

Oxidation and Reduction (9.1)

- Oxidation

- Defined as: the addition of oxygen to a substance or the loss of hydrogen from a substance.



- The magnesium has gained oxygen and we say that this magnesium has been oxidised.



- The HCl loses hydrogen and therefore is oxidised.

- Redox reactions are reactions where oxidation & reduction occur.

- Reduction

- Reduction is the opposite of oxidation, and is defined as: the loss or removal of oxygen from a substance or the addition of hydrogen to a substance.



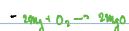
- The copper (II) oxide loses oxygen to the hydrogen gas, meaning that the Cu will be reduced and the H₂ will be oxidised.



- The C₂H₅O₂ (ethanoic acid) will gain hydrogen, meaning it will be reduced.

- One definition of oxidation change is the loss of electrons from a substance.

- One definition of reduction change is the gain of electrons by a substance.



- The Mg will still be oxidised, but in terms of electrons, each Mg molecule will gain 2 electrons from each oxygen molecule.



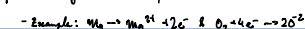
- Full oxidation equation is: $2\text{Mg} + \text{O}_2 + 4e^- \rightarrow 2\text{Mg}^{2+} + 4e^- + 2\text{O}^{2-}$



- The new definition of oxidation and reduction means that reactions where oxygen and hydrogen aren't involved will also count as redox reactions.



- Half-reactions only describe one of the two reactions that count occur together.



- To have a balanced ion-electron equation, you have to have the same oxidation amount on both sides of the equation.

- Illustration: Photochromic lenses

- Photochromic lenses use chemical changes to compensate for changes in brightness.

- Sun glass is made photochromic by adding small amounts of silver chloride (AgCl) and copper (II) chloride to the ordinary glass as it was.

- This traps the crystals within the structure of the glass.

- When sunlight hits the lenses, the light causes to form silver atoms, which make the lenses darker.



- The chloride particles will react with the $\text{Cu}^{2+}\text{Cl}_6^{4-}$ forming copper (II) ions and chloride ions:



- Once intense light stops, the copper (II) ions are reduced by silver atoms to re-form silver chloride and copper (II) chloride.



- Oxidation numbers

- In the reaction: $\text{AsO}_3^{3-} + \text{O}_2 \rightarrow \text{AsO}_4^{3-}$, it is said that sulfur has been oxidised, but the product compound isn't electrically charged.

- The concept oxidation number, is used to combine the old & new method.

- Making the definition of oxidation: the increase in oxidation number.

- And that of reduction: a decrease in oxidation number.

- The rules of oxidation are:

- The oxidation number of any uncombined element is zero.

- E.g. O_2 oxidation number 0.

- For a simple ion, the oxidation number of the ion is equal to the charge on the ion.

- E.g. Cl^- & Fe^{2+} , have the oxidation number -1 & +2 respectively.

- NOTE: the charges are written with the signs (+/-) after them, but for the oxidation number, they have to be before the number.

- For a compound, the sum of the oxidation numbers of the elements is zero.

- E.g. NaCl [$\text{Na}^{+}\text{Cl}^{-}$] the sum of the oxidation numbers is: $(+1) + (-1) = 0$.

- In a polyatomic ion (an ion with more than just one atom in it), will have an oxidation number which is equal to the sum of the charge on the ion.
 - E.g. nitrate ion, NO_3^- , the sum of the oxidation numbers is -2, that is, $(+5) + (-2 \times 3) = -2$.
- Hydrogen oxidation number is always +1 except when it's bonded with a reactive metal (Group 1 & 2 metals).
 - E.g. NaH ($\text{Na}:+1$, $\text{H}:-1$)
- The reason that with transition metals hydrogen is +1, is because of the fact that transition metals have oxidation states that are more than +1 or +2, meaning that hydrogen can't reduce the oxidation number.
- The oxygen number is always -2, except when it's in H_2O_2 (hydrogen peroxide) where it's -1, or when it's bonded with fluorine in OF_2 where it's +2.
- In covalent bonding, the more electronegative element is given the negative oxidation number while the less electronegative one has a positive oxidation number.
 - E.g. ClF , where chlorine is less electronegative than fluorine, meaning that it will have an oxidation number of +1 & fluorine has one of -1.
- By convention, the less electronegative element is written first in the formula.
- The idea of oxidation number considers all compounds, even covalent ones, to be ionic.
- A negative sign for an oxidation number means the atom has gained "control" of the electrons (compared to the element), while a positive sign shows that the atom has lost control of the atoms.
 - Essentially, the numbers show how many electrons an atom has either gained or lost.
 - A positive number means that it has lost x amount of electrons.
 - A negative one will mean that the atom has gained x amount of electrons.
 - The reason that a negative sign is given in brackets is because of the fact that the electrons have a negative charge.

