

### Definitions

**Electromotive force** is the voltage generated by any source of electrical energy.

**Potential difference** is the difference in voltage between the anode and the cathode in a cell.

**Standard hydrogen electrode** is a reference half-cell that is used to measure the electrode potentials of other half-cell.

**Electrode potential** is the EMF that is generated by a half-cell when it is connected to the standard hydrogen electrode.

**Standard conditions** is a set of consistent reaction conditions that is used when measuring cell potentials.

**Standard electrode potential** is the EMF that is generated by a half-cell when it is connected to the standard hydrogen electrode under standard conditions.

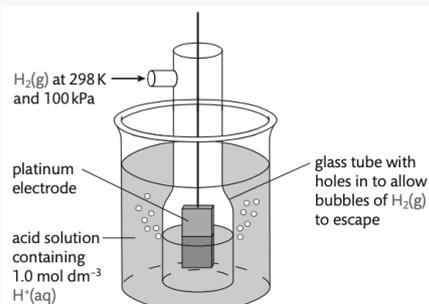
**Electrolysed** occurs when a compound is converted into simpler compounds using electrolysis.

**Electrolysis** is a process in which electrical current is used to make non-spontaneous redox reactions occur.

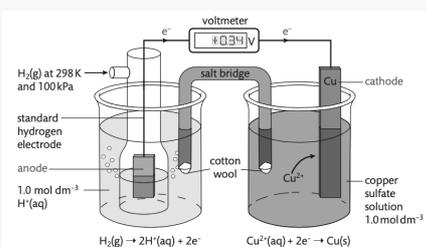
**Faraday constant** is the total charge carried by 1 mol of electrons. It has the symbol  $F$  and has a value  $96\,500\text{ C mol}^{-1}$ .

**Electroplating** is a process that uses electrolysis to deposit a layer of metal on another conducting object.

### Standard hydrogen electrode



### Sample setup for standard electron potential



### Electrolysis of aqueous solutions

When aqueous solutions are electrolysed, water can be oxidized to oxygen at the anode and reduced to hydrogen at the cathode.

#### Cathode

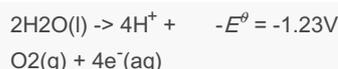
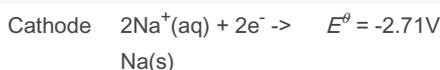
|        |  |         |
|--------|--|---------|
| Cation | $M^+(aq) + e^- \rightarrow M$                    | Reduced |
| Water  | $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ | Reduced |

#### Anode

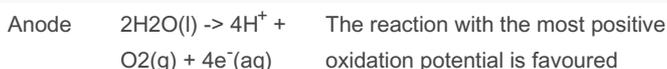
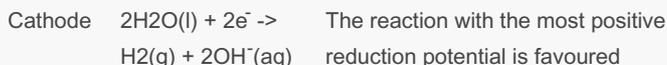
|       |   |          |
|-------|---|----------|
| Anion | $A^- \rightarrow A + e^-$                       | Oxidised |
| Water | $2H_2O(l) \rightarrow 4H^+ + O_2(g) + 4e^-(aq)$ | Oxidised |

### Electrolysis of NaCl(aq)

#### Possible reactions at electrodes

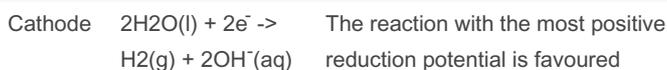


#### Low concentration of NaCl(aq)



Colourless  $H_2(g)$  bubbles at cathode, and colourless  $O_2(g)$  bubbles at anode

#### High concentration of NaCl(aq)



### Electrolysis of NaCl(aq) (cont)

Anode  $2\text{Cl}^- \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$  The two possible oxidation reactions have similar potentials, at high  $[\text{Cl}^-]$  the oxidation of  $\text{Cl}^-$  is favoured

Overall equation  $2\text{H}_2\text{O}(\text{l}) + 2\text{NaCl}(\text{aq}) \rightarrow \text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) + 2\text{NaOH}(\text{aq})$

Colourless  $\text{H}_2(\text{g})$  bubbles at cathode, green  $\text{Cl}_2(\text{g})$  bubbles at anode, and the pH increases as  $\text{OH}^-$  is formed

As the oxidation reactions take place at the anode, the sign of the electrode potentials has been reversed to convert it from a reduction potential to an oxidation potential.

