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Electrochemistry

Definitions

Redox reactions – reactions involving the transfer of electrons

Oxidation – the loss of electrons

Reduction – the gain of electrons

Oxidising agent – a substance that accepts electrons

Reducing agent – a substance that donates electrons

Anode – the electrode where oxidation takes place

Cathode – the electrode where reduction takes place

Electrolyte – a substance that can conduct electricity by forming free ions when molten or when dissolved in solution

Dissociation – the splitting of an ionic compound into its ions

Oxidation numbers

The oxidation number is the number given to a bonded atom to show how oxidised or reduced the atom is

Pure elements and diatomic elements	0
Hydrogen	+1 (except when bonded to a metal then -1)
Oxygen	-2 (except in peroxides like H_2O_2 where it is -1 and when bonded to fluorine then +2)
Group 17	-1
Group I	+1
Group II	+2
Group III	+3
Monoatomic ions / polyatomic ions as whole	Same as the charge
Transitional metals	Indicated with stock notation
In neutral compound, sum of oxidation numbers is 0	
In polyatomic ions the sum of oxidation numbers = to overall charge of ions	

Redox reactions

- Oxidation and reduction take place simultaneously
- **O**xidation **I**s the **L**oss of e, **R**eduction **I**s the **G**ain of e
- There is NO SUBTRACTION of electrons when writing redox reactions

Redox table

shows the half cell reactions, 1 oxidation, 1 reduction

→ reduction

← oxidation

Values

- SHE values – standard hydrogen electron (reference number)
- Emf value
- Electrodes in which the oxidizing agent can be reduced better than H^+ are assigned a positive sign.
- Chemical species that can undergo reduction better than H^+ , have a positive value.
- Electrodes in which the reducing agent is oxidized better than H_2 are assigned negative signs.
- Chemical species that can undergo oxidation better than H_2 have a negative value

Determining the overall balanced equation using the Redox table

1. Identify oxidising agent and reducing agent by circling them on redox table
2. Write down reduction half reaction
3. Write down oxidation half reaction
4. Compare number of electrons in each equation
5. Find lowest common multiple and multiply each equation by multiple to get equal number of electrons in both
6. Combine both equations into one – leaving out electrons
7. Add spectator ions **if instructed**

Spontaneous reactions

- Strong oxidising agent
- Strong reducing agent
- Energy is released
- Chemical energy is converted to electrical energy (in cell)

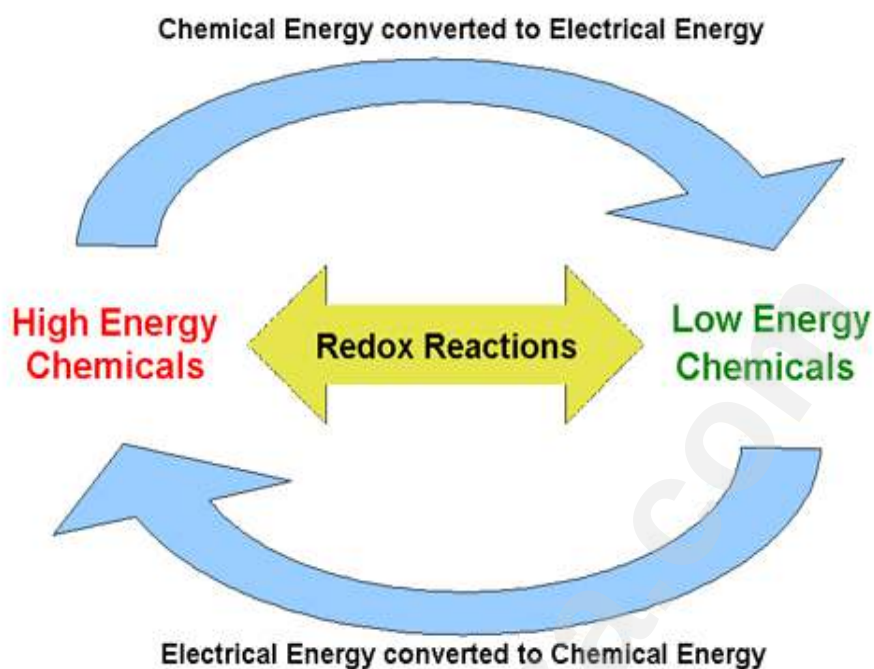
How to know if it is spontaneous with Redox table

- Bottom Left Top Right
- Positive gradient between reactants

Cell with spontaneous reaction is galvanic cell

Nonspontaneous reactions

- Requires electrical current to make it happen
- Weak oxidising agent
- Weak reducing agent
- Electrical energy converted to chemical energy
- Negative gradient between reactants on Redox table