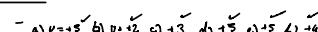
Differences with oxidation numbers

- Bonds between elements
 - Another rule for determining the oxidation number is that bonds between atoms of the same element don't count towards the oxidation number.
 - E.g., hydrogen peroxide (H_2O_2). $\text{H}:+1$ & $\text{O}:-1$, where the oxidation numbers will be zero overall.
- To find the oxidation number, use the periodic table & find where the elements are.
 - Closer to the noble gases by right side = gainers (-1 full charge).
 - Closer to the noble gases by left side = losers (+1 full charge)
 - Metals are always losers.

Organic chemistry

- We stick to use the old definition of oxidation for organic chemistry:
 - The gain of oxygen or loss of hydrogen.

Questions (1)



Naming inorganic compounds

- Stock notation is used to write the names of elements
- In this system the oxidation number is inserted immediately after the name of an ion
 - E.g. $\text{FeCl}_2 \rightarrow [\text{Fe}^{+2} + 2\text{Cl}^-] \rightarrow$ iron (II) chloride
 - E.g. $\text{FeCl}_3 \rightarrow [\text{Fe}^{+3} + 3\text{Cl}^-] \rightarrow$ iron (III) chloride
- This notation is only used for transition metals, i.e., and lead from group 14 (IV) of the periodic table where variable or multiple oxidation states are exhibited.
- An example of where a compound contains two cations in the "mixed oxide" of lead:
 - Pb_3O_4 $[\text{Pb}^{2+} \text{ Pb}^{4+} \text{ Pb}^{2+}]$ lead (II) and (IV) oxide

- The stock system is also used to name complex ions.

- E.g. $[\text{Fe}(\text{CN})_6]^{4-}$, where the iron is +3 (iron (III) ion) surrounded by six cyano ions: $\text{Fe}^{3+} 6\text{CN}^-$, named hexacyanoferrate (III) ion.
- Nox names are used for the following oxyanions:
 - Chromate (VI) CrO_4^{2-} , dichromate (VII) $\text{Cr}_2\text{O}_7^{2-}$, manganate (VII) MnO_4^- , manganite (VI) MnO_4^{2-} , chlorate (VI) ClO_4^- , chlorite (III) ClO_4^{2-} , chlorite (V) ClO_3^- , chlorite (VI) ClO_4^{2-} , chlorite (VII) ClO_4^{2-} .
 - Chlorite and manganite aren't precise enough, and therefore, the oxidation number is used to determine the species.
- For compounds between non-metals the stock system isn't used, and the name & % of atoms is shown.
 - E.g. N_2O = nitrogen oxide & nitrogen (I) oxide.

Q&A

- $\text{K}_2\text{Cr}_2\text{O}_7$ = Potassium dichromate - $2\text{K}^{+} \text{Cr}_2\text{O}_7^{-}$ - Potassium chromate - $2\text{K}^{+} (\text{Cr}_2\text{O}_7^{2-})$ - 2 potassium (VI) chromate
- U_2O_8 = Uranium (V) oxide - $2\text{U}^{+4} \text{O}_8^{-}$ - $2\text{U}^{+4} (\text{O}_8^{-})$ - 2 uranium (VI) oxide
- K_2CrO_4 = Potassium chromate - $2\text{K}^{+} \text{CrO}_4^{-}$ - Potassium (VI) chromate

