

## Oxidation and Reduction (9.1)

### Oxidation

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



- The Magnesium has gained oxygen and we say that the magnesium has been oxidized.



- The HCl has hydrogen and therefore is oxidized.

- 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."



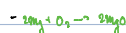
- The copper (II) oxide loses oxygen to the hydrogen gas, meaning that the Cu will be reduced and the  $\text{H}_2$  will be oxidized.



- The  $\text{C}_2\text{H}_4$  (ethene) will gain hydrogen, meaning it will be reduced.

- The definition of oxidation changes to the loss of electron from a substance.

- The definition of reduction changes to the gain of electron by a substance.



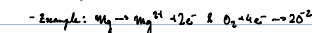
- The Mg will still be oxidized, but in terms of electron, each Mg molecule will gain 2 electrons from each oxygen molecule.



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



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



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

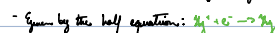
### Application: Photochromic Lenses

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

- Ion glass is made photochromic by adding small amounts of silver chloride ( $\text{AgCl}$ ) and copper (I) chloride to the surface glass or it coats.

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

- When sunlight hits the lenses, the  $\text{AgCl}$  changes to form silver atoms, which makes the lenses darker.



- The chloride particles will react with the  $\text{CuCl}$ , forming copper (II) ion and chloride ions:



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



### Oxidation numbers

- In the reaction:  $2\text{Cu} + \text{O}_2 \rightarrow 2\text{CuO}$ , it is said that copper has been oxidized, but the product compound isn't electrically charged.

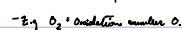
- The concept oxidation number, is used to combine the old & new method.

- Using the definition of oxidation the increase in oxidation number.

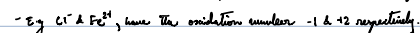
- And that of reduction a decrease in oxidation number.

- The rules of oxidation are:

- The oxidation number of any uncombined element is zero.

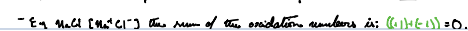


- For a simple ion, the oxidation number of the ion is equal to the charge on the ion.



- NOTE: the charges are written with the sign (+/-) after the name, 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.



- For 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,  $\text{NO}_3^-$ , the sum of the oxidation numbers is -2, that is,  $(+5 + (-2)(3)) = -2$ .
- Hydrogen's oxidation number is always +1 except when it's bonded with a reactive metal (group 1 & 2 metals).
  - E.g.  $\text{NaH}$  ( $\text{Na} = +1, \text{H} = -1$ )
  - 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  $\text{H}_2\text{O}_2$  (hydrogen peroxide) where it's -1, or when it's bonded with fluorine in  $\text{OF}_2$  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.  $\text{HF}$ , where fluorine is less electronegative than hydrogen, 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 numbers 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 atom.
  - Essentially, the number shows how many electrons an atom has either gained or lost.
    - A positive number means that it has lost an amount of electrons.
    - A negative one will mean that the atom has gained an amount of electrons.
    - The reason that a negative sign is given in electrons is because of the fact that the electrons have a negative charge.

Difficulties with oxidation numbers

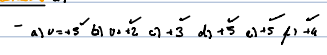
Bonds between elements

- 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 ( $\text{H}_2\text{O}_2$ )  $\text{H} = +1$  &  $\text{O} = -1$ , where the oxidation numbers will be zero overall.
- To find the oxidation number, use the periodic table & find where the element are.
  - Closer to the noble gases by right side = greater (-) final charge.
  - Closer to the noble gases by left than hydrogen donors (+) final charge.
  - Metals are always donors.