Electricity in relation to Redox

In order to use the current that is generated in redox reactions, there needs to be separate places where oxidation and reduction take place

Electrolyte examples

- Sodium chloride
- Potassium nitrate
- Ionic substances that are molten or in aqueous solution

Electrodes

- A solid electric conductor through which allows electric current to enter or leave an electrolytic cell or other medium.
- It is where the reactions take place!
- E.g. Carbon or platinum
- Anode
 - AN OX (anode is where oxidation takes place)
 - Connected to positive end of battery in electrolytic cell
 - Loses mass in electrolytic cell
- Cathode
 - RED CAT (reduction takes place at cathode)
 - Cations are attracted to it
 - Connected to negative side in electrolytic cell
 - Gains mass in electrolytic cell – where plating takes place in electroplating

Emf

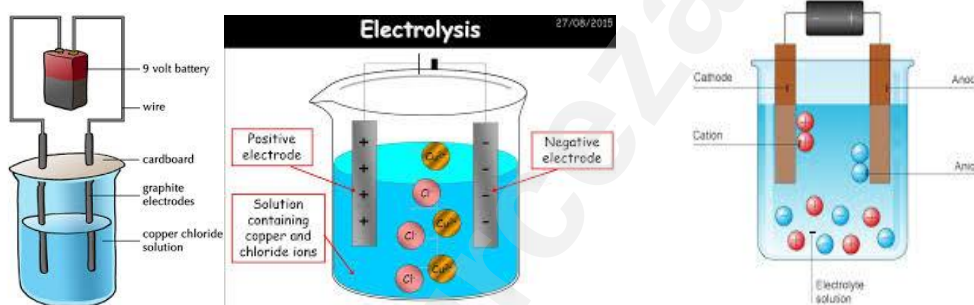
- Determined by half cell reactions
- Reduction half-cell potential – oxidation half cell potential
- $E_{Red}^{\circ} - E_{Ox}^{\circ}$
 - if positive – spontaneous reaction
 - if negative – nonspontaneous reaction
- as chemical reactants in the cell run out, the emf will decrease
- no more chemical reactants left to react then cell is flat

Types of cells

Galvanic / voltaic cells

- spontaneous reactions
- chemical energy converted to electrical energy

Electrolytic cells



- non spontaneous reactions (energy supply required)
- electrolysis
 - decomposition of a substance by electric current
 - voltage increased until electrons flow in opposite directions
 - in pure compounds
 - must be in molten / liquid state
 - electrodes normally graphite
 - cations are reduced at the cathode to metal element.
 - anions oxidized at anode to non-metal element.
- electrical energy to chemical energy
- **cations** pick up electrons from the **cathode** (-) and are **reduced**,
- **anions** release electrons to the **anode** (+) and are **oxidized**
- selective discharge
 - if two substances are in the solution normally the one with the stronger reducing agent would undergo oxidation however if one is highly concentrated then that one will be reduced even if it has a lower oxidising ability

Predicting whether a metal will dissolve in an acid

- will dissolve if oxidation of metal ion is easier than the reduction of $H^+(aq)$
- will dissolve if metal ion reduction lies above H^+ reduction on Redox table

Corrosion / oxidation of metal

- a spontaneous reaction
- many metals will develop a thin layer of metal oxide on the outside that prevents further oxidation
- metals that are relatively difficult to oxidise
 - copper
 - gold
 - silver
 - platinum

Corrosion of iron

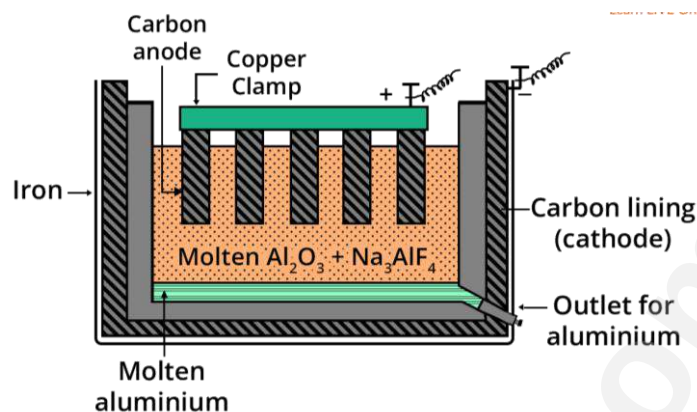
- anodic regions
 - regions of steel alloy where iron is easily oxidised
- cathodic regions
 - areas resistant to oxidation
 - electrons flow through anodic regions and react with oxygen
- water and oxygen need to be present
- salt acts as a catalyst and speeds up corrosion by increasing electron conduction from anodic to cathodic regions
- Rusting
 - Hydrated iron (III) oxide
 - Moisture must be present as water is a reactant and it is required for flow between cathode and anode
 - Electrolytes promote rusting as they enhance current flow
 - Acids also promote rusting as lower pH = lower E°_{red}

