9.1 – Introduction to Oxidation and Reduction

9.1.1 - Define oxidation and reduction in terms of electron loss and gain

Oxidation – The loss of electrons from a substance. This may happen through the gain of oxygen or loss of hydrogen

Reduction – The gain of electrons. This may happen though the loss of oxygen, or gain of hydrogen, or decrease in oxidation number

9.1.2 - Deduce the oxidation number of an element in a compound

When oxidation numbers are assigned to an atom, we assume that the electron transfer was complete, even if this is not the case.

In order to deduce the oxidation number, we **use the following rules**:

- The oxidation number of each atom in a pure element is **zero** (such as O_2)
- The oxidation number of an atom in a monatomic ion is equal to the **charge of the ion** (such as S^{2-})
- In compounds that contain oxygen, each oxygen atom has an oxidation number of **-2** (such as H_2O and CO_2). The exceptions include OF_2 (**+2**) and peroxides (**-1**)
- In compounds containing hydrogen, each hydrogen atom has an oxidation number of **+1** (such as NH_3 and H_2O). The exceptions include metal hydrides, like NaH (**-1**)
- For a molecule, the sum of the oxidation numbers of the constituent atoms equals **zero** (such as $CH_4 = C^{-4} + 4H^{+1} = 0$)
- For a polyatomic ion, the sum of the oxidation numbers of the constituent atoms equals the **charge of the ion** (such as $PO_4^{-3} = P^{+5} + 4O^{-2} = -3$)
- In a compound, the most electronegative atom is assigned the **negative oxidation number** (such as $SF_6 = F^{-1}$ and S^{+6})

By convention, the sign (+ or -) is written **before the oxidation number**, for example: Mn^{+7}

9.1.3 - State the names of compounds using oxidation numbers

Since elements like the transition metals can have a few oxidation states, the oxidation number is written with the name of the element in a compound using **Roman numerals**.

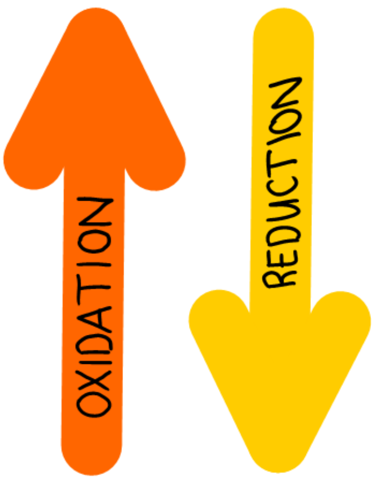
Examples include iron (II) oxide or nitrogen (IV) oxide. The oxidation number is always written in brackets after the name of the element.

9.1.4 - Deduce whether an element undergoes oxidation or reduction in reactions using oxidation numbers

Using the **change in oxidation number** of an atom, we can determine whether oxidation or reduction has occurred in a reaction. In the equation, the numbers are written above the element.

$$\overset{0}{C}_{(s)} + \overset{0}{O}_{2\,(g)} \rightarrow \overset{+4}{C}\overset{-2}{O}_{2\,(g)}$$

In the carbon atom, the oxidation number has increased by four, whilst the oxygen atoms have decreased by two. If the oxidation number **increases**, then oxidation has occurred, whilst if the number **decreases**, then reduction has occurred.



9.2 – Redox Equations

9.2.1 - Deduce simple oxidation and reduction half-equations given the species involved in a redox reaction

The half equations break up the whole equation to show what is happening with each element or molecule. Since one element or molecule will be oxidised while the other is reduced, one half equation will show reduction and the other will show oxidation.

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$$

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

OXIDATION

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

REDUCTION

Using these half-equations, it is easy to see where the electron transfer is taking place, and thus determine which species is undergoing reduction or oxidation. The equations must be balanced for the number of electrons being transferred.