### Quantitative Electrolysis

$\Delta G^\theta = -nFE^\theta$ . When  $E$  is positive,  $\Delta G$  is negative, indicating of a spontaneous process. When  $E$  is negative,  $\Delta G$  is positive, indicating of a non-spontaneous process. When  $E$  is 0,  $\Delta G$  is 0.

The Cell potential of a voltaic cell is related to the Gibbs free energy change for the overall redox reaction occurring in the cell:  $\Delta G^\theta = -nFE^\theta$

Where,

$\Delta G$  is the difference in the standard free energy of reactants and products,

$n$  is the number of moles of electrons transferred in the reaction,

$F$  is the Faraday constant,

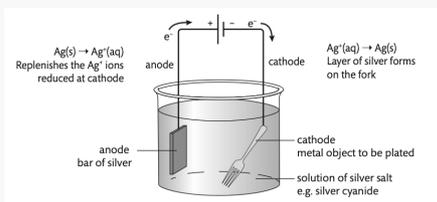
$E^\theta$  is the standard cell potential.

$-\Delta G^\theta$  is spontaneous, and  $+\Delta G^\theta$  is non-spontaneous.

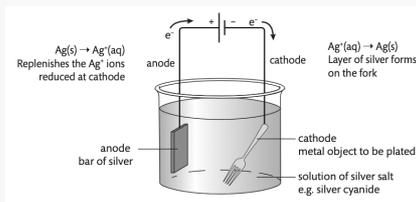
This means that the cell potential  $E^\theta_{\text{cell}}$ , also indicates if the redox reaction occurring is spontaneous or non-spontaneous.

| $E^\theta_{\text{cell}}$ | $\Delta G^\theta$ | Spontaneity            |
|--------------------------|-------------------|------------------------|
| positive                 | negative          | spontaneous            |
| negative                 | positive          | non-spontaneous        |
| zero                     | zero              | cell is at equilibrium |

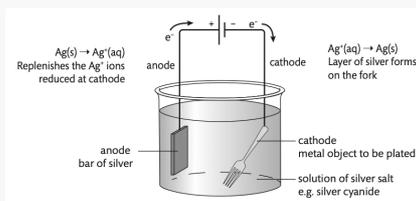
### Electroplating



### Electroplating



### Electroplating



### Voltaic cells

A voltaic cell generates an electromotive force (EMF) resulting in the movement of electrons from the anode (negative electrode) to the cathode (positive electrode) via the external circuit. The EMF is termed the cell potential ( $E$ ).

The electromotive force (EMF) of a voltaic cell:

is also known as the cell potential

is the potential difference between the anode and cathode

has the symbol  $E$

changes with different combinations of half cells.

### Standard hydrogen electrode

The standard hydrogen electrode (SHE) consists of an inert platinum electrode in contact with 1 mol  $\text{dm}^{-3}$  hydrogen ion and hydrogen gas at 100 kPa and 298 K. The standard electrode potential ( $E^\theta$ ) is the potential (voltage) of the reduction half-equation under standard conditions measured relative to the SHE. Solute concentration is 1 mol  $\text{dm}^{-3}$  or 100 kPa for gases. The  $E^\theta$  of the SHE is 0 V.

The standard hydrogen electrode(SHE):

- is a half-cell that can be combined with other half-cells to make a voltaic cells

- is used as a reference half-cell

- has a standard electrode potential of 0V

- has the redox equilibrium between aqueous  $\text{H}^+$  ions and  $\text{H}_2(\text{g})$

- uses an inert platinum electrode

- uses standard conditions

Electrode potentials are affected by temperature, concentration, and pressure. This means that a standard set of conditions must be used when measuring electrode potentials.



