_2(g) + (2+n)H_2O(l) \rightarrow Fe_2O_3{\cdot}nH_2O(s) + 4H^+(aq)$$

Annex C: The Pain of a Dental Voltaic Cell (Enrichment)

Have you ever felt a jolt pain when biting down with a filled tooth on a scrap of foil left on a piece of food? Here's why.

The aluminium foil acts as an active anode $\left(E^{\ominus}\left(\mathrm{A}l^{3+}(\mathrm{aq})\middle|\mathrm{A}l(\mathrm{s})\right) = -1.66\ \mathrm{V}\right)$, saliva as the electrolyte, and the filling (usually a silver/tin/mercury alloy) as an inactive cathode. $O_2(g)$ is reduced to $H_2O(l)$, and the short circuit between the foil in contact with the filling creates a current that is sensed by the nerve of the tooth.



Annex D: The Nernst Equation (Enrichment)

The Nernst equation is used to determine the e.m.f. of an electrochemical cell under non-standard conditions.

The free energy change, ΔG, for a reaction can be expressed as:

$$\Delta G = \Delta G^{\ominus} + RT\ln Q$$

where Q is the reaction quotient (for a reaction $a\mathbf{A} + b\mathbf{B} \rightleftharpoons c\mathbf{C} + d\mathbf{D}$, $Q = \dfrac{[\mathbf{C}]^c[\mathbf{D}]^d}{[\mathbf{A}]^a[\mathbf{B}]^b}$, where [**A**], [**B**], [**C**] and [**D**] are concentration values at any given time).

Since $\Delta G = -nFE_{\text{cell}}$ and $\Delta G^{\ominus} = -nFE^{\ominus}_{\text{cell}}$,

$$-nFE_{\text{cell}} = -nFE^{\ominus}_{\text{cell}} + RT\ln Q$$

Simplifying,

$$E_{\text{cell}} = E^{\ominus}_{\text{cell}} - \frac{RT}{nF}\ln Q \qquad \textit{(Nernst equation)}$$

The Nernst equation is often expressed in terms of base-10 logarithm of Q:

$$E_{\text{cell}} = E^{\ominus}_{\text{cell}} - \frac{2.303RT}{nF}\lg Q$$

At T = 298 K,

$$E_{\text{cell}} = E^{\ominus}_{\text{cell}} - \frac{0.0257}{n}\ln Q = E^{\ominus}_{\text{cell}} - \frac{0.0592}{n}\lg Q$$

where R = 8.314 J K^{-1} mol^{-1} and F = 96500 C mol^{-1}.

The Nernst equation enables us to calculate E_{cell} as a function of reactant and product concentrations in a redox reaction and vice versa.

The Nernst equation also helps us understand why the e.m.f. of a voltaic cell drops as it discharges. As reactants are converted to products, Q increases and hence E_{cell} decreases, eventually reaching 0 V. When E_{cell} = 0, the cell reaction has reached an equilibrium and there is no net transfer of electrons. At equilibrium, $Q = K$, where K is the equilibrium constant. The Nernst equation gives:

$$\begin{aligned} 0 &= E^{\ominus}_{\text{cell}} - \frac{RT}{nF}\ln K \\ E^{\ominus}_{\text{cell}} &= \frac{RT}{nF}\ln K \\ &= \frac{0.0257}{n}\ln K \ \ (\text{at } 298\text{ K}) \end{aligned} \qquad \textit{or} \qquad \begin{aligned} 0 &= E^{\ominus}_{\text{cell}} - \frac{2.303RT}{nF}\lg K \\ E^{\ominus}_{\text{cell}} &= \frac{2.303RT}{nF}\lg K \\ &= \frac{0.0592}{n}\lg K \ \ (\text{at } 298\text{ K}) \end{aligned}$$

In summary,

$\Delta G^{\ominus}$	$E^{\ominus}_{\text{cell}}$	K	**Reaction under standard conditions**
Negative	Positive	> 1	Spontaneous
0	0	= 1	At equilibrium
Positive	Negative	< 1	Non-spontaneous (reverse reaction is spontaneous)