

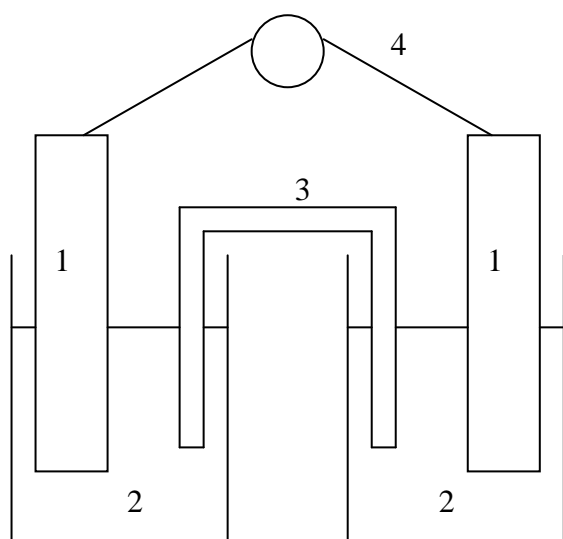
# Electrochemistry

Redox reactions involve the transfer of electrons by definition. This transfer of flow of electrons is in essence an electric current and therefore we can produce electricity from redox reactions. Also by the similar thinking we can use electricity, or a flow of electrons, to force some redox reactions to occur. There are two main types of electrochemical cells, galvanic and electrolytic cells and we will consider each separately.

## Galvanic Cells

We probably use galvanic cells everyday when you turn on your mp3 player, start up your car, look at your watch as all of these objects contain batteries. Batteries are by far the most used application of galvanic cells.

Galvanic cells use **spontaneous redox reactions** which generate an electrical current. Spontaneous redox reactions that occur automatically in everyday conditions, you do not need to initiate or start the reaction using heat or electricity. Below is a diagram of an electrochemical cell and we will discuss each part and how the overall cell works.



Electrodes (1) – These are where the half reactions occur. The electrodes are normally made of metal or graphite as they both conduct electricity very well as solids.

There are two names given to the electrodes the **anode** is where oxidation occurs and the **cathode** is where reduction occurs

Anode, oxidation (vowels)

Cathode, reduction (consonants)

Electrolyte (2) – These are any liquids containing mobile ions, therefore they are generally molten or aqueous salts. Electrolytes are used to conduct electricity and allow the electrons to flow. There are 3 different electrolytes in each galvanic cell one in each of the half cells and one in the salt bridge (3).

Salt bridge (3) – This is used to complete the electrical circuit and without it there would be no flow of electricity. It is a barrier that connects the two half cells and allows the flow of ions.

There are two different types of ions, **anions** which have a negative charge flow towards the anode, and **cations** which have a positive charge flow towards the cathode.

External wire (4) – This is where the electrical flows through and a meter can be attached to show the direction of electron flow.

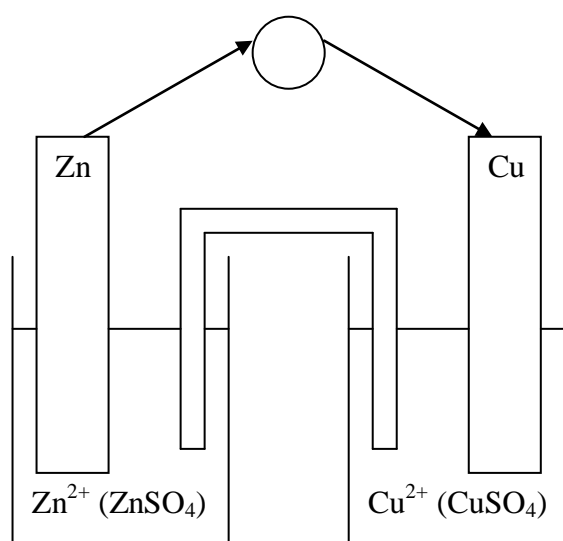
Now that we know all the parts we can figure out how it works and it occurs in a series of steps.

1. There is a loss of electrons at the anode, this is where oxidation occurs.
2. These electrons move through the external wire to the cathode.
3. Reduction occurs to cathode to the ions in solution as electrons are gained.
4. Anions and Cations move through the salt bridge to balance out the circuit.

As there is a collection of anions at the anode, and since anions are negatively charged, the anode is the **negative** electrode, making the cathode **positive**.

There are many types of galvanic cells but the principle remains the same for each a oxidising agent is separated from a reducing agent forcing the electrons to flow through a wire in order for redox to occur.