Identifying redox reactions

- Redox reactions are easily recognizable b/c:
 - Reducing all of the oxidation numbers of the atoms in the chemical species present in the molecular, ionic, or half-equation.
 - Equations don't have to be balanced.
- Examining if the oxidation numbers have changed.
 - If it has, then the reaction is a redox reaction.
 - An increase in the oxidation number means that the atom has been oxidized.
 - If it decreased, then it's a reduction.
- If there is no change in oxidation numbers means that the reaction isn't a redox reaction.
- Non-redox reactions are most acid-base reactions, precipitation reactions, and complex ion formation.
- $\text{Fe}(\text{Cl}_3)_3 \text{aq} + \text{Cl}_2 \text{g} \rightarrow \text{Fe}(\text{Cl}_4)_3 \text{aq}$
 - The oxidation numbers of iron are +2 and +3 respectively.
 - The iron has undergone oxidation, and chloride has been reduced.
 - $\text{Fe}^{+2} \rightarrow \text{Fe}^{+3}, \text{Cl}^{-2} \rightarrow \text{Cl}^{-1}$.
- $[\text{Co}(\text{H}_2\text{O})_6]^{2+} \text{aq} + 4\text{H}_2\text{O}_2 \text{aq} \rightarrow [\text{Co}(\text{H}_2\text{O})_6]^{3+} \text{aq} + 4\text{H}_2\text{O}_{\text{liq}}$
 - Not a redox reaction b/c there is no change in oxidation.

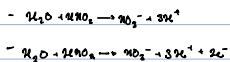
Dissproportionation

- Dissproportionation occurs when a single species is both oxidized & reduced simultaneously.
- E.g. $\text{H}_2\text{O}_2 \text{aq} \rightarrow \text{H}_2\text{O}_{\text{liq}} + \frac{1}{2}\text{O}_2 \text{g}$
 - One of the oxygen atoms in the hydrogen peroxide molecule becomes part of an oxygen radical, changing from $+1$ to 0 .
 - Oxidation: O .
 - One of the oxygens will be reduced, going from -1 to -2 .
 - Reduction: O .
- Another example of disproportionation is the reaction between chlorine & water to form hydrochloric acid & chlorine (Cl_2) (hypochlorous) acid:
 - $\text{Cl}_2 \text{g} + \text{H}_2\text{O}_{\text{liq}} \xrightarrow{\text{O}} \text{HCl}_{\text{aq}} + \text{HClO}_{\text{aq}}$
 - One of the chlorine atoms become a chloride ion, where the oxidation number decreases from 0 to -1 .
 - One more chlorine atom goes from 0 to $+1$. Chlorite (ClO^-) ion.
- Other examples of disproportionation include:
 - Chlorine and cold dilute aqueous sodium hydroxide.
 - Soluble copper (Cu) compounds, such as copper (Cu^{+2}) sulphate, and water.
 - The overall cell reaction that occurs in a lead-acid car battery during discharge.

Half-equations

Continuity half-equations

- Half-equations can be described by the following steps:
 - Write down the formulae of the reactant and products, e.g.
 - $\text{Cr}_2\text{O}_7^{2-} \rightarrow \text{Cr}$
 - Balance with respect to the chromium.
 - $\text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+}$
 - Balance the oxygen atoms of the dichromate ($\text{Cr}_2\text{O}_7^{2-}$) ion with water molecules:
 - $\text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$
 - Balance the hydrogen atoms present in the water with hydrogen ions:
 - $14\text{H}^+ + \text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$
 - Determine the total charge on both sides of almost completed half-equation:
 - $14(+1) - 6 = 12$
 - Balance the equation with electrons:
 - $14\text{H}^+ + \text{Cr}_2\text{O}_7^{2-} + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$
 - In identical process is done for reducing agents, with a difference. But the electrons go on the right side of the equation:
 - $2\text{NO}_2 \rightarrow \text{NO}_3^-$
 - $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O}_{\text{liq}}$

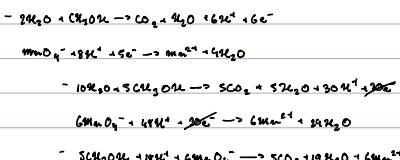


Gaining oxidation equations

Two-electron method

- Redox reactions are written by combining two half-equations: one using the action of the oxidizing agent, and the other using the action of a reducing agent.
- They must be balanced, so that the number of electrons gained by one equation is the same as the loss of electrons of the other.
- The electrons can then be cancelled out on both sides.