Organic Chemistry

- We have 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 system is only used for transition metals, this, 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 oxides" of lead:
      - $\text{Pb}_3\text{O}_4$  [ $2\text{Pb}^{2+}, \text{Pb}^{4+}, 4\text{O}^{2-}$ ] lead (II) lead (IV) oxide
- The Stock system is also used to name complex ions.
  - E.g.  $[\text{Fe}(\text{CN})_6]^{3-}$ , where the iron is +3 (iron (III) ion) surrounded by six cyanide ions:  $\text{Fe}^{3+} 6\text{CN}^-$ , named hexacyanoferrate (III) ion.
- Stock names are used for the following occasions:
  - Chromate (VI)  $\text{CrO}_4^{2-}$ , dichromate (VI)  $\text{Cr}_2\text{O}_7^{2-}$ , manganate (VII)  $\text{MnO}_4^-$ , permanganate (VII)  $\text{MnO}_4^{2-}$ , chlorate (V)  $\text{ClO}_3^-$ , chlorite (III)  $\text{ClO}_2^-$ , chlorate (I)  $\text{ClO}_2^-$ , chlorite (I)  $\text{ClO}_2^-$ .
  - Chlorite and manganate aren't present 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 is of atoms in them.
  - E.g.  $\text{H}_2\text{O}$  - dihydrogen oxide & nitrogen (I) oxide.

Answers

- $\text{K}_2\text{Cr}_2\text{O}_7$  - Potassium dichromate -  $\text{KMnO}_4$  - Potassium permanganate -  $\text{Zn}(\text{NO}_3)_2$  - Zinc nitrate (I) (NO-3)
- $\text{U}_3\text{O}_8$  - Uranium (IV) oxide -  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  - Calcium sulfate (II) dihydrate
- $\text{K}_2\text{Cr}_2\text{O}_7$  - Potassium dichromate -  $\text{Cu}_2\text{SO}_4$  - Copper (I) sulfate

Identifying redox reactions

- Redox reactions are easily recognizable by:
  - Balancing 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 number have changed.
    - If it has, then the reaction is a redox reaction.
      - An increase in the oxidation number means that the atom has been oxidised.
      - If it decreased, then it's a reduction.
  - If there is no change in oxidation number means that the reaction isn't a redox reaction.
    - Non-redox reactions are most acid-base reactions, precipitation reactions, and complex ion formation.
- $2FeCl_2(aq) + Cl_2(g) \rightarrow 2FeCl_3(aq)$ 
  - The oxidation number of iron are +2 and +3 respectively.
  - The iron has undergone oxidation, and chlorine has been reduced.
    - $2Fe^{+2} + 2Cl^- \rightarrow 2Fe^{+3} + 2Cl^{-1}$
- $[Co(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightarrow [Co(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O(l)$ 
  - Not a redox reaction because there is no change in oxidation.

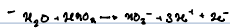
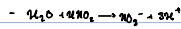
Disproportionation

- Disproportionation occurs when a single species is both oxidised & reduced simultaneously.
  - E.g.  $H_2O_2(aq) \rightarrow H_2O(l) + \frac{1}{2}O_2(g)$ 
    - One of the oxygen atoms in the hydrogen peroxide molecule becomes part of an oxygen molecule, changing from -1 to 0.
      - Oxidation ↑
    - One of the oxygens will be reduced, going from -1 to -2.
      - Reduction ↓
  - Another example of disproportionation is the reaction between chlorine & water to form hydrochloric acid and chloric (I) (hypochlorous) acid:
    - $Cl_2(aq) + H_2O(l) \rightarrow HCl(aq) + HOCl(aq)$ 
      - One of the chlorine atoms becomes a chloride ion, where the oxidation number decreases from 0 to -1.
        - The second chlorine atom goes from 0 to +1. Chlorate (I) ion.
  - Other examples of disproportionation include:
    - Chlorine and cold dilute aqueous sodium hydroxide.
    - Soluble copper (I) compounds, such as copper (I) sulphate, and water.
    - The small cell reaction that occurs in a lead-acid car battery during discharge.