Prevention of corrosion

Coating metal that forms oxide coat to protect metal that would not develop protective coat

- Alloying
 - The addition of metals that change steel's reduction potential
 - E.g. Nickel and chromium alloyed to iron
- Galvanising
 - Placing a "sacrificial" metal that is more easily oxidised on top of the original metal to protect it
 - E.g. Zinc / aluminium over iron
 - Zinc or aluminium easily form Oxide which is actually the greater protection and forms impenetrable layer
- Cathodic protection
 - When an anode made from an easily oxidised metal is connected to a less easy oxidising metal to keep it from experiencing corrosion
 - This anode will corrode quickly and needs to be replaced periodically
 - E.g. Magnesium as anode to iron pipe or titanium as anode to steel ship's hull

Extraction of aluminium (Hall-Heroult Process)



- The electrolyte is molten Al_2O_3 or Alumina which has been extracted from bauxite (ore)
- The process requires very high currents (40 000A a day) to melt the alumina which makes aluminium extraction very expensive
- To lower the melting point of the alumina (and lower the cost), cryolite (Na_3AlF_6) is used to dissolve the alumina
- Al^{3+} ions are reduced at the cathode, producing molten Al which is tapped off at the bottom of the cell
- O^{2-} ions are oxidised at the anode, producing O_2 gas
- The O_2 produced can react with the carbon anodes used, this results in a combustion reaction that produces CO_2 and leads to the disintegration of the anodes which means that they must be replaced regularly – this adds to the expense

The equations:

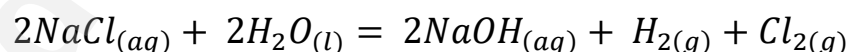
Oxidation $\frac{1}{2}$ reaction: $2\text{O}^{2-} \rightarrow \text{O}_2 + 4\text{e}^-$

Reduction $\frac{1}{2}$ reaction: $\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$

Overall reaction: $4\text{Al}^{3+} + 6\text{O}^{2-} \rightarrow 2\text{Al} + 3\text{O}_2$

The chlor-alkali industry

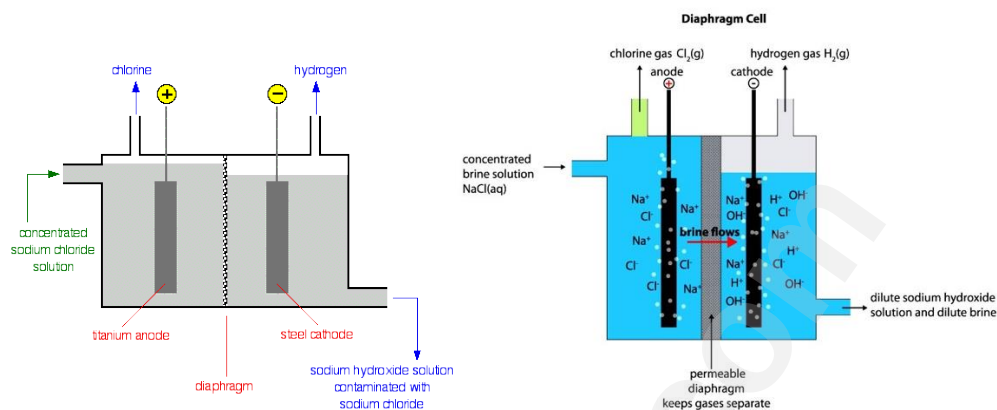
The industry exploits the following equation:



Cl_2 (anode)	NaOH (caustic soda)	H_2 (cathode)
Purify water	Makes soap and cleaning products	Saturation of double bonds – making margarine
Disinfectant	Purify bauxite	Making ammonia
Production of HOCl (used in drinking water)	Make paper	Fuel cells
Production of food, paper, paints, PVC, etc.	Make rayon	