Worked example

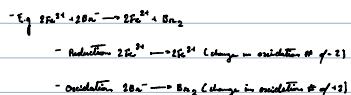


Oxidation number method

The steps are:

- Identify the elements that have undergone a change in oxidation number.
- Balance the atoms that have undergone a change in oxidation number.
- Find the change in oxidation number, and the number of electrons transferred for each redox species.
- Balance charge with $2e^-$.
- Balance oxygen with H_2O .

- In a redox reaction, the sum of the increases in the oxidation number of oxidized species equals the sum of the decreases in the oxidation number of the reduced species.



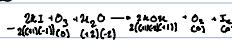
Redox titration

- A redox titration involves the transfer of one or more electrons from a reducing agent to a oxidizing agent.
- Reducing agent loses electrons, oxidizing itself.
- Oxidizing agent gains electrons, reducing itself.
- Indirect methods needed for titrations that involve manganese (MnO_4^-) ions, dichromate ($\text{Cr}_2\text{O}_7^{2-}$) ions, or iodine since there is a significant color change.

Oxidizing agents

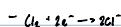
- Oxidizing agent is defined as a substance that brings about the oxidation of another by accepting electrons from the substance they oxidize.
- Oxidizing agents are reduced.
- The strengths of oxidizing agents are described by their standard electrode potentials.

E.g. Oxone



- O_3 is oxidizing agent

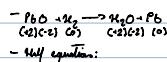
Aktoxine



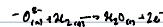
Reducing agents

- A reducing agent is a substance that brings about the reduction of another by donating electrons to the substance it reduces.
- The strengths of reducing agents are described by their standard electrode potentials.

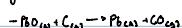
Hydrogen (e.g.)



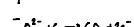
- Half equation:



Carbon (e.g.)



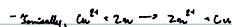
- Half equation:



metals

- The more reactive the metal, the stronger it is as a reducing agent

- Eg zinc acts as a reducing agent with aqueous copper (II) sulphate solution:



natural antioxidants

- An antioxidant is a natural or synthetic substance that delays the onset, or slows down the rate of oxidation.

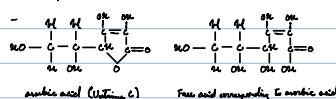
- Used to extend the shelf life of food.

- An example of a natural antioxidant is vitamin C and E.

- Vitamin C is a water-soluble vitamin, and is oxidised by exposure to air.

- The rate of oxidation is increased with temperature, and with the presence of alkalis.

- Vitamin C (also referred to as ascorbic acid) while called an acid, doesn't contain a free carboxylic acid functional group.

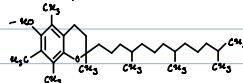


ascorbic acid (vitamin C) Furan-2-carboxylic acid

- Vitamin E is the main lipid-soluble antioxidant.

- It occurs in all membranes together with polyunsaturated fatty acids in phospholipids, and vegetable oils are a major dietary source.

- It is a phytolc antioxidant, or an antioxidant.



Utilisation of redox reactions

Batteries

- A battery is a voltage cell that is used as an energy source.

- A cell battery will have multiple voltage cells in series, combining their pds, and forming a large pd at the output terminal.

- There are two types of batteries, a primary battery (can't recharge), and secondary battery (rechargeable battery).

- The dry cell battery is an example of a primary cell and a lead-acid battery, lithium-ion battery, and nickel-cadmium (Ni-Cd) battery are examples of secondary cells.

- A fuel cell is an electrochemical cell designed so that reactants, often gases, are replenished all the time, therefore, recharging isn't ever necessary.

Solar cells

- One form of solar cells consists of two joined layers of silicon.

- One layer doped with a small amount of arsenic or phosphorous.

- Known as p-type silicon.

- The atoms in the element release an extra electron into the silicon lattice, creating a current.

- The second layer is doped with boron atoms, and is called n-type silicon.

