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 sued 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.

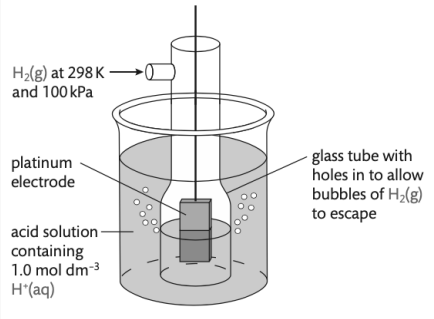
Electrolysedoccurs when a compound is converted into simpler compounds using electrolysis.

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

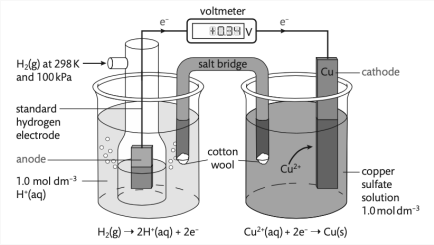
Faraday constant is the total charge carried by 1 mol of electrons. It has the symbol *F* and has a value 96 500 C mol^{-1}.

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	$2H2O(l) + 2e^- \rightarrow H2(g) + 2OH^-(aq)$	Reduced
Anode		
Anion	$A^- \rightarrow A + e^-$	Oxidised
Water	$2H2O(l) \rightarrow 4H^+ + O2(g) + 4e^-(aq)$	Oxidised

Electrolysis of NaCl(aq)

Possible reactions at electrodes		
Cathode	$2Na^+(aq) + 2e^- \rightarrow Na(s)$	$E^\theta = -2.71V$
	$2H2O(l) + 2e^- \rightarrow H2(g) + 2OH^-(aq)$	$E^\theta = -0.83V$
Anode	$2Cl^- \rightarrow Cl2(g) + 2e^-$	$-E^\theta = -1.36V$
	$2H2O(l) \rightarrow 4H^+ + O2(g) + 4e^-(aq)$	$-E^\theta = -1.23V$
Low concentration of NaCl(aq)		
Cathode	$2H2O(l) + 2e^- \rightarrow H2(g) + 2OH^-(aq)$	The reaction with the most positive reduction potential is favoured
Anode	$2H2O(l) \rightarrow 4H^+ + O2(g) + 4e^-(aq)$	The reaction with the most positive oxidation potential is favoured
Overall equation	2H2)(l) -> 2H2(g) + O2(g)	
Colourless H2(g) bubbles at cathode, and colourless O2(g) bubbles at anode		
High concentration of NaCl(aq)		
Cathode	$2H2O(l) + 2e^- \rightarrow H2(g) + 2OH^-(aq)$	The reaction with the most positive reduction potential is favoured

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Electrolysis of NaCl(aq) (cont)

Anode	$2Cl^- \rightarrow Cl_2(g) + 2e^-$	The two possible oxidation reactions have similar potentials, at high [Cl^-] the oxidation of Cl^- is favoured
Overall equation	$2H_2O(l) + 2NaCl(aq) \rightarrow 2H_2(g) + Cl_2(g) + 2NaOH(aq)$	

Colourless $H_2(g)$ bubbles at cathode, green $Cl_2(g)$ bubbles at anode, and the pH increases as 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, ΔG is negative, indicating of a spontaneous process. When E is negative, ΔG is positive, indicating of a non-spontaneous process. When E is 0, ΔG 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: $\Delta G^\theta = -nFE^\theta$

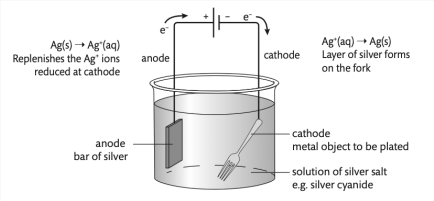
Where,
ΔG is the difference in the standard free energy of reactants and products,
n is the number of moles of electrons transferred in the reaction,
F is the Faraday constant,
E^θ is the standard cell potential.

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

This means that the cell potential E^θcell, also indicates if the redox reaction occurring is spontaneous or non-spontaneous.

E^θcell	ΔG^θ	Spontaneity
positive	negative	spontaneous
negative	positive	non-spontaneous
zero	zero	cell is at equilibrium

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 electode (SHE) consists of an inert platinum electrode in contact with 1 mol dm–3 hydrogen ion and hydrogen gas at 100 kPa and 298 K. The standard electrode potential (E) is the potential (voltage) of the reduction half-equation under standard conditions measured relative to the SHE. Solute concentration is 1 mol dm–3 or 100 kPa for gases. The E 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 H^+ ions and $H_2(g)$
- 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.

The standard conditions for electrochemical cells are:
- a concentration of 1.0mol 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^θ) 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^θcell = E^θhalf-cell - E^θSHE
E^θSHE=0, E^θcell = E^θhalf-cell

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Standard hydrogen electrode (cont)

E^{θ}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 induced 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^{θ} value.
- oxidation will occur at the half-cell with the more negative E^{θ}value.

E^{θ} values are given for a large number of half-cells in section 24 of the IB data booklet.

Electrolysis of CuSo4(aq)

Inert electrodes

Possible reactions at electrodes

Cathode	Cu^{2+} + $2e^{-}$ -> Cu(s)	E^{θ} = +0.34V
	2H2O(l) + $2e^{-}$ -> H2(g) + $2OH^{-}$(aq)	E^{θ} = -0.83V
Anode	$2SO4^{2-}$(aq) -> $S2O8^{2-}$(g)+$2e^{-}$	$-E^{\theta}$ = -2.01V
	2H2O(l) -> $4H^{+}$ + O2(g) + $4e^{-}$(aq)	$-E^{\theta}$ = -1.23V

Actual reactions

Cathode	Cu^{2+} + $2e^{-}$ -> Cu(s)	The reaction with the most positive reduction potential is favoured
Anode	2H2O(l) -> $4H^{+}$ + O2(g) + $4e^{-}$(aq)	The reaction with the most positive oxidation potential is favoured
Overall equation	2CuSO4(aq) + 2H2O(l) -> 2Cu(s) + O2(g) + $4H^{+}$(aq) + $2SO4^{2-}$(aq)	

Pink/brown metal layer of Cu(s) forms on cathode, blue colour of solution fades as Cu2+(aq) is depleted, and colourless O2(g) bubbles at anode pH decreases as H^{+} formed

Copper Electrodes

Possible reactions at electrodes

Electrolysis of CuSo4(aq) (cont)

Cathode	Cu^{2+} + $2e^{-}$ -> Cu(s)	E^{θ} = +0.34V
	2H2O(l) + $2e^{-}$ -> H2(g) + $2OH^{-}$(aq)	E^{θ} = -0.83V
Anode	$2SO4^{2-}$(aq) -> $S2O8^{2-}$(g)+$2e^{-}$	$-E^{\theta}$ = -2.01V
	2H2O(l) -> $4H^{+}$ + O2(g) + $4e^{-}$(aq)	$-E^{\theta}$ = -1.23V
	Cu(s) -> Cu^{2+}(aq) + $2e^{-}$	$-E^{\theta}$ = -0.34V

Actual reactions

Cathode	Cu^{2+} + $2e^{-}$ -> Cu(s)	The reaction with the most positive reduction potential is favoured
Anode	Cu(s) -> Cu^{2+}(aq) + $2e^{-}$	The reaction with the most positive oxidation potential is favoured

No overall change is observed

Pink/brown metal layer of Cu(s) forms on cathode, Cu anode reduces in mass as it oxidizes to 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: $m=nM$

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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.

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