NET EQUATION $$Fe_{(s)} + 2Ag^+_{(aq)} \longrightarrow Fe^{2+}_{(aq)} + 2Ag_{(s)}$$

OXIDATION HALF-EQUATION $$Fe_{(s)} \longrightarrow Fe^{2+}_{(aq)} + 2e^-$$

REDUCTION HALF-EQUATION $$2Ag^+_{(aq)} + 2e^- \longrightarrow 2Ag_{(s)}$$

9.2.2 - Deduce redox equations using half-equations

You may be given two half equations for a complete reaction and be asked to use them to find the whole equation. The individual half-equations allow us to see what is happening to each substance, but can be put back together to give the whole equation. In doing so, the electrons present in these equations will cancel out.

$$2H^{+}{}_{(aq)} + 2e^{-} \rightarrow H_{2\,(g)} \qquad and \qquad Mg_{(s)} \rightarrow Mg^{2+}{}_{(aq)} + 2e^{-}$$

$$\boldsymbol{2H^{+}{}_{(aq)} + Mg_{(s)} \rightarrow H_{2\,(g)} + Mg^{2+}{}_{(aq)}}$$

The Seven Steps to Deducing Redox Equations

1. Identify what is oxidised and what is reduced, and to what.
2. Balance for elements other than hydrogen and oxygen
3. Balance for oxygen by adding water (H_2O) to the side that is deficient in oxygen
4. Balance for hydrogen by adding H^+ to the side that is deficient in hydrogen
5. Balance for charge by adding electrons (e^-) to the more positive side of the equation
6. Equate the electrons lost and gained by multiplying by the small whole integer
7. Add the two half equations, cancelling the electrons, H_2O and H^+ if possible. All the e^- should cancel out.

These reactions often take place in acidified solutions, accounting for the presence of H^+ ions.

Example:

① $Fe^{2+} \rightarrow Fe^{3+}$ Fe^{2+} is oxidised, and is the reducer
$MnO_4^- \rightarrow Mn^{2+}$ MnO_4^- is reduced, and is the oxidiser

② Fe and Mn are both already balanced:

$Fe^{2+} \rightarrow Fe^{3+}$
$MnO_4^- \rightarrow Mn^{2+}$
} Both are in a 1:1 ratio

③ Additional oxygen is needed to balance out the MnO_4^-

$Fe^{2+} \rightarrow Fe^{3+}$
$MnO_{\underline{4}}^- \rightarrow Mn^{2+} + \underline{4H_2O}$

④ Additional hydrogen is needed to balance out the H_2O

$Fe^{2+} \rightarrow Fe^{3+}$
$MnO_4^- + \underline{8H^+} \rightarrow Mn^{2+} + \underline{4H_2O}$

⑤ Add electrons to balance the charge

$Fe^{2+} \rightarrow Fe^{3+} + e^-$ both sides now = 2+
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ both sides now = 2+

⑥ Equate the electrons

$5Fe^{2+} \rightarrow 5Fe^{3+} + 5e^-$ multiplied by 5 to form $5e^-$
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

⑦ Add the half equations

$$5Fe^{2+} + MnO_4^- + 8H^+ + \cancel{5e^-} \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O + \cancel{5e^-}$$

the electrons cancel

$$\underbrace{5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O}_{\text{Final Redox Equation}}$$

9.2.3 - Define the terms oxidising agent and reducing agent

Oxidising Agent – A substance that causes another reactant to be oxidised

Reducing Agent – A substance that causes another reactant to be reduced

9.2.4 - Identify the oxidising and reducing agents in redox equations

Looking at a redox equation, you will need to determine what is happening to the electrons. The species that loses electrons is the **reducing agent**, whilst the species that gains electrons is the **oxidising agent**.

Species being reduced = Oxidising agent

Species being oxidised = Reducing agent

In the example before, the following reaction was used:

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$$

In this equation, zinc is oxidised and copper is reduced. Therefore, zinc is the reducing agent and copper is the oxidising agent.