Redox equations

Constructing half-equations

- Half-equations can be described by the following steps:
  - Write down the formulae of the reactant and products, e.g.
    - $Cr_2O_7^{2-} \rightarrow Cr$
  - Balance with respect to the chromium.
    - $Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$
  - Balance the oxygen atoms of the dichromate (VI) ion with water molecules.
    - $Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$
  - Balance the hydrogen atoms present in the water with hydrogen ions.
    - $14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$
  - Determine the total charge on both sides of almost completed half-equation.
    - $14 - 2 = 12$
    - $12 / 6$
  - Balance the equation with electrons.
    - $14H^+ + Cr_2O_7^{2-} + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$
  - The identical process is done for reducing agents, with a difference that the electrons go on the right side of the equation.
    - $3NO_2 \rightarrow NO_3^-$
    - $2H_2O + 9e^- \rightarrow H_2O_2^-$



### - Combining redox equations

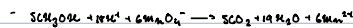
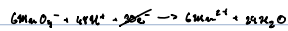
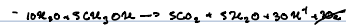
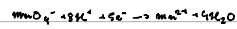
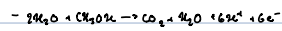
#### - Ion-electron method

- Redox reactions are written by combining two half equations: one being the action of the oxidizing agent, and the other being 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.

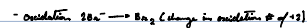
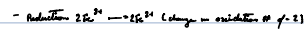
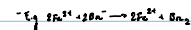
- Balance the atoms that have undergone a change in oxidation number.

- Find the change in oxidation number, and the number of electrons transferred for each redox species.

- Balance charge with  $\text{H}^+$ .

- Balance oxygen with  $\text{H}_2\text{O}$ .

- 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 an oxidizing agent.

- Reducing agent loses electrons, oxidizing itself.

- Oxidizing agent gains electrons, reducing itself.

- Indicators aren't needed for titrations that involve conjugate (Ox) ions, dichromate (Ox) ions, or iodine since there is a significant color change.

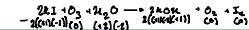
### - Oxidizing agents

- Oxidizing agent is defined as a substance that brings about the oxidation of a substance by accepting electrons from the substance being oxidized.

- Oxidizing agents are reduced.

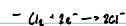
- The strengths of oxidizing agents are described by their standard electrode potentials.

- Eg bromine



-  $\text{O}_2$  is oxidizing agent

- Chlorine

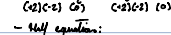
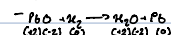


### - Reducing agents

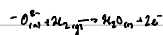
- A reducing agent is a substance that brings about the reduction of a substance by donating electrons to the substance it reduces.

- The strengths of reducing agents are described by their standard electrode potentials.

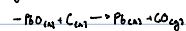
- Hydrogen (e.g.)



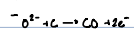
- Half equation:



- Carbon (e.g.)



- Half equation

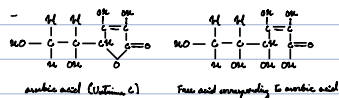


- Metals

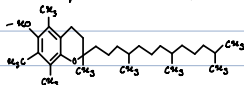
- The more reactive the metal, the stronger it is as a reducing agent
- E.g zinc acts as a reducing agent with aqueous copper (II) sulfate solution:
  - $CuSO_4 + Zn \rightarrow ZnSO_4 + Cu$
  - Similarly,  $Cu^{2+} + Zn \rightarrow Zn^{2+} + Cu$

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 oxidized by exposure to air.
  - The rate of oxidation is increased with temperature, and with the presence of alkali.
  - Vitamin C (also referred to as ascorbic acid) which called an acid, doesn't contain a free carboxylic acid functional group.



- 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 phenolic antioxidant, an antioxidant.



Classification of redox reactions

Batteries

- A simple battery is a voltage cell that is used as an energy source.
  - An battery cell have multiple voltage cells in series, combining their pots, and forming a large pd at the output terminals.
- There are two types of batteries, a primary battery (not rechargeable), 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.
- The fuel cell is an electrochemical cell designed so that reactants, after gone, are replenished all the time, therefore, recharging isn't our necessity.

Zinc cells

- One form of zinc cells consists of two joined layers of zinc.
  - One layer is coated with a small amount of arsenic or phosphorous.
    - known as an-type selenium.
  - The atoms in the element release an extra electron into the selenium lattice, creating a current.
  - The second layer is coated with copper atoms, and is called p-type selenium.
    - The layer has a shortage of electrons.
    - Electrons will flow from an-type to p-type layer through a wire.
  - An equilibrium is established with a pd between the two layers.
    - The equilibrium is disturbed when sunlight is incident on the an-type cell surface.
    - The electrons move from p-type to an-type, and then back to p-type 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 oxidize and convert to brown melanins.
  - The presence of iron & copper increases the rate of reaction.
  - The browning can be slowed down with sulfite ions (sulfite (SO<sub>3</sub>) ions), ascorbic acid (vitamin C), and citric acid (lemon).