- This layer has a shortage of electrons.

- Electrons will flow from n-type to p-type layers through a wire.

- Ion equilibrium is established with a pd between the two layers.

- The equilibrium is disturbed when sunlight is incident on the solar cell surface.

- The electrons move from p-type to n-type, and then back to p-types and generate an electrical current.

Browning of food

- When fruits and vegetables are cut and peeled, the enzymes in the plant are released.

- In the presence of oxygen, they'll oxidise and convert to brown melanins.

- The presence of iron & copper increases the rate of oxidation.

- The browning can be slowed down with sulphur ion (sulphite (SO₃)²⁻), ascorbic acid (vitamin C), and citric acid (L-ascorbic acid).

Reactions of metals with metal ions in solution

- Metals often act as reducing agents, and the greater the chemical reactivity of the metal, the greater the ability to bring about reduction.

- To test the reactivity of metals, the following experiment can be performed.

- Dissolve an aqueous solution of different metals, and place different metals in those solutions.

- If a change occurs on the surface of the metal, then a reaction has taken place.

- The more metals react with the aqueous solution, the more reactive the metal in the solution is.

- The more reactive the metal is, the greater their reducing power (ability to donate electrons (reduction)) is.

| Metal | Number of replacement reactions |
|-------|---------------------------------|
| Mg | 5 ← most reactive metal. |
| Zn | 4 |
| Fe | 3 |
| Sn | 2 |
| Pb | 1 |
| Cu | 0 |

Table 9.6 An activity series for selected metals based on replacement reactions

- The reactions that take place are called **replacement reactions**.

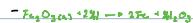
- Due to the fact that the more reactive metal will replace the less reactive metal in the salt.

- Eg equations:



- Replacement reactions can also take place in the solid state using powdered samples of metals, and metal compounds.

- Eg reaction between iron (II) oxide and aluminium are heated together, a very exothermic reaction takes place, known as **thermitic reaction**, the will result in the formation of aluminium oxide and molten iron.



- The reason that the thermitic reaction occurs is because aluminium is a more powerful reducing agent than iron.

- Meaning that it will lose its electrons easier than iron.



- Actual half-equations:

Corrosion and galvanisation

Rusting

- Rusting requires liquid water & oxygen.



- The number of water molecules present in the rust is uncertain or variable.

- It's steel coils which has a drop of ferricron indicator added shows two important electrochemical aspects of this redox reaction.

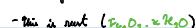
- It blue colour shows that iron (II) ions are present.



- The pink colour indicates the presence that hydroxide ions are present.



- The iron (II) hydroxide formed from precipitation will oxidise to form hydrated iron (III) oxide.



- Method to combat rusting is with the use of stoichiometric principle.

- Pair of iron are usually protected by a block of zinc or magnesium, which are electrically attached to the iron object.

- Zinc & magnesium being more reactive than iron will oxidise before the iron will.

- Iron is the cathode here.



- The electrons released reduce the O₂ molecules to form hydroxides:



Galvanisation

- A coating of zinc protects iron from rusting and is known as galvanised iron.

- It's protected because in an electrochemical cell it's an oxidiser because of the fact that zinc is preferred.

- Zinc is higher up on the activity cell than iron.

- Since zinc would run out of another reaction wouldn't simultaneously occur, the reaction between zinc hydroxide (formed with H₂O), and carbon dioxide.

- This reaction will form zinc carbonate, a compound that adheres firmly to iron to give further protection.

- Using the activity series

- Aluminium won't react because of the fact that it has a very thin layer of aluminium oxide that prevents the metal under from reacting.
- metals above one another will replace the others in a reaction

- E.g:



- metals above carbon in the activity series, such as sodium & aluminium, can't be produced by reduction of metal oxides with carbon, instead electrolysis has to be used.
- metals below carbon can be produced by reducing metal oxides with carbon.



- Replacement reaction also occurs with non-metals, in particular halogens, where a more reactive halogen will replace a less reactive halogen.

- The activity series can also be contrasted similarly to the metals.

- moving up the activity series the halogen becomes increasingly chemically reactive, thus oxidising power will also increase.