9.3 – Reactivity

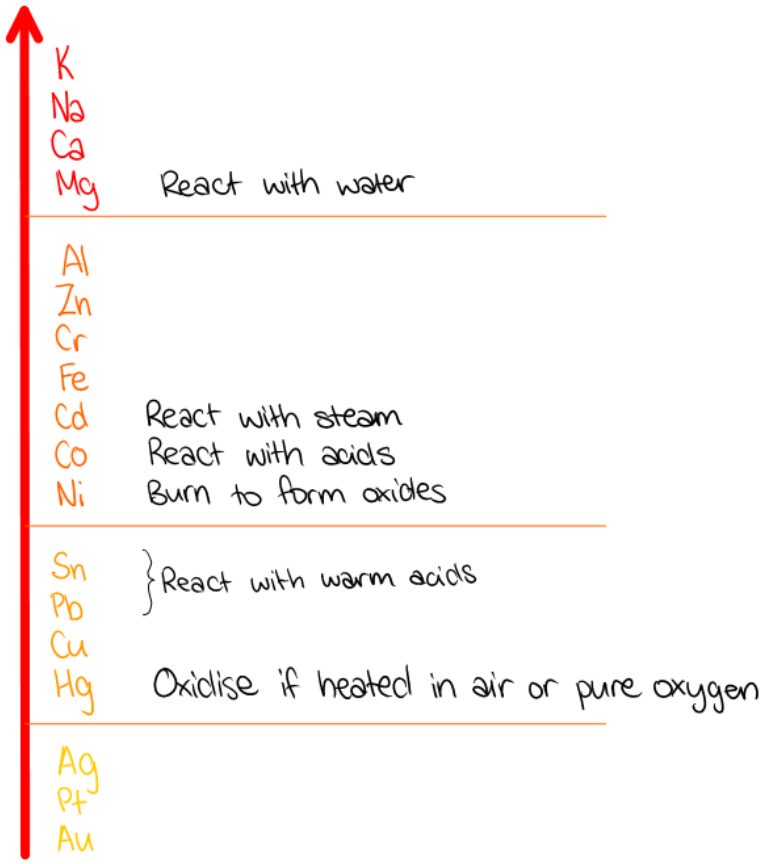
9.3.1 - Deduce a reactivity series based on the chemical behaviour of a groups of oxidising and reducing agents

When a metal is replaced by another metal in a compound, this is called a **metal displacement reaction**. For this to occur, the metal in the compound must be less reactive than the metal it is being replaced by. This new metal is the reducing agent, or electron donor. Although all solid metals act as reducing agents, some are more reactive than others.

We can compare the reactivity of different metals based on a number of factors, including reactivity with:

- Oxygen
- Water
- Dilute acids
- Other metal salts

These are then organised into the reactivity series:



Since all solid metals are oxidised, losing electrons, the reactivity series orders the metals in order of **increasing ease of oxidation**.

Since hydrogen occurs above copper on the reactivity series, any metals below it will not react with acids.

$$Zn_{(s)} + 2H^{+}{}_{(aq)} \rightarrow Zn^{2+}{}_{(aq)} + H_{2\,(g)}$$

A more reactive metal will displace a less reactive metal from its salt. This is because the more reactive metal is a **stronger reducing agent**.

A more reactive halogen will displace a less reactive halogen from a compound. This is because the more reactive halogen is a **stronger oxidising agent**.

Some reactivity series will not only show metals, but oxidising agents as well (non-metals), including the halogens. The reactivity of metals and non-metals is compared using **half-cells**. These all have the same conditions:

- 1 mol dm^{-3} concentration of aqueous solutions
- 25°C temperature
- 1 atm pressure for gases.

Using these cells, the **potential difference** can be measured to determine which element is more reactive.

9.3.2 - Deduce the feasibility of a redox reaction from a given reactivity series

The greater the **difference in reactivity** of two metals, the more rapidly the reaction would occur. However, the metal acting as the reducing agent must occur higher in the reactivity series that the one being reduced. The one being displaced is the oxidising agent.

It is also important to remember that the ions of a less reactive metal will act as stronger oxidising agents. Therefore, they are more likely to oxidise the metals at the top of the series.

This may be done using these steps:

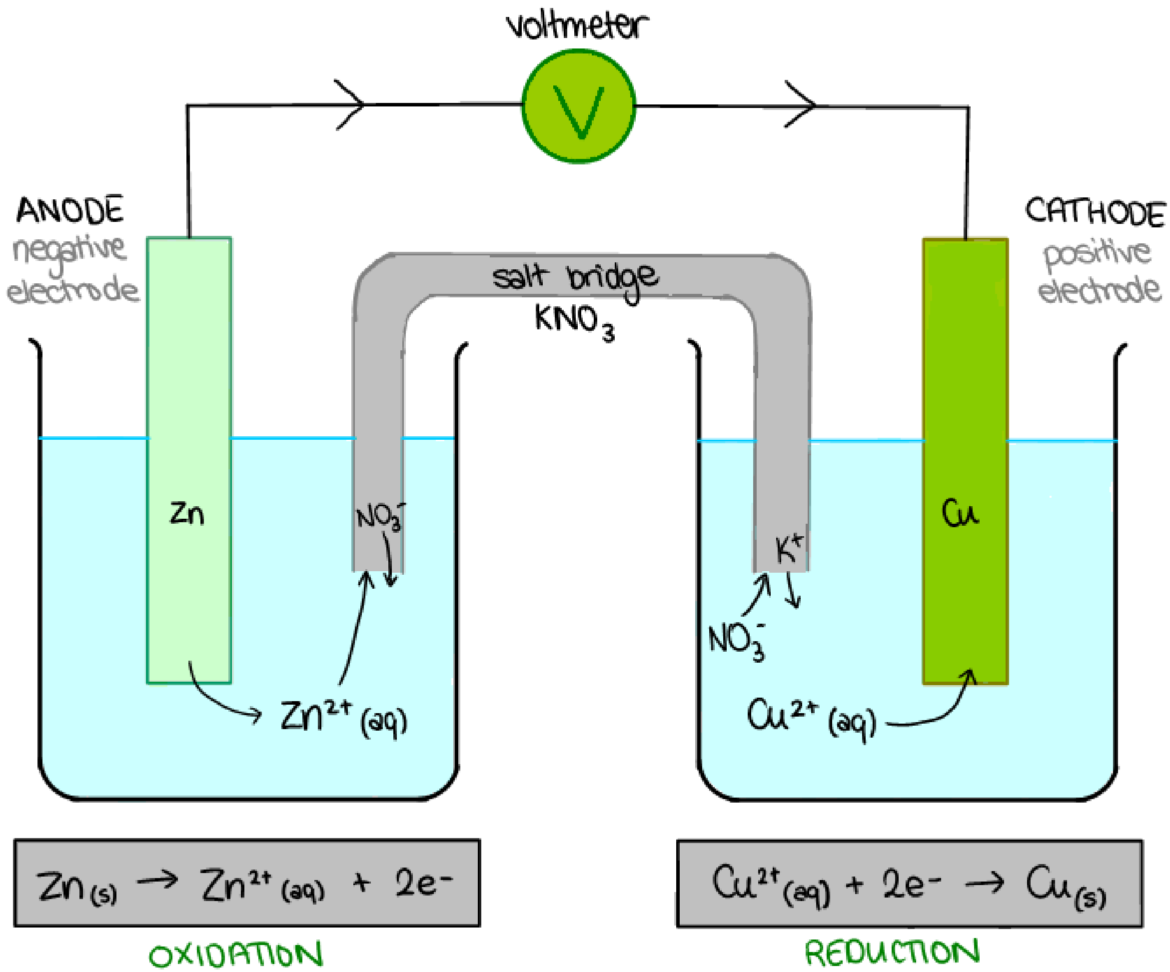
1. Identify all reactants and find their **half-equations** on the electrochemical series. You should have some on each side (the oxidising and reducing agents)
2. The oxidising agent on the **left** must be lower down the series than the reducing agent on the **right**.
3. The half-equation for the reducing agent needs to be **reversed**, then the two half-equations can be balanced and added together

9.4 – Voltaic Cells

9.4.1 - Explain how a redox reaction is used to produce electricity in a voltaic cell

In a half-cell, a metal electrode is placed in an aqueous solution of its ions. Two half cells are connected to form a **voltaic cell**, allowing electrons to flow during the redox reaction and produce electrical energy. The half-cells are joined by a wire to transfer electrons and a salt bridge to transfer ions.

The direction of electron flow is determined by the reactivity of the metals that form the half cells. In the diagram below, the electrons flow from the zinc half-cell to the copper half-cell because zinc is located higher up the reactivity series than copper. In any voltaic cell, the voltage produce during the reaction will depend on the difference in reactivity between the two metals.



In this setup, the anode is sitting in a solution of $Zn(NO_3)_2$ and the cathode is in a solution of $Cu(NO_3)_2$. As the reaction proceeds, the NO_3^- ions in the copper cell flow up into the salt bridge while the Cu^{2+} ions attach to the cathode as the electrons flow down, maintaining charge balance in the cell. The NO_3^- ions replace those moving into the zinc solution to join the Zn^{2+} ions being produced. Hence, the salt bridge is essential for maintaining each half-cell as electrically neutral. The salt usually used in KNO_3 because it will not react with any other substances in the cells.