Reactivity of metals with metal ions in solution

- Metals after act on 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.
    - Place 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 metals are the greater their reducing power (ability to donate electrons (oxidation)) 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.

- E.g. equations:



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

- E.g. reaction between iron (II) oxide and aluminium are heated together, a very exothermic reaction takes place, known as the thermite reaction. The salt results in the formation of aluminium oxide and molten iron.



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

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



- Advanced half equations.

- Corrosion and galvanization

- Rusting

- Rusting requires liquid water & oxygen.



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

- The steel coil which has a drop of ferronitric indicator added shows two important electrochemical aspects of the rusting reaction.

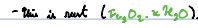
- It shows iron forms showing that iron (II) ions are present.



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



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



- Method to construct rusting is with the use of electrochemical principles.

- Pairs 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 oxidize before the iron will.

- Iron is the cathode here.



- The electrons released reduces the  $O_2$  molecules to form hydroxide:



- Galvanization

- The coating of zinc protects iron from rusting and is known as galvanized iron.

- It's protected because in an electrochemical cell it won't oxidize because of the fact that zinc is preferred.

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

- Hence zinc would run out of another reaction wouldn't simultaneously occur, the reaction between zinc hydroxide (formed with  $H_2O$ ), and carbon dioxide.

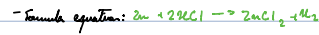
- This reaction will form zinc carbonate, a compound that adheres firmly to iron to give further protection.

- Using the activity series

- Aluminium isn't used because of the fact that it has a very thin layer of aluminium oxide that prevents the metal under from reacting.

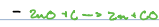
- Metals above one another will replace the other in a reaction

- 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.

- Metal below carbon can be produced by reducing metal oxides with carbon.

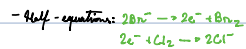
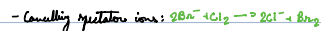


- Replacement reactions also occur with non-metals, in particular halogens, where a more reactive halogen will replace a less reactive halogen.

- An activity series can also be constructed similarly to the metals.

- Moving up the activity series the halogens become increasingly chemically reactive, their oxidising power will also increase.

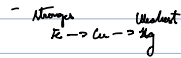
- E.g reaction:



- The bromide ions have 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 Molar method

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

- If it's too low then  $\leq 5 \text{ mg dm}^{-3}$  most species will die.

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

- Manganese (II) ions are rapidly oxidised to manganese (III) by dissolved oxygen, producing  $Mn(OH)_3$ :



- Manganese (III) 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.

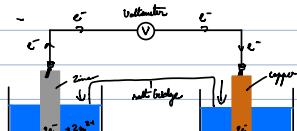
- A salt bridge which is used to maintain the charge of the two substances.

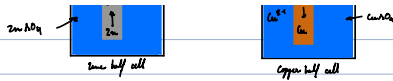
- This is done by having ions move from the salt bridge into the beakers.

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

- These 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 travel from the zinc to the copper.
- the copper (II) ions on the surface of the copper will be reduced.

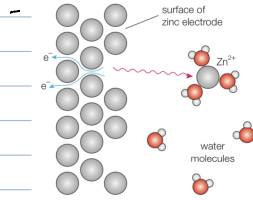


Figure 9.40 Zinc atoms forming hydrated zinc ions on the surface of the zinc electrode of a Daniell cell

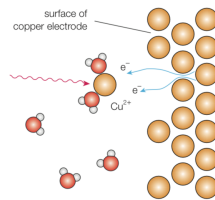


Figure 9.41 Hydrated copper(II) ions forming copper atoms on the surface of the copper electrode of a Daniell cell

- 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 oxidizing agent.
- By definition, the anode is the electrode in which 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 is the same as if zinc was added to copper sulfate.
- 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 ions, but also on the concentration of the ions and the temperature at which the cell is operated.