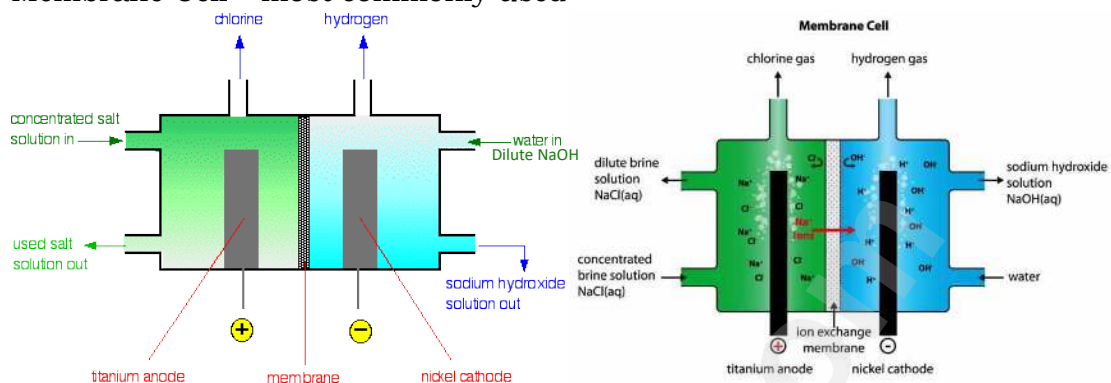
The three different cells

1. Diaphragm Cell



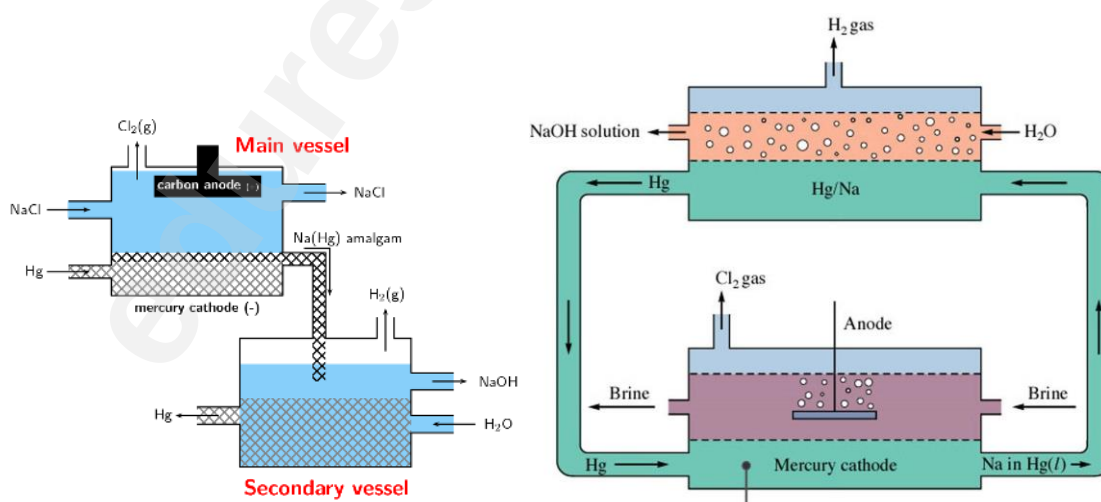
- Most important part is the diaphragm that separates the cathode and the anode compartment
 - Usually made of asbestos which is porous and allows the electrolyte to pass through to pass slowly from anode to cathode
 - Pressure gradient is maintained to ensure flow of electrolyte remains anode to cathode and back flow is limited
- Concentrated brine is pumped into the anode compartment where the oxidation of chloride ions will take place
 - Although oxidation of the water is preferential under standard conditions, the concentration of the NaCl ensures that the chloride ions are oxidised in preference
 - Chlorine gas is collected from anode compartment and stored separately
- Electrolyte (now containing Na⁺ ions and water) moves to cathode compartment where water is reduced to form H₂ gas
 - H₂ gas is collected from cathode compartment and stored separately
- Remaining Na⁺ ions and OH⁻ ions combine to form NaOH which is tapped out of the cell
- Equations
 - Oxidation $\frac{1}{2}$ reaction: $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$
 - Reduction $\frac{1}{2}$ reaction: $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^-$
 - Overall reaction: $2\text{Cl}^- + 2\text{H}_2\text{O} \rightarrow \text{H}_2 + \text{Cl}_2 + 2\text{OH}^-$
- Limitations
 - Asbestos is toxic and very dangerous to use and dispose of
 - Cl⁻ ions can pass through the diaphragm into the cathode compartment and contaminate the NaOH with NaCl – the NaOH must then be purified further before use which adds to expenses
 - Although the pressure gradient prevents back flow, it is possible for the OH⁻ ions produced to move back into the anode compartment and be further oxidised to form O₂. This contaminates the Cl₂ collected requiring further purification and cost