9.4.2 - State that oxidation occurs at the negative electrode (anode) and reduction occurs at the positive electrode (cathode)

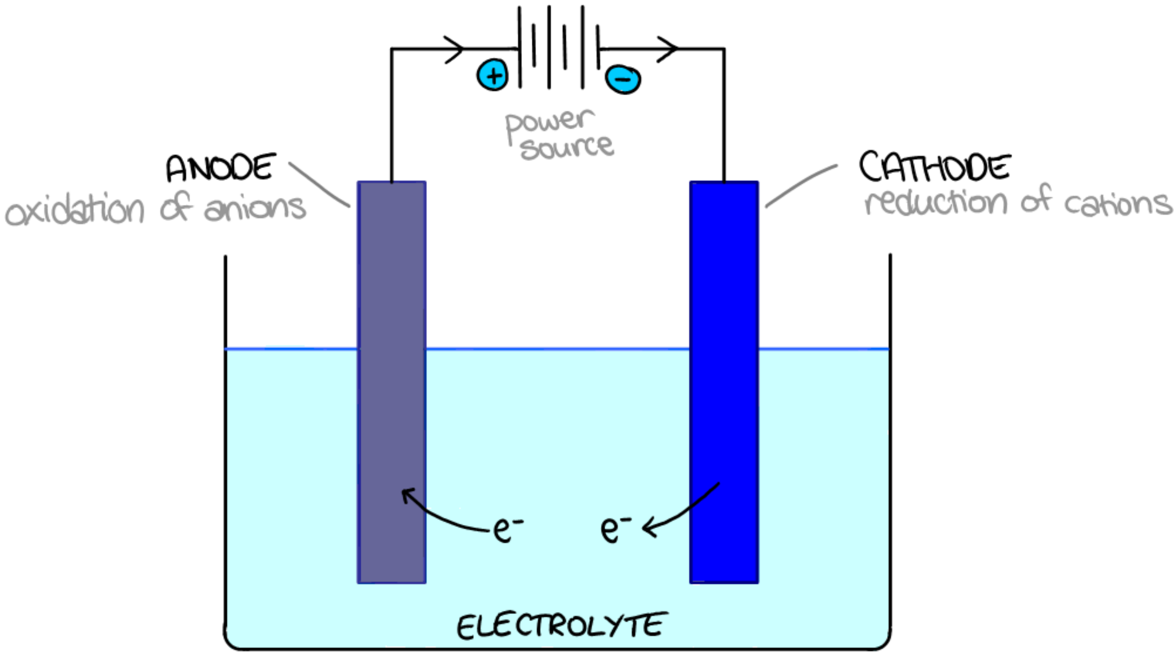
The metal that is more reactive will form the **anode**, since electrons flow from it to the other cell. The electrons are lost from the electrode in an <u>oxidation</u> reaction. The ions formed as the electrons leave the electrode then move into the solution.

On the other hand, the metal that is less reactive will receive the electrons, forming the **cathode**. It accepts the electrons in a <u>reduction</u> reaction. The ions in the solution will combine with the electrons to form solid metal on the electrode.

9.5 – Electrolytic Cells

Electrolysis is used to isolate highly reactive metals, such as sodium and potassium, which would not react in a voltaic cell, but require electrical energy for the reaction to occur. The reactions taking place here are non-spontaneous.

9.5.1 - Describe, using a diagram, the essential components of an electrolytic cell



The power source should be a battery or a DC power source. The electrodes are placed in the electrolyte, connected to the power supply by electrical wires. They must not touch each other.

The electrical energy supplied by the power source induces a flow of electrons from the anode to the cathode. However, unlike in voltaic cells, the **anode is the positive electrode** and the **cathode is the negative electrode**.

When the current reaches the electrolyte, the electrical energy is carried by ions, which migrate to the electrodes. The redox reactions taking place at the electrodes take the ions of out solution and allow it to continue.

9.5.2 - State that oxidation occurs at the positive electrode (anode) and reduction occurs at the negative electrode (cathode)

The power source causes the polarity of the electrodes to change.

The negative electrode, or the **cathode**, has excess electrons, which are removed in a reduction reaction. The cations present in solution will act as oxidising agents and accept the electrons.

The positive electrode, or the **anode**, is deficient in electrons, which are added back in an oxidation reaction. The anions present in solution will act as reducing agents and donate the electrons.

9.5.3 - Describe how current is conducted in an electrolytic cell

The flow of energy in an electrolytic cell has two forms. From the anode to the cathode, the electrons pass along a conductive wire in the form of **electrical energy**. Therefore, the current is conducted by the movement of electrons in the external part of the circuit.

However, electrical energy cannot move through the electrolyte, so the current moves in a different form. At the cathode, electrons are accepted by the positive ions. The flow of current in the electrolyte is facilitated by ions, or **chemical energy**- the positive ions flow towards the cathode and the negative ions flow towards the anode.

