Electrolysis Notes

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Electrolysis can seem a bit odd at first but it's very straightforward. That is, once we get used to the **half equations** and what happens in terms of **reduction** and **oxidation** of course 😊 Let's start there, with half equations.

Half Equations

They are quite short equations which only deal with one species and the electrons that are involved with it.
But, what is the definition of a half equation and how do we use them?

A half equation: is a way of showing either reduction or oxidation in a redox reaction.

A redox reaction: is a reaction in which both reduction and oxidation take place. Or oxidation and reduction if we want to think of it in that order. Most chemical reactions are redox reactions but not all of course.

Let's look at the half equations for copper(II) ions and chloride ions.

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad 2Cl^- \rightarrow Cl_2 + 2e^-$$

Did you spot the difference? We can see that the apart from the atoms themselves being different the main difference is on which side of the reaction the electrons are. Yes, it does matter what side of the reaction the electrons are on.

Half equation rule:

Electrons on the left hand side is reduction.

Electrons on the right hand side is oxidation.

So for the two half equations above we can now say that…

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad 2Cl^- \rightarrow Cl_2 + 2e^-$$

Shows reduction **Shows oxidation**

Now, let's make sure that we understand reduction and oxidation before we look at electrolysis itself.

Reduction and Oxidation

Reduction and oxidation are one of those really important parts of chemistry that we really do need to understand. It can seem a bit odd at first but once we understand it it's fine 😊 First, let's look at the key definitions.

Reduction: the gain of electrons or the loss of oxygen.

Oxidation: the loss of electrons or the gain of oxygen.

We can use **OILRIG** to help us remember this. **O**xidation **I**s **L**oss (of electrons) **R**eduction **I**s **G**ain (of electrons).

A reducing agent: is the substance that causes reduction to happen by losing electrons itself. The substance is oxidised in the process.

An oxidising agent: is the substance that causes oxidation to happen by gaining electrons itself. The substance is reduced in the process.

Redox Equations

A redox equation: a type of chemical equation that represents a redox reaction.

A redox equation is really just the two half equations for a reaction combined and then the electrons cancel each other out 😊 Let's look at a few examples.

Example 1: Magnesium is a more reactive metal than silver. When a piece of magnesium metal is placed into a solution of silver nitrate, a redox reaction occurs. Magnesium atoms (Mg) are oxidised and silver ions (Ag^+) are reduced. Give the redox reaction for this reaction.

Step 1: Write the two half-equations for the reaction.

Oxidation: $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$

Reduction: $Ag^+(aq) + e^- \rightarrow Ag(s)$

Step 2: Balance the electrons.

The oxidation half-equation for magnesium shows 2 electrons being lost, but the reduction half-equation for silver shows 1 electron being gained. For a redox reaction to happen, **the number of electrons transferred must be equal**.

So, we'll need two silver ions to react with every one magnesium atom. To show this, we must multiply the entire silver half-equation by 2.

The magnesium half-equation involves 2 electrons, while the silver half-equation only involves 1 electron. Therefore, the silver half-equation must be multiplied by 2.

The adjusted half-equation is: $2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$

Step 3: Combine the balanced half-equations.

Now that the electrons are balanced, we can add the two equations together. We write everything from the left side of both equations on one side, and everything from the right side on the other. Then we'll cancel out the species that appear on both sides (which in this case is going to be the electrons).

Write the two balanced half-equations:

$$Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$$

$$2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$$

Add them together:

$$Mg(s) + 2Ag^+(aq) + 2e^- \rightarrow Mg^{2+}(aq) + 2Ag(s) + 2e^-$$

Cancel the $2e^-$ from both sides to get the final equation:

$$Mg(s) + 2Ag^+(aq) + \cancel{2e^-} \rightarrow Mg^{2+}(aq) + 2Ag(s) + \cancel{2e^-}$$