2. Membrane Cell – most commonly used



- small change in design but huge increase in effectiveness
- diaphragm replaced by ion-selective membrane which only allows positive ions to pass between compartments which negates the need for a pressure gradient
- increase in purity of NaOH produced
- processes at anode and cathode are identical to the diaphragm cell
- ion-selective membrane prevents negative ions from crossing between compartments
 - Cl^- ions cannot travel into cathode compartment and contaminate the NaOH
 - OH^- ions cannot travel into anode compartment and be oxidised to form O_2
- Most effective cell in chlor-alkali industry
- Equations
 - Oxidation $\frac{1}{2}$ reaction: $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$
 - Reduction $\frac{1}{2}$ reaction: $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^-$
 - Overall reaction: $2\text{Cl}^- + 2\text{H}_2\text{O} \rightarrow \text{H}_2 + \text{Cl}_2 + 2\text{OH}^-$

3. Mercury Cell



- When the cathode is mercury, the lower energy option for a cathode reaction ceases to be reduction of hydrogen and instead becomes $\text{Na}^+ + \text{e}^- \rightarrow \text{Na(Hg)}$
- Mercury cell provides the ultimate way of keeping the chlorine away from the sodium hydroxide, since no sodium hydroxide has been made yet

- Concentrated brine is pumped into the first compartment where the Cl^- ions are oxidised to form Cl_2 at the anode
- The cathode is made from liquid mercury which attracts the Na^+ ions, which are preferentially reduced to form a sodium-mercury amalgam, Na(Hg)
- Amalgam is then transported into a second compartment where it is reacted with water
 - The Na will react as predicted with water according to the equation – $\text{Na} + \text{H}_2\text{O} \rightarrow \text{NaOH} + \text{H}_2$
 - The Hg will not react with water and can be recycled back into the first compartment
- Products remain NaOH , Cl_2 , and H_2 , albeit produced slightly differently
- Chlorine gas produced is very pure
- Equations
 - Oxidation $\frac{1}{2}$ reaction: $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$
 - Reduction $\frac{1}{2}$ reaction: $\text{Na}^+ + \text{e}^- + \text{Hg} \rightarrow \text{Na(Hg)}$
 - Net ionic equation: $2\text{Cl}^- + 2\text{Na}^+ \rightarrow 2\text{Na} + \text{Cl}_2$
- Limitations
 - Mercury is very toxic and is difficult to work with safely
 - > Very dense and once in lungs it cannot be coughed up
 - Cell operates with higher energy requirements than the others and as such is seldom used industrially anymore

Summary

Diaphragm	Membrane	Mercury
Low energy requirements	NaOH is more pure than in diaphragm cell	Very pure Cl_2 gas produced
Asbestos is toxic and needs to be replaced regularly	Most energy efficient	Mercury is toxic and inevitably escapes to products and environment
NaOH contaminated with NaCl – needs to be repurified	No toxic components	High energy requirements
Cl_2 contaminated with O_2	Cheapest cell to run	Not really used anymore
Not very cost effective		

Quantitative Electrolysis

- The mass of a substance produced at an electrode during electrolysis is proportional to the time over which a constant electric current is applied and the strength of the electric current
- Amount of substance produced is proportional to the number of electrons transferred from anode to cathode

Charge of an electron = $1,6 \times 10^{-19} \text{ C}$
 Charge of 1 mole of e^- = $(6,02 \times 10^{23})(1,6 \times 10^{-19}) \approx 96\,500 \text{ C.mol}^{-1}$
 $F = 96\,500 \text{ C.mol}^{-1}$
- A Faraday (F) is the quantity of electric charge carried by 1 mole of electrons

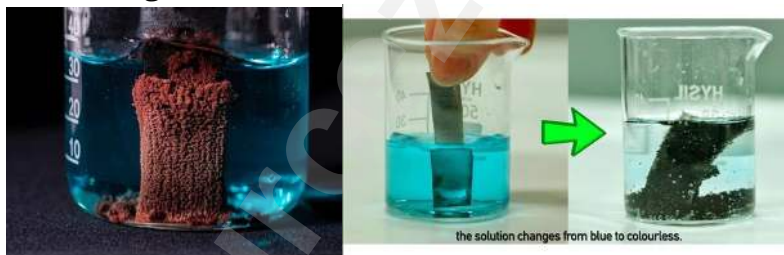
- Formulae: $q = It$
 $q = nF$

Galvanic Cells

Direct electron transfer

- Galvanic cells convert chemical energy to electrical energy through spontaneous electrochemical process
- Electrons readily move from a good reducing agent to a good oxidising agent
- Example