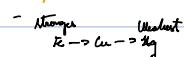
- E.g. reaction:



- The bromide ion has undergone oxidation and the chlorine has undergone reduction.

- The reactivity and oxidising power of halogens are related to their size, the smaller they are, the more reactive and stronger oxidising agents.

- Worked example:



- The Daniell method

- Fish can only survive in water because of the dissolved O_2 in it.

- If the air pressure is 5 kg dm^{-2} most species will die.

- One method for calculating the O_2 dissolved in water is the Daniell method.

- Manganese (II) ions are rapidly oxidised to manganese (III) by dissolved oxygen, producing MnO_4^- :



- Magnesium (II) is reacted with excess potassium iodide, which oxidises to iodine:



- The amount of iodine is then determined with a titration between sodium thiosulfate of known concentration.



9.2 Electrochemical cells

- Voltaic cells

- A simple cell can be constructed by placing a zinc electrode (solid electric conductor that carries current) in a solution of zinc sulfate, and a copper electrode in a solution of copper (II) sulfate.

- The electrodes are connected by a wire, and a high-resistance voltmeter.

- This allows the flow of electrons, and is known as the external circuit.

- This is a spontaneous process and doesn't require an external energy source.

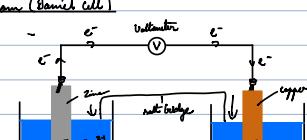
- A salt bridge which is used to maintain the charge of the two substances.

- This is done by having ions move from the salt bridge into the liquids.

- The salt bridge is a piece of filter paper soaked in saturated potassium acetate.

- There are chosen because they won't react with other ions in solution or with the electrodes.

- Diagram (Daniell cell)



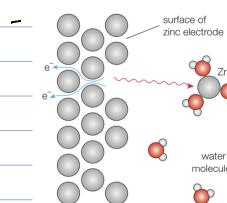


- Zinc is higher than copper in the activity series, this means it will undergo oxidation releasing electrons.

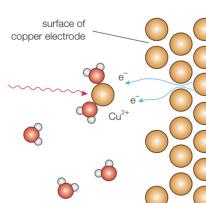
- The zinc ions will dissolve in the water.

- The electrons will move from the zinc to the copper.

- The copper (II) ions on the surface of the copper will be reduced.



■ Figure 9.40 Zinc atoms forming hydrated zinc ions on the surface of the zinc electrode of a Daniell cell



■ Figure 9.41 Hydrated copper(II) ions forming copper atoms on the surface of the copper electrode of a Daniell cell

- The process continues until either all the zinc electrode or copper (II) ions run out.

- The zinc is acting as a reducing agent, while the copper (II) ions are acting as an oxidising agent.

- By definition, the anode in the electrode is where oxidation occurs.

- In this example, zinc would be the electrode.

- By definition, the cathode is the electrode where the reduction takes place.

- Half-equations:



- The overall reaction in this source is if zinc was added to copper sulphate.

- The difference is that rather than just being reduced, electrical energy is released.

- There is a current from the anode to the cathode because there is a pd between the cathode and anode.

- Pd is called "cell potential".

- The anode will always be the more reactive metal, and it will always donate the electrons.

- The voltage will depend on the nature of the electrodes and the ion, but also on the concentration of the ion and the temperature at which the cell is operated.

Fuel cells

- Fuel cells use the reaction between molecular hydrogen (or carbon) and molecular oxygen to produce water.

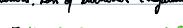
- The energy released will be in the form of electrical energy.

- The reactants are released, more are added to continue the supply of electricity.

- The electrolyte is a strong base, usually aqueous sodium hydroxide.

- The container within the fuel cell uses porous electrodes, which allow the movement of gas and water molecules.

- Oxidation: loss of electrons (negative electrode):



- Reduction: gain of electrons (positive electrode):



- A problem with fuel cells is that to store them, they need to kept at -253°C which is 4 times the cost of storing petrol.

- It's expensive because of the fact that the only waste product is H₂O.

- Magnesium hydride, MgH₂, is 7.7 percent hydrogen by mass and the hydrogen is released by the following reaction:



Heterogeneous cells

Conductors and insulators

- A conductor is a substance that allows the flow of electrons/electricity through it.