$$Mg(s) + 2Ag^+(aq) \rightarrow Mg^{2+}(aq) + 2Ag(s)$$

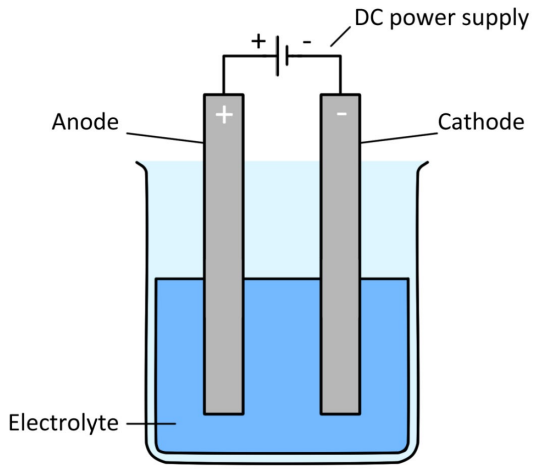
That's it 😊 that's redox equations 😊

Electrolysis

Electrolysis: is the decomposition (breakdown) of an ionic compound using electricity.

Lysis: is the Latin to split or to burst and **electro** clearly means using electricity.

In order to do an electrolysis of a compound we need to have a few things. We need to have a source of electricity, an anode, a cathode, an electrolyte and the compound being decomposed. Check out the figure below 😊



The figure shows the basic set up of an electrolysis practical. It has all the things we need 😊

You may have done a practical that looked quite like this.

Source of electricity: in practicals at school we can use simple cells or batteries or power packs set to direct current.

We really do want to use direct current (DC) as it allows us to have a continuous flow of electrons. Alternating current (AC) can be used in electrolysis but because the current changes direction many times per second and that would change the position of the cathode and anode many times per second. Basically confusing the process.

Anode: is the positively charged electrode. **Cathode**: is the negatively charged electrode.

These two are a weird part of electrolysis! Normally, we would think that the negative electrode would be called the anode and the positive electrode would be called the cathode **but no!** In electrolysis the electrodes are not named after the charge that they actually have. They are named for the ions that they attract!

The positive electrode attracts anions (negative ions) so it is called the anode.

The negative electrode attracts cations (positive ions) so it is called the cathode.

What is an electrode? It's just a conductor that allows current to flow from one medium to another.

For electrolysis these electrodes are usually made out of graphite (because it's cheap) or copper. Both of these materials are good conductors of electricity. Graphite is **inert** (unreactive).

Electrolyte: a substance, either molten or aqueous that contains ions that are free to move and can conduct electricity.

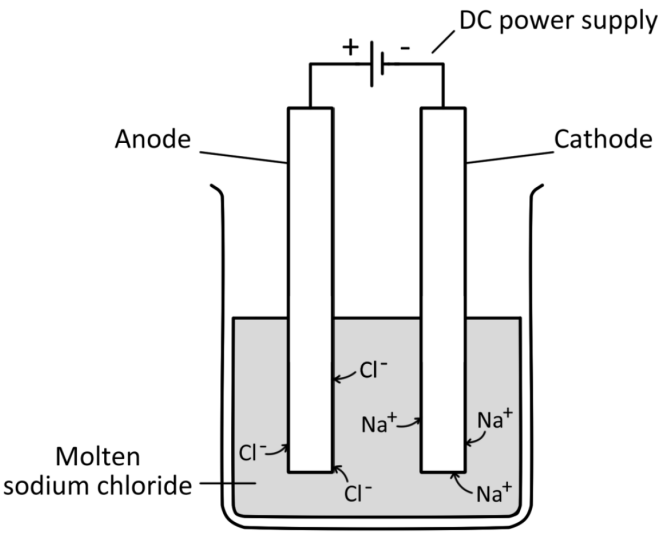
A quick reminder that ionic compounds need to be either molten (so hot it melted) or aqueous (dissolved in water) to conduct electricity. In these states the ions are free to move and carry charge.

Solid ionic compounds do not conduct electricity. As the ions are not free to move and carry charge.

Compound decomposed: will be an ionic compound as these are made of ions that can be separated.

Electrolysis Process

Let's look at a few examples of electrolysis where we can see what happens to the ions of the compounds. The figure below shows the electrolysis of **molten** sodium chloride.



What is happening in this electrolysis?
The cations are attracted to the cathode and the anions are attracted to the anode.

Why are they attracted there?
They are attracted due to the law of opposite charges.

<u>Opposite charges attract, like charges repel</u>.

What are the products of this electrolysis?