- When placing a strip of Zinc metal into a solution of Cu^{2+} ions
- A spontaneous transfer of electrons takes place between the Zn metal and the Cu^{2+} ions
- $\text{Zn}_{(s)} + \text{Cu}_{(aq)}^{2+} \rightarrow \text{Zn}_{(aq)}^{2+} + \text{Cu}_{(s)}$
- The Zn metal disintegrates and a copper coloured solid is formed in its place and the blue colour of the solution starts to become clear due to the concentration of the Cu^{2+} ions decreasing and Zn^{2+} ions are colourless

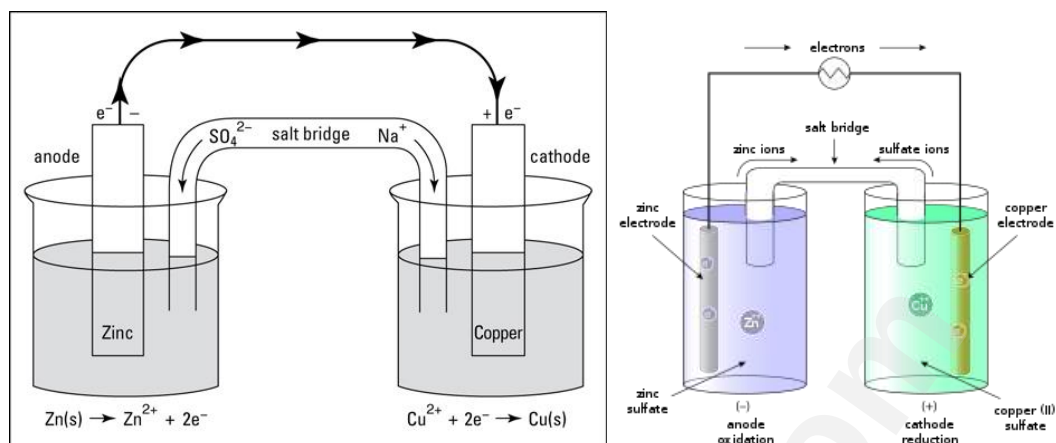


- Zn is a good reducing agent and therefore readily loses electrons (E^0 value is very negative meaning it does not attract electrons towards itself strongly)
- Cu^{2+} is a good oxidising agent and therefore readily gains electrons (E^0 value is positive meaning it strongly attracts electrons towards itself)
- Electrons will readily move from where they are loosely attracted to where they are strongly attracted
- The E_{cell}^0 value = $E_{\text{cat}} - E_{\text{an}} = 0,34 - (-0,76) = +1,10 \text{ V}$ which is a positive value and therefore the reaction is spontaneous
- However if a piece of copper metal is placed into a solution of Zn^{2+} ions, no reaction would take place
 - > Zn^{2+} is a poor oxidising agent and does not have the strength to pull electrons away from the Cu atom
 - > The E_{cell} for this reaction would be $-1,10 \text{ V}$ therefore the reaction would not occur spontaneously

Indirect electron transfer

The Daniel Cell – example of galvanic cells

Since electrons spontaneously move from Zn to Cu^{2+} ions, if we separate these two species with a low resistance wire, we can force the electrons to travel through the connecting wire and create a current flow. This is the basic principle of a battery



- Zn is a better reducing agent (has a more negative E^0 value / is more likely to be oxidised) than Cu and so oxidation will take place at the Zn electrode
 - The Zn electrode is the anode
 - The Zn electrode submerged in the electrolyte (of Zn^{2+} ions) is the Zn $\frac{1}{2}$ cell or the anode $\frac{1}{2}$ cell
 - Since the Zn is losing electrons from its atoms, the surface of the Zn electrode is (relatively) negative
- Cu^{2+} is mostly likely to accept electrons, and so the copper electrode is the site of reduction
 - The Cu electrode is the cathode
 - The Cu electrode submerged in the electrolyte (of Cu^{2+} ions) is the cathode $\frac{1}{2}$ cell or the Cu $\frac{1}{2}$ cell
 - Since the Cu^{2+} ions are continually accepting electrons from the electrode, there is a (relative) positive charge on the electrode
- The electrons travel from Zn to the Cu^{2+} via the external circuit (the connecting wire)
 - In all galvanic cells, electrons will always travel from the anode $\frac{1}{2}$ cell to the cathode $\frac{1}{2}$ cell
 - Electrons do not move through the solution or the salt bridge, they can only move through the external circuit
 - A voltmeter can be placed between the $\frac{1}{2}$ cells to measure the E^0_{cell} value, but this would prevent current flow
- A salt bridge is necessary to allow a complete circuit to exist
 - A salt bridge is usually an inverted U tube, plugged with cotton wool, containing an inert electrolyte, such as KNO_3 or Na_2SO_4
 - The salt bridge can also be made from string or filter paper soaked in the electrolyte
- The cell will continue to deliver current until each of the reactions taking place in the half-cell reach equilibrium
 - As the Zn is oxidised, more and more Zn^{2+} is produced and according to LCP, the equilibrium point will shift to reduce the Zn^{2+} concentration and therefore the reduction of the Zn^{2+} would begin to occur instead of further oxidation of Zn
 - Eventually, a point will be reached where the rate of oxidation of the Zn is equal to the rate of the reduction of Zn^{2+}