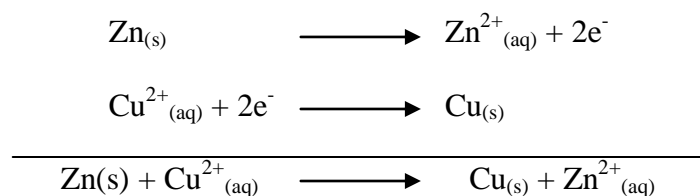
Lets look at a galvanic cell and see what is happening:



In this case as you can see indicated by the arrows the flow of electrons is from the zinc to the copper. This is because zinc is a more reactive metal than zinc and will therefore be the one more likely to lose electrons.

Therefore the zinc electrode will be the anode as there is a loss of electrons hence oxidation is occurring. This makes the copper the cathode as there is a gain of electrons and hence reduction is occurring.

The half reactions and overall redox reaction are shown below

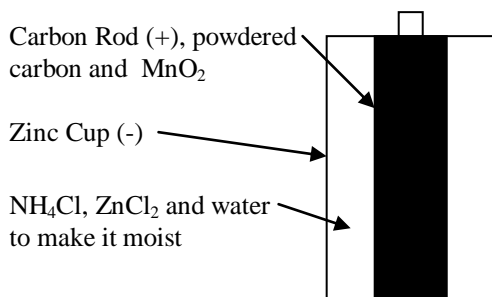


Notice that although we have used both copper and zinc sulfate that the sulfate ions are not included in the half reactions or the overall equation. This is because they do not take part in the reaction even though they are in the solutions, these are known as **spectator ions**.

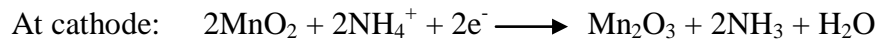
Batteries are a series of cells that have been connected to be able to produce larger electrical currents. There are two main types of cells. **Primary cells** are cells that cannot be recharged, once they have been used you throw them away. Secondary cells can be recharged many times and reused, however they do have a limited lifetime as recharging does damage the battery.

It is important to note that in primary cells the electricity flow will only last as long as the chemical reaction. If the reaction stops then so does the flow of electricity. When there are no materials close to the electrodes then the reaction will stop, therefore the choice of electrolyte to maximise the mobility of ions is very important. There are many types of cells and some of these are shown below.

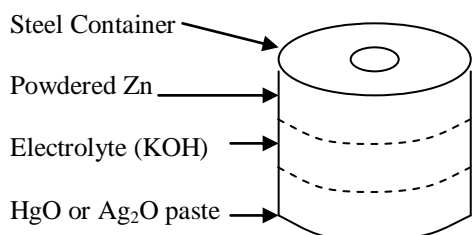
## Dry Cells



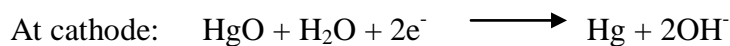
The dry cell is the most common form of battery used. This cell gives off approximately 1.5 volts. The reactions are:



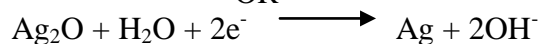
## Minature Cells



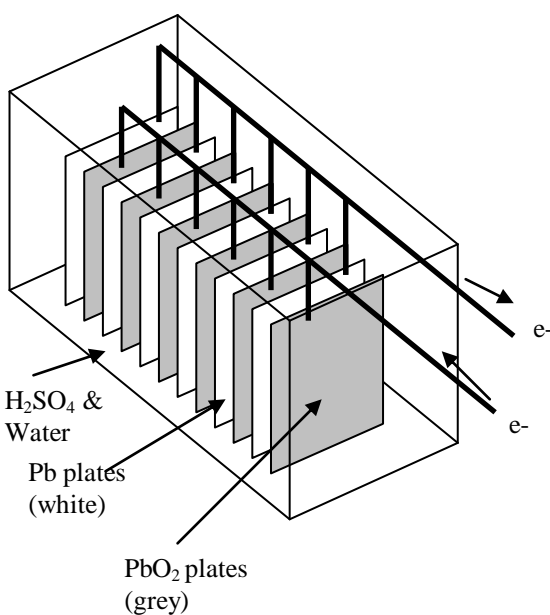
Minature cells are used where you need a small battery and you want it to put out a constant voltage over the time that it is discharging. They have a voltage of 1.35 volts. The reactions are:



OR

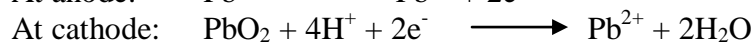
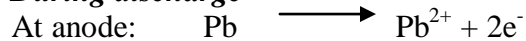


## Lead-Acid Cells

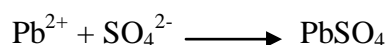


Lead-acid cells are secondary cells, which means that they can be recharged. They are the most common form of secondary cell used. Secondary cells rely on being able to generate another power to be able to reverse the redox reaction and therefore turning products back into reactants. They are widely used as they are cheap although you must be careful as they produce hydrogen and can explode near flames The reactions for discharge and recharge are shown below:

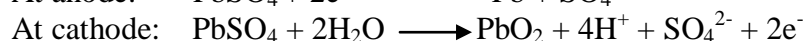
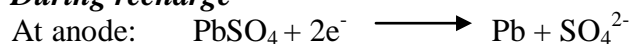
### *During discharge*



Lead ions are trapped as PbSO<sub>4</sub> during discharge and we get the following



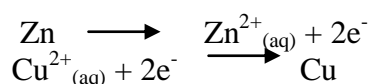
### *During recharge*



## Standard Reduction Potentials

All galvanic cells produce a voltage and the voltage or potential for each half reaction is a characteristic amount and will remain the same no matter what other half reaction you pair it with. Therefore we can predict the voltage we can achieve from a redox reaction simply by adding the voltages of the half reactions.

Lets take the galvanic cell formed between copper and zinc the half reactions are

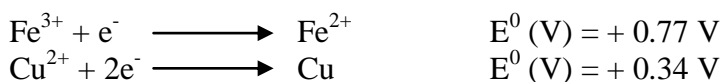


From the table opposite we can see that for the copper equation the voltage is +0.34 volts. However the zinc equation is reversed on the sheet. This is because it is a list of reduction potentials and the zinc has been oxidised. So we need to reverse the equation and therefore reverse the sign of the voltage so we get a voltage of +0.76 volts for zinc. Therefore overall we should get an overall cell voltage of 1.10 volts.

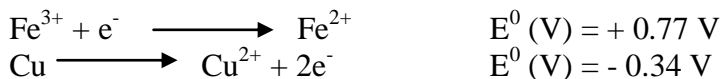
In this case we knew which one was oxidised and which was reduced. If this was not the case but we knew what roughly what the half equations were you can still figure out the cell voltage by reversing the voltage sign and equation of the one lowest on the list before adding them.

Let us take another example of another galvanic cell and see how much voltage a copper/iron (III) cell produces.

The two reactions from the list we are looking for are



However we can not simply add these as they both have electrons on the reactants side and therefore we have two reduction equations. The copper equation has the lowest reduction potential so we need to reverse this equation to get.