9.5.4 - Deduce the products of the electrolysis of a molten salt

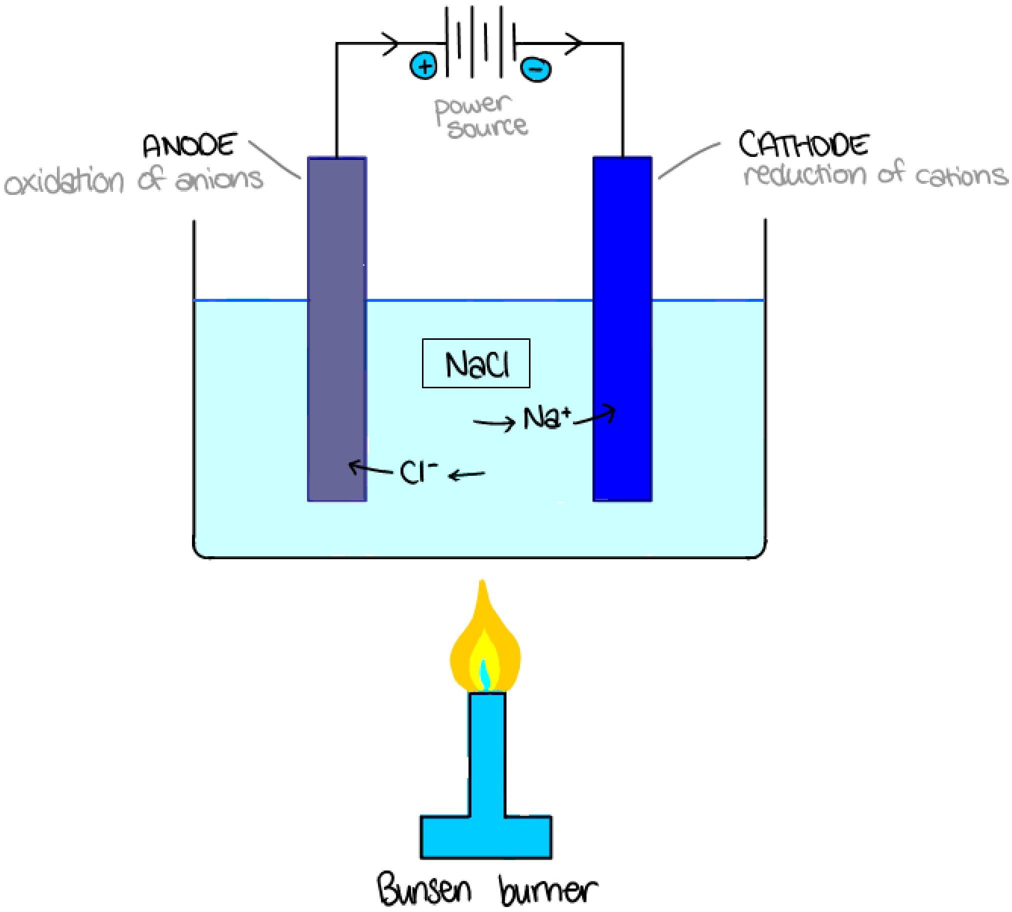
Since sodium ions and chlorine ions do not react spontaneously, they require energy in order for the reaction to proceed. In the electrolysis of molten sodium chloride, sodium metal and chlorine gas are formed.

In this electrolytic cell, the electrolyte is molten NaCl. The electrical current flows towards the negative electrode, causing the **positive Na^+ ions** to be attracted to it. These ions accept the excess electrons in a reduction reaction, forming sodium metal on the cathode. As the electrical current continues to flow, this in turn creates a flow of Na^+ ions towards the negative electrode.

$$Na^+_{(l)} + e^- \rightarrow Na_{(l)}$$

At the **positive electrode**, electrons are pulled away, making the anode electron deficient. As a result, the negative Cl^- ions in the electrolyte are attracted to it. These will donate electrons to the anode in an oxidation reaction, forming chlorine gas in the process.

$$2Cl^-_{(l)} \rightarrow Cl_{2\,(g)} + 2e^-$$



The general half-equations for these reactions are:

Cathode: $M^+ + e^- \rightarrow M$

Anode: $A^- \rightarrow A + e^-$

Summary of Voltaic and Electrolytic Cells:

	Voltaic Cell		Electrolytic Cell	
Anode	oxidation	negative	oxidation	positive
Cathode	reduction	positive	reduction	negative

^ This comes up in exams a lot!