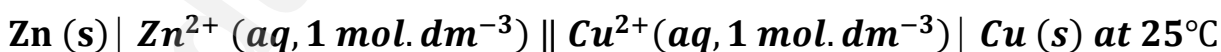
- This means that no electrons will be transferred to the Cu $\frac{1}{2}$ cell and the cell will stop functioning
 - Once the half cells reach equilibrium, the potential difference between the cells would be zero
- Equations
- The oxidation $\frac{1}{2}$ equation: $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$
 - The reduction $\frac{1}{2}$ equation: $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$
 - Overall ionic equation: $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$
 - The E°_{cell} for this cell is $E_{\text{cell}} = E_{\text{cat}} - E_{\text{an}} = +0,34 - (-0,76) = +1,10\text{V}$

Cell notation in a galvanic cell

Certain conventions should be used:

1. Reaction at anode (the oxidation reaction) is written on the left side while the reaction at the cathode (the reduction reaction) is on the right side and the two reactions are separated by a salt bridge
2. Cell notation is written using the following order convention
reducing agent | oxidised species || oxidising agent | reduced species
 Or
Electrode | reducing agent | oxidised species || oxidising agent | reduced species | electrode
3. A single vertical line (|) represents a phase boundary and is drawn between two chemical species that are in different phases but in contact with each other
4. When both chemical species in a half-cell are in the same phase they are separated by a comma
5. The salt bridge is represented by 2 vertical line (||) and the identity of the salt bridge does not need to be shown in the cell notation
6. Spectator ions and numbers used for balancing are not shown
7. State symbols need only be shown when requested (s, aq, g, l)
8. If requested, standard conditions are given in brackets after
 - > Aqueous solution of ions – (aq, 1 mol.dm⁻³)
 - > Gases – (g, 1atm)
 - > Temperature - (at 25°C) shown at the end of cell notation

Example:



The Salt Bridge

Essential component of any galvanic cell

Two main functions

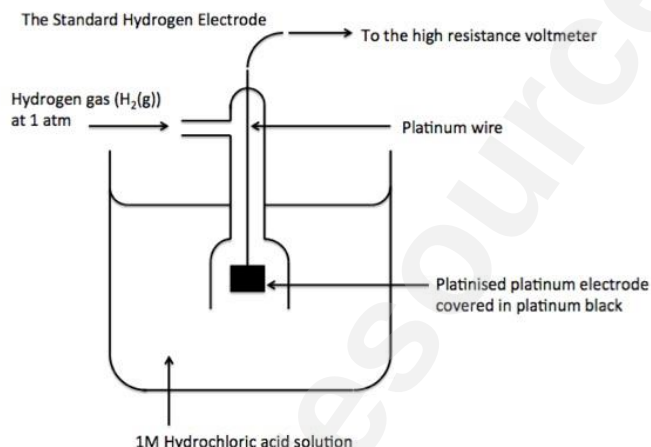
1. Completes the circuit by allowing charged ions to move towards the two half cells
2. Maintains cell neutrality by neutralising the build-up of charge in each half cell

How does it work?

- In the anode half-cell, oxidation is taking place and so positive ions are being produced. This causes a build-up of positive charge in the electrolyte. If left unchecked, the electrons would no longer move readily away from the increasingly positively charged half-cell
- Similarly, in the cathode half-cell, reduction is taking place and removing the positive ions from solution. The $\frac{1}{2}$ cell therefore becomes negative, and electrons would cease to move toward it
- The salt bridge contains positive and negative ions
 - Negative ions migrate into the anode $\frac{1}{2}$ cell to neutralise the build up of positive ions produced by oxidation
 - Positive ions migrate into the cathode $\frac{1}{2}$ cell to neutralise the excess of negative ions left over after reduction