Now we can add them to get and overall cell voltage of + 0.43 V

## Standard Reduction Potentials at 25°C 1 M 1 atm

HALF-REACTION	E° (V)
F <sub>2(g)</sub> + 2 e <sup>-</sup> → 2 F <sup>-</sup> (aq)	+2.87
O <sub>3(g)</sub> + 2 H <sup>+</sup> (aq) + 2 e <sup>-</sup> → O <sub>2(g)</sub> + H <sub>2</sub> O(l)	+2.07
Co <sup>3+</sup> (aq) + e <sup>-</sup> → Co <sup>2+</sup> (aq)	+1.82
H <sub>2</sub> O <sub>2(aq)</sub> + 2 H <sup>+</sup> (aq) + 2 e <sup>-</sup> → 2 H <sub>2</sub> O(l)	+1.77
PbO <sub>2(s)</sub> + 4 H <sup>+</sup> (aq) + SO <sub>4</sub> <sup>2-</sup> (aq) + 2 e <sup>-</sup> → PbSO <sub>4(s)</sub> + 2 H <sub>2</sub> O(l)	+1.70
Ce <sup>4+</sup> (aq) + e <sup>-</sup> → Ce <sup>3+</sup> (aq)	+1.61
MnO <sub>4</sub> <sup>-</sup> (aq) + 8 H <sup>+</sup> (aq) + 5 e <sup>-</sup> → Mn <sup>2+</sup> (aq) + 4 H <sub>2</sub> O(l)	+1.51
Au <sup>3+</sup> (aq) + 3 e <sup>-</sup> → Au(s)	+1.50
Cl <sub>2(g)</sub> + 2 e <sup>-</sup> → 2 Cl <sup>-</sup> (aq)	+1.36
Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> (aq) + 14 H <sup>+</sup> (aq) + 6 e <sup>-</sup> → 2 Cr <sup>3+</sup> (aq) + 7 H <sub>2</sub> O(l)	+1.33
MnO <sub>2(s)</sub> + 4 H <sup>+</sup> (aq) + 2 e <sup>-</sup> → Mn <sup>2+</sup> (aq) + 2 H <sub>2</sub> O(l)	+1.23
O <sub>2(g)</sub> + 4 H <sup>+</sup> (aq) + 4 e <sup>-</sup> → 2 H <sub>2</sub> O(l)	+1.23
Br <sub>2(l)</sub> + 2 e <sup>-</sup> → 2 Br <sup>-</sup> (aq)	+1.07
NO <sub>3</sub> <sup>-</sup> (aq) + 4 H <sup>+</sup> (aq) + 3 e <sup>-</sup> → NO(g) + 2 H <sub>2</sub> O(l)	+0.96
2 Hg <sup>2+</sup> (aq) + 2 e <sup>-</sup> → Hg <sub>2</sub> <sup>2+</sup> (aq)	+0.92
Hg <sub>2</sub> <sup>2+</sup> + 2 e <sup>-</sup> → 2 Hg(l)	+0.85
Ag <sup>+</sup> (aq) + e <sup>-</sup> → Ag(s)	+0.80
Fe <sup>3+</sup> (aq) + e <sup>-</sup> → Fe <sup>2+</sup> (aq)	+0.77
O <sub>2(g)</sub> + 2 H <sup>+</sup> (aq) + 2 e <sup>-</sup> → H <sub>2</sub> O <sub>2(aq)</sub>	+0.68
MnO <sub>4</sub> <sup>-</sup> (aq) + 2 H <sub>2</sub> O(l) + 3 e <sup>-</sup> → MnO <sub>2(s)</sub> + 4 OH <sup>-</sup> (aq)	+0.59
I <sub>2(s)</sub> + 2 e <sup>-</sup> → 2 I <sup>-</sup> (aq)	+0.53
O <sub>2(g)</sub> + 2 H <sub>2</sub> O + 4 e <sup>-</sup> → 4 OH <sup>-</sup> (aq)	+0.40
Cu <sup>2+</sup> (aq) + 2 e <sup>-</sup> → Cu(s)	+0.34
AgCl(s) + e <sup>-</sup> → Ag(s) + Cl <sup>-</sup> (aq)	+0.22
SO <sub>4</sub> <sup>2-</sup> (aq) + 4 H <sup>+</sup> (aq) + 2 e <sup>-</sup> → SO <sub>2(g)</sub> + 2 H <sub>2</sub> O(l)	+0.20
Cu <sup>2+</sup> (aq) + e <sup>-</sup> → Cu <sup>+</sup> (aq)	+0.15
Sn <sup>4+</sup> (aq) + 2 e <sup>-</sup> → Sn <sup>2+</sup> (aq)	+0.13
2 H <sup>+</sup> (aq) + 2 e <sup>-</sup> → H <sub>2(g)</sub>	0.00
Pb <sup>2+</sup> (aq) + 2 e <sup>-</sup> → Pb(s)	-0.13
Sn <sup>2+</sup> (aq) + 2 e <sup>-</sup> → Sn(s)	-0.14
Ni <sup>2+</sup> (aq) + 2 e <sup>-</sup> → Ni(s)	-0.25
Co <sup>2+</sup> (aq) + 2 e <sup>-</sup> → Co(s)	-0.28
PbSO <sub>4(s)</sub> + 2 e <sup>-</sup> → Pb(s) + SO <sub>4</sub> <sup>2-</sup> (aq)	-0.31
Cd <sup>2+</sup> (aq) + 2 e <sup>-</sup> → Cd(s)	-0.40
Fe <sup>2+</sup> (aq) + 2 e <sup>-</sup> → Fe(s)	-0.44
Cl <sup>-</sup> (aq) + 3 e <sup>-</sup> → Cl(s)	-0.74
Zn <sup>2+</sup> (aq) + 2 e <sup>-</sup> → Zn(s)	-0.76
2 H <sub>2</sub> O(l) + 2 e <sup>-</sup> → H <sub>2(g)</sub> + 2 OH <sup>-</sup> (aq)	-0.83
Mn <sup>2+</sup> (aq) + 2 e <sup>-</sup> → Mn(s)	-1.18
Al <sup>3+</sup> (aq) + 3 e <sup>-</sup> → Al(s)	-1.66
Be <sup>2+</sup> (aq) + 2 e <sup>-</sup> → Be(s)	-1.85
Mg <sup>2+</sup> (aq) + 2 e <sup>-</sup> → Mg(s)	-2.37
Na <sup>+</sup> (aq) + e <sup>-</sup> → Na(s)	-2.71
Ca <sup>2+</sup> (aq) + 2 e <sup>-</sup> → Ca(s)	-2.87
Sr <sup>2+</sup> (aq) + 2 e <sup>-</sup> → Sr(s)	-2.89
Ba <sup>2+</sup> (aq) + 2 e <sup>-</sup> → Ba(s)	-2.90
K <sup>+</sup> (aq) + e <sup>-</sup> → K(s)	-2.93
Li <sup>+</sup> (aq) + e <sup>-</sup> → Li(s)	-3.05

↑ strong oxidizing agents