- alkaline fuel cells

- fuel cells are the reaction between molecular hydrogen (or methanol) and molecular oxygen to produce water.

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

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

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

- the contained within the fuel cell being porous electrodes, which allow the movement of gases and water molecules.

- Oxidation: loss of electrons (negative electrode):



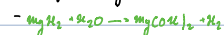
- Reduction: gain of electrons (positive electrode):



- the problem with fuel cells is that to store them, they need to kept at  $-253^{\circ}\text{C}$  which is 4 times the cost of creating petrol.

- the principal because of this fact that the only waste product is  $\text{H}_2\text{O}$ .

- Magnesium hydroxide,  $\text{Mg}(\text{OH})_2$ , is 77 percent hydrogen by mass and the hydrogen is released by the following reaction.



- electrolytic cells

- conductors and insulators

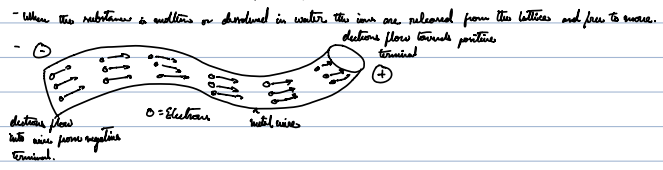
- a conductor is a substance that allows the flow of electrons/electricity through it.

- substances that conduct slightly are semi-conductors.

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



- Non-metallic elements are insulators.
- For a substance to conduct, there must be electrically charged particles which are free to move when a pd is subjected.
  - In a metal in the liquid or molten state, the conduction of electricity uses the valence electrons.
  - The flow of these electrons through the metal 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.



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 metal's chemical properties will remain unchanged.
- When a current goes through an ionic substance, either molten 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.
  - Electrolyte is defined as a chemical compound that conducts electricity by changing into ions when molten or in a solution.
  - The process of decomposing an electrolyte is known as electrolysis. Electrolysis is chemical decomposition produced by an electrical current.
- Electrolysis will need a constant input of energy or it's not spontaneous.
- The 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 surface, they will undergo redox 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 inactive (inert) electrodes are used, and the decomposition products are molten lead and bromine vapor.
    - $PbBr_2 \rightarrow Pb + Br_2$
  - The lead is formed at the cathode, and the bromine vapor is formed at the anode.

At the anode:

- At the anode the negatively charged bromide ions will be attracted to the anode.
- They will lose electrons and form bromine molecules.
  - $2Br^{-} \rightarrow Br_2 + 2e^{-}$

At the cathode:

- Positively charged lead (II) ions will be attracted to the cathode. They gain electrons then become molten lead.
- $Pb^{2+} + 2e^{-} \rightarrow Pb$

Electrolysis of other compounds

- All ionic compounds undergo electrolysis in the molten state and obey the rules:
  - Metals change from cations which go to the cathode to discharge.
  - Non-metals will change from anions which move to the anode and form atoms by donating electrons.
- The following table shows different examples of electrolysis of molten or fused electrolytes.

Electrolyte substance	Overall decomposition	Cathode $\ominus$ half-equation	Anode $\oplus$ half-equation
Sodium chloride, NaCl	$2NaCl(l) \rightarrow 2Na(l) + Cl_2(g)$	$Na^{+} + e^{-} \rightarrow Na$	$2Cl^{-} \rightarrow Cl_2 + 2e^{-}$
Potassium iodide, KI	$2KI(l) \rightarrow 2K(l) + I_2(g)$	$K^{+} + e^{-} \rightarrow K$	$2I^{-} \rightarrow I_2 + 2e^{-}$
Copper(II) chloride, $CuCl_2$	$CuCl_2(l) \rightarrow Cu(l) + Cl_2(g)$	$Cu^{2+} + 2e^{-} \rightarrow Cu$	$2Cl^{-} \rightarrow Cl_2 + 2e^{-}$
Aluminium oxide, $Al_2O_3$	$2Al_2O_3(l) \rightarrow 4Al(l) + 3O_2(g)$	$Al^{3+} + 3e^{-} \rightarrow Al$	$2O^{2-} \rightarrow O_2 + 4e^{-}$