The standard hydrogen electrode

The standard electrode potential table was created by deeming how likely the substance would reduce in comparison to hydrogen gas. In order to generate the E^0 values, each $\frac{1}{2}$ cell was connected to a standard hydrogen half-cell, and the potential difference measure under standard conditions



The standard hydrogen half-cell consists of:

- A platinum wire electrode over which H_2 gas is bubbled at 1 atmosphere pressure
 - Pt is used as it is unreactive and absorbs H_2 gas effectively and because it catalyses the reaction between H_2 and H^+
- A 1 mol. dm^{-3} solution of H^+ ions
- At 25°C

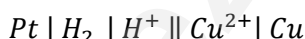
When being used to calculate Standard Electrode Potentials it must be connected as the anode

- It will always be connected to the negative terminal of the voltmeter
- Substances which are better oxidising agents (more likely to be reduced) than H^+ ions will pull electrons away from the hydrogen $\frac{1}{2}$ cell. This results in a positive voltmeter reading and a positive E^0 value

- Substances which are worse oxidising agents (less likely to be reduced) than H^+ , will have their electrons pulled away by the H^+ and so the electrons will travel towards the hydrogen $\frac{1}{2}$ cell. This results in a negative voltmeter value and a negative E^0 value
- The E^0 value for the reduction of H^+ is 0V since it would be comparing the likelihood of reduction of H^+ to itself (electrons will not transfer between the two $\frac{1}{2}$ cells)
- The Standard Hydrogen Electrode is connected as the anode however this is not necessarily the site of oxidation. That is determined by the chemical properties of the substances involved. Connecting the Standard Hydrogen Electrode as the anode only changes the sign of the voltmeter reading, allowing us to determine if the substance in the other $\frac{1}{2}$ cell is being oxidised or reduced

Cell notation and the Standard Hydrogen Electrode

- Standard Hydrogen Electrode is always the anode
- Therefore when writing the cell notation for cells containing the Standard Hydrogen Electrode, it will always be written on the left side
- Example:



The voltmeter reading would be +0,34V

- For Zn



The voltmeter reading would be -0,76V. the negative sign tells us that the electrons are not moving from H_2 to the Zn^{2+} but are in fact moving from the Zn to the H^+ . If asked for the oxidation $\frac{1}{2}$ reaction, the answer would be

$$Zn \rightarrow Zn^{2+} + 2e^-$$

Galvanic cells and equilibrium considerations

The changing the concentration of the electrolyte can change the likelihood of reduction or oxidation of a species

Example : $Cu^{2+} + 2e^- \rightleftharpoons Cu$ $E^0 = +0,34 V$

- if the concentration of the Cu^{2+} solution is increased, according to LCP, the reduction of Cu^{2+} will be favoured
- Relative to a standard hydrogen electrode, the Cu $\frac{1}{2}$ cell would now be even more positive and so the E_{cell} value would become more positive
- A decrease in concentration of Cu^{2+} would, conversely, favour the oxidation of Cu and make the E_{cell} value less positive
- With time, this $\frac{1}{2}$ cell will reach equilibrium, and no further (net) reduction or oxidation will take place. The E^0 value tends to zero (this is true of all $\frac{1}{2}$ cells and is why batteries eventually stop working)

in galvanic cells, any changes to the $\frac{1}{2}$ cells (in terms of concentration, pressure, and temperature) will affect the EMF of the galvanic cell. For example, in the Daniel cell if the Cu^{2+} concentration is increased in the cathode $\frac{1}{2}$ cell, according to the above reasoning, the E_{cat} will increase and therefore the EMF value will also increase

General rule:

- Changes that favour oxidation at the anode and reduction at the cathode INCREASE the EMF of the cell
- Changes that favour reduction at the anode and oxidation at the cathode DECREASE the EMF of the cell

The only factors that can affect the EMF of a galvanic cell are those factors which change the likelihood of reduction or oxidation of the species in the $\frac{1}{2}$ cells. The concentration of electrolytes, temperature and pressure (where appropriate) may change the likelihood of reduction, thereby changing the E^0 value for the $\frac{1}{2}$ cell and affecting the EMF

Changing factors that increase the rate of electron transfer or ion movement do not change the EMF but can change the efficiency of the cell and the amount of current it can deliver. These factors are:

- Increasing electrode surface area – increases the rate of oxidation or reduction and so would increase the current delivery by the cell, but the EMF would not change
- Increasing the size of the salt bridge – increases the ease with which ions transfer between $\frac{1}{2}$ cells and efficiency lowers the internal resistance of the cell. Again, current delivery would increase but there would be no effect on EMF