- Substances that conduct slightly are semi-conductors.

- An insulator is a substance material that resists the flow of electrons/electricity to pass through it.

- Non-metals elements are insulators.

- For a substance to conduct, there must be electrically charged particles which can free to move when a pd is applied.

- In a metal in the liquid or melt state, the conduction of electricity uses the valence electrons.

- The flow of the electrons through the melt constitutes the electric current.

- Substances that melt a metal but contain ions, the current is transferred by means of ions.

- Ionic substances won't conduct as ions are held in place by bonds.

- When the substance is melted or dissolved in water the ions are released from the lattice and free to move.



The electrolysis of a molten salt

- The difference between a metal's or graphite's electrical conduction compared to an aqueous material is that the metals' chemical properties will remain unchanged.

- When a current goes through an ionic substance, either melting or in a solution, the substance will undergo chemical decomposition.

- A substance that will decompose by the passage of electricity is known as an electrolyte.

- Electrolysis is defined as a chemical compound that conducts electricity by changing into ions when melted or in a solution.

- The process of decomposing an electrolyte is known as electrolysis. Electrolysis is chemical decomposition produced by an electric current.

- Electrolysis will need a constant input of energy or it's not spontaneous.

- In electrolysis, electricity passes through an electrolyte, entering and leaving via an electrode.

- Electrodes are usually metals or graphite.

- The electrode connected to the positive terminal of the cell or battery is known as the anode.

- The electrode connected to the negative terminal of the cell or battery is known as the cathode.

- Negative ions, or anions, are attracted to the positive terminal.

- Cations are attracted to the negative terminal.

- When the ions reach the electrode surfaces, they will undergo reduction reactions.

- The simplest form of electrolysis is the electrolysis of a molten binary salt.

- E.g. lead (II) bromide, $PbBr_2$ [$Pb^{2+}, 2Br^-$]

- Chemically inert (inert) electrodes are used, and the decomposition products are neither hot nor caustic vapors.



- The lead is formed at the anode, and the bromine vapor is formed at the anode.

To the anode:

- At the anode the negatively charged bromide ion will be attracted to the anode.

- They will lose electrons and form bromide molecules.



To the cathode:

- Positively charged lead (II) ion will be attracted to the cathode. They gain electrons since they are ions.



Electrolysis of other compounds

- All ionic compounds undergo electrolysis in the molten state and obey two rules:

- Metals always form cations which go to the cathode to discharge.

- Non-metals will always form anions which move to the anode and form them by donating electrons.

- The following table shows different examples of electrolysis of molten or fused electrolytes.

| Electrolyte | Dissociation | Overall decomposition | Cathode O | Anode O |
|---|--|---|--|------------------|
| Sodium chloride, NaCl | $2\text{NaCl}(l) \rightarrow 2\text{Na}(l) + \text{Cl}_2(g)$ | $\text{Na}^+ + e^- \rightarrow \text{Na}$ | $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e^-$ | |
| Potassium iodide, KI | $2\text{KI}(l) \rightarrow 2\text{K}(l) + \text{I}_2(g)$ | $\text{K}^+ + e^- \rightarrow \text{K}$ | $2\text{I}^- \rightarrow \text{I}_2 + 2e^-$ | |
| Copper(II) chloride, CuCl_2 | $\text{CuCl}_2(l) \rightarrow \text{Cu}(l) + \text{Cl}_2(g)$ | $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$ | $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e^-$ | |
| Aluminum oxide, Al_2O_3 | $2\text{Al}_2\text{O}_3(l) \rightarrow 4\text{Al}(l) + 3\text{O}_2(g)$ | $\text{Al}^{3+} + 3e^- \rightarrow \text{Al}$ | $2\text{O}^{2-} \rightarrow \text{O}_2 + 4e^-$ | |

Differences between a voltaic cell and electrolytic cell:

A voltaic cell

Oxidation occurs at the anode (positive)

Reduction occurs at the cathode (negative)

It uses a redox reaction to produce a voltage

It involves a spontaneous redox reaction (exothermic)

It converts chemical energy to electrical energy

The cathode is the positive electrode and the anode is the negative electrode (during discharge)

There is a salt bridge and an external circuit

An electrolytic cell

Oxidation occurs at the anode (positive)

Reduction occurs at the cathode (negative)

It uses electricity to carry out a redox reaction

It involves a non-spontaneous redox reaction (endothermic)

It converts electrical energy to chemical energy

The cathode is the negative electrode and the anode is the positive electrode

There is no salt bridge

- Oxidation (Reaction #6)

- Lithium bromide, LiBr.