Differences between a voltaic and electrolytic cell:

A voltaic cell	An electrolytic cell
<ul style="list-style-type: none"> <li>Reaction occurs at the anode (negative).</li> <li>Reduction occurs at the cathode (positive).</li> <li>It uses a redox reaction to produce a voltage.</li> <li>It involves a spontaneous redox reaction (exothermic).</li> <li>It converts chemical energy to electrical energy.</li> <li>The cathode is the positive electrode and the anode is the negative electrode (during discharge).</li> <li>There are two separate aqueous solutions connected by a salt bridge and an external circuit.</li> </ul>	<ul style="list-style-type: none"> <li>Reaction occurs at the anode (positive).</li> <li>Reduction occurs at the cathode (negative).</li> <li>It uses electricity to carry out a redox reaction.</li> <li>It involves a non-spontaneous redox reaction (endothermic).</li> <li>It converts electrical energy to chemical energy.</li> <li>The cathode is the negative electrode and the anode is the positive electrode.</li> <li>There is one solution (liquid).</li> </ul>

- Reduction (Oxidation + R)

- Lithium bromide, LiBr
  - Anode  $Li \rightarrow Li^+ + e^-$  attracted to cathode,  $Br^+ + e^- \rightarrow Br$
- Calcium nitrate,  $Ca(NO_3)_2$ 
  - $3Ca \rightarrow 3Ca^{2+} + 3e^-$  attracted to cathode,  $9NO_3^- + 3e^- \rightarrow 9N$
- Iron (II) bromide,  $FeBr_2$ 
  - $Fe \rightarrow Fe^{2+} + 2e^-$  attracted to cathode,  $2Br^- + 2e^- \rightarrow 2Br$

- distinction between electrochemical & voltaic cells

- Ion flow in the electrolyte of both electrolytic & voltaic cells.
- Electron only flows in the external circuit of all types of electrochemical cells.

- Electrolytic cell

- In an electrolytic cell, power originates at the electrodes with the opposite charge.
- Cathodes are positively charged, and are attracted to anodes which are negatively charged.
  - NO the cathode reduction will occur.
- Anodes are negatively charged, and are attracted to anodes which are positively charged.
  - NO the anode oxidation will occur.
- The electron 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 electrode 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 cations undergo reduction to form atoms.
- Salt bridge is used to maintain neutrality.

- the difference between metallic and electrolytic conduction

Metallic conduction	Electrolytic conduction
Conduction through metals is carried out by the movement of delocalized valence electrons	Conduction through electrolytes is carried out by the movement of cations and anions
No change is observed in the chemical properties of the conductors.	It involves a chemical change resulting in the decomposition of electrolytes
It does not involve any transfer of matter	It involves the transfer of matter as ions
It shows an increase in resistance with an increase in temperature.	It shows a decrease in resistance with an increase in temperature.
The conductivity of metals is generally high	The conductivity of electrolytic solutions is generally low
Measured using an ohmmeter	Measured using a conductivity meter

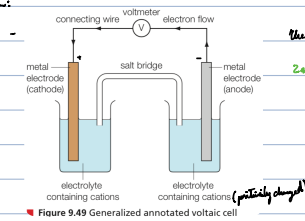
- When a direct current is passed through a solution electrolysis occurs and ions are removed from the solution.

- This can be reversed with an alternating current

- Constructing and annotating basic types of electrochemical cells

- Cells often have to be drawn with:
  - Two half cells
  - A salt bridge
  - An external circuit with:
    - A wire
    - A voltmeter

- Diagram:



The entire voltaic cell can be described with:



- The electrodes and electrolyte should be labelled.
- The electrolyte should be drawn with a power pack or battery connected to two electrodes.
  - The anode is + and cathode is -.
- Diagrams:

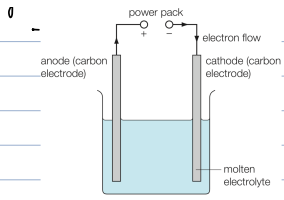


Figure 9.50 Generalized electrolytic cell

- worked example