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### Standard hydrogen electrode (cont)

The standard conditions for electrochemical cells are:

- a concentration of  $1.0 \text{ mol dm}^{-3}$  for all solutions
- a pressure of 100kPa for all gases
- a temperature of 298K
- a platinum electrode if the half-cell does not include a metal

the standard electrode potential ( $E^\ominus$ ) of a half-cell is the EMF that is measured when it is connected to a SHE to make a voltaic cell under standard conditions.

$$E^\ominus_{\text{cell}} = E^\ominus_{\text{half-cell}} - E^\ominus_{\text{SHE}}$$

$$E^\ominus_{\text{SHE}} = 0, E^\ominus_{\text{cell}} = E^\ominus_{\text{half-cell}}$$

$E^\ominus_{\text{half-cell}}$  values:

- are always given for the reduction reaction of the half-cell
- do not depend on the number of electrons involved in the reduction reaction
- are positive when the half-cell is more easily reduced than the SHE
- are negative when the half-cell is harder to reduce than the SHE

When two half-cells are combined:

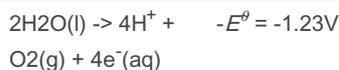
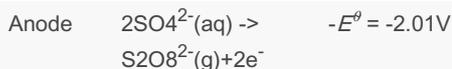
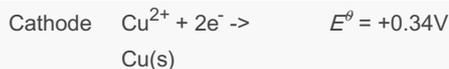
- reduction will occur at the half-cell with the more positive  $E^\ominus$  value.
- oxidation will occur at the half-cell with the more negative  $E^\ominus$  value.

$E^\ominus$  values are given for a large number of half-cells in section 24 of the IB data booklet.

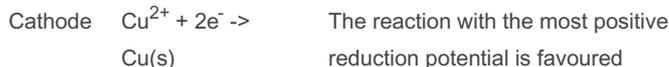
### Electrolysis of $\text{CuSO}_4(\text{aq})$

#### Inert electrodes

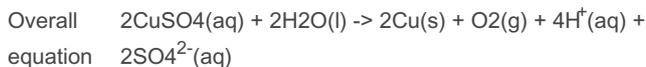
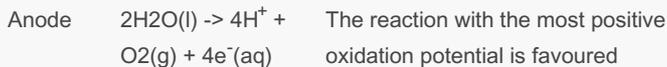
#### Possible reactions at electrodes



#### Actual reactions



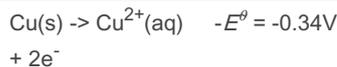
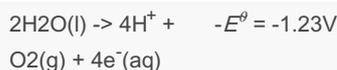
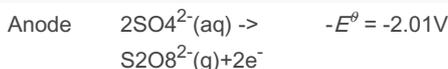
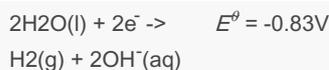
### Electrolysis of $\text{CuSO}_4(\text{aq})$ (cont)



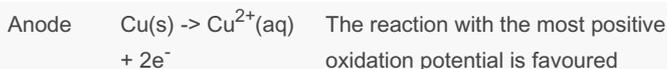
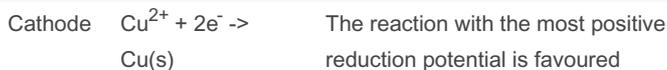
Pink/brown metal layer of  $\text{Cu(s)}$  forms on cathode, blue colour of solution fades as  $\text{Cu}^{2+}(\text{aq})$  is depleted, and colourless  $\text{O}_2(\text{g})$  bubbles at anode pH decreases as  $\text{H}^+$  formed

#### Copper Electrodes

#### Possible reactions at electrodes



#### Actual reactions



No overall change is observed

Pink/brown metal layer of  $\text{Cu(s)}$  forms on cathode, Cu anode reduces in mass as it oxidizes to  $\text{Cu}^{2+}$ , blue colour of solution is constant, and no change in pH.



### Product of electrolysis

*Current, duration of electrolysis, and charge on the ion affect the amount of product formed at the electrodes during electrolysis.*

The amount of product that is produced in an electrolysis reaction depends on:

- the amount of current
- the amount of time that the current is flowing
- the charge on the ion being oxidised or reduced.

*Determination of the relative amounts of products formed during electrolytic processes.*

Determine the total charge (Q) produced by the current flow:  $Q=It$ .

Determine the number of moles of electrons contained in the total charge:  $n(e^-) = Q/F$ .

Use the balanced oxidation (or reduction) reaction to determine the moles of product formed.

Determine the mass of product formed:  $m=nM$

### Electroplating

*Electroplating involves the electrolytic coating of an object with a metallic thin layer.*

Electroplating is when a layer of metal is deposited on an object made of a different metal or another conductive material such as graphite.

Electroplating uses an electrolytic cell that contains:

- a salt solution containing the cations of the metal to be deposited onto the object
- a cathode made of the conducting object that will be electroplated
- an anode made of the metal being electroplated.