- Calcium nitrate, Ca_3N_2 .



- Iron (II) bromide, FeBr_2 .



- Difference between electrochemical & voltaic cells

- Ion flow in the electrolyte of both electrochemical & voltaic cells.

- Electrons only flow in the external circuit of all types of electrochemical cells.

- Electrolytic cell

- In an electrolytic cell, ions migrate to the electrode with an opposite charge.

- Cations are positively charged, and are attracted to cathodes which are negatively charged.

- At the cathode reduction will occur.

- Anions are negatively charged, and are attracted to anodes which are positively charged.

- At the anode oxidation will occur.

- The electrons flow from the anode to the cathode.

- Voltaic cells

- In an electrochemical cell, the more reactive metal acts as the anode and the metal atoms undergo oxidation and lose electrons.

- The electrons on the surface of the electrodes make it negative.

- The electrons flow to the cathode via the external circuit.

- The electrons on the surface react with the cations in the half cell forming the cathode.

- The anode undergoes reduction to form stones.

- Salt bridge is used to maintain neutrality.

- The difference between metallic and electrolytic conductors

Metallic conduction

Conduction through metals is carried out by the movement of delocalized valence electrons

No change is observed in the chemical properties of the conductors

It does not involve any transfer of matter

It shows an increase in resistance with an increase in temperature

The conductivity of metals is generally high

Measured using an ohmmeter

Electrolytic conduction

Conduction through electrolytes is carried out by the movement of cations and anions

It involves a chemical change resulting in the decomposition of electrolytes

It involves the transfer of matter as ions

It shows a decrease in resistance with an increase in temperature

The conductivity of electrolytic solutions is generally low

Measured using a conductivity meter

- When a direct current is passed through a solution electrolysis occurs and ions are removed from the solution.

- This can be remedied with an alternating current.

- Constructing and annotating two types of electrochemical cells

- Volt cells have to be shown with:

- Two half cells

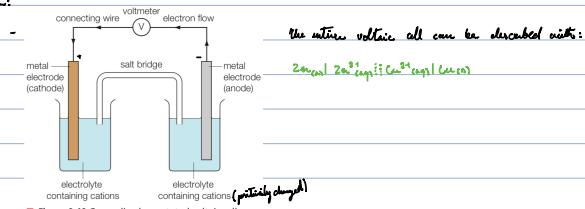
- A salt bridge

- An external circuit with:

- Wires

- Voltmeter

- Diagram:



- The electrodes and electrolytes should be labelled.

- The electrolyte should be shown with a power pack or battery connected to two electrodes.

- The anode is + and cathode is -.

- Diagram:

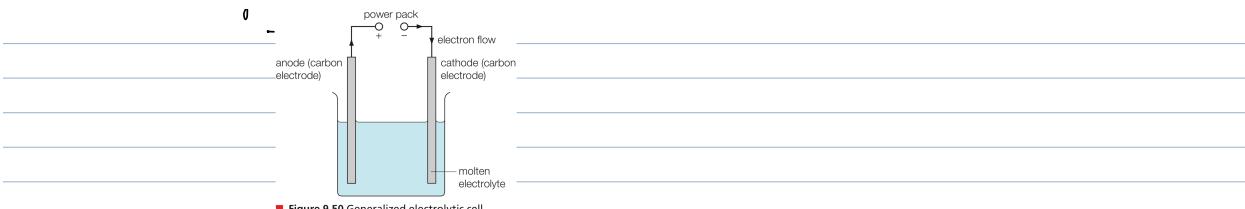


Figure 9.50 Generalized electrolytic cell

- Worked example