1. Sodium metal.
2. Chlorine gas.

Why are there no other products?
There's nothing else there 😊 This electrolysis is being done on a molten compound. There is no water present.

What happens to each Na^+ ion when they get to the cathode?
Each Na^+ ion will gain one electron and become a neutral sodium atom. As this will happen to each Na^+ ion in the molten compound as the process goes on… more and more sodium metal will be deposited at the cathode.

How do we figure out the half equation for this reaction?
First let's ask ourselves, is this oxidation or reduction? Well… the Na^+ gained an electron so it's reduction. For a reduction half equation the electron will be on the left hand side of the equation. That's it 😊

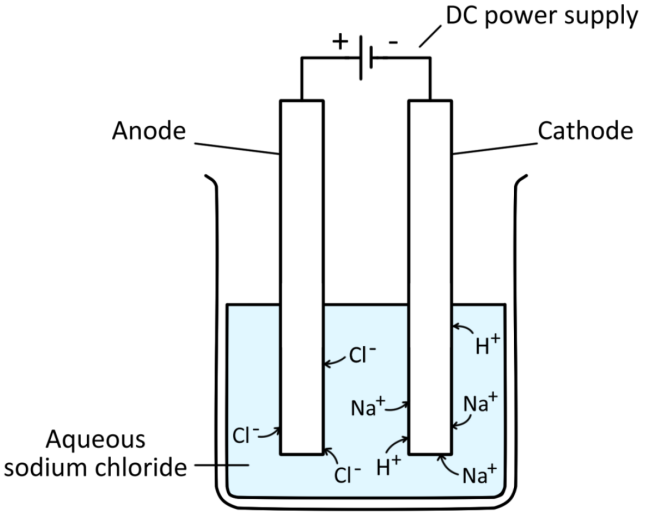
$$Na^+ + e^- \rightarrow Na$$

What happens to Cl^- when it gets to the anode?
Each Cl^- ion will lose one electron and become a neutral chlorine atom. Wait, isn't that <u>oxidation</u>? Yes indeed. Anyway, each chlorine atom will form a covalent bond with another chlorine atom as they both have seven electrons in their outer shells. This will form a molecule of chlorine gas, Cl_2. So, Cl_2 gas will be given off as the process goes on.

How do we figure out the half equation for this reaction?
First let's ask ourselves again, is this oxidation or reduction? Well the Cl^- lost an electron so it's oxidation. For an oxidation half equation the electron will be on the right hand side of the equation. We also need to take into account that Cl_2 gas is the product so we will need two Cl^- ions and two electrons.

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

Next let's look at the electrolysis of sodium chloride solution. The fact it says "solution" tells us that this is the electrolysis of aqueous sodium chloride.



What is happening in this electrolysis?
The cations are again attracted to the cathode and the anions are attracted to the anode.

Why are they attracted there?
They are attracted due to the law of opposite charges.

Opposite charges attract, like charges repel.

What are the products of this electrolysis?

1. Sodium hydroxide.
2. Chlorine gas.
3. Hydrogen gas.

Why are hydrogen gas and sodium hydroxide solution formed in this electrolysis? When the sodium ion went to the cathode and gained an electron that formed a sodium atom. This newly formed sodium atom is immediately surrounded by water molecules.

As an alkali metal, sodium reacts vigorously with water. In this reaction, sodium displaces a hydrogen ion from a water molecule because it is more reactive than hydrogen. The displaced hydrogen forms hydrogen gas, while the sodium combines with the remaining hydroxide (OH^-), resulting in the formation of sodium hydroxide (NaOH).

The equation for sodium reacting with water is:

$$2Na\ (s) + 2H_2O\ (l) \rightarrow 2NaOH\ (aq) + H_2\ (g)$$

The half equation for H^+ at the cathode would be:

$$2H^+ + 2e^- \rightarrow H_2$$

What are the products of the electrolysis of sodium chloride solution used for?

1. **Sodium hydroxide** – is used to make soaps and bleach. It is also used to make paper.
2. **Chlorine gas** – is used in water treatment to kill bacteria and any harmful microorganisms.
3. **Hydrogen gas** – is used in the Haber process to make fertilisers. It can also be used in "Hydrogenation" reactions where hydrogen is added to a compound. For example, alkenes can be hydrogenated (saturated) to become alkanes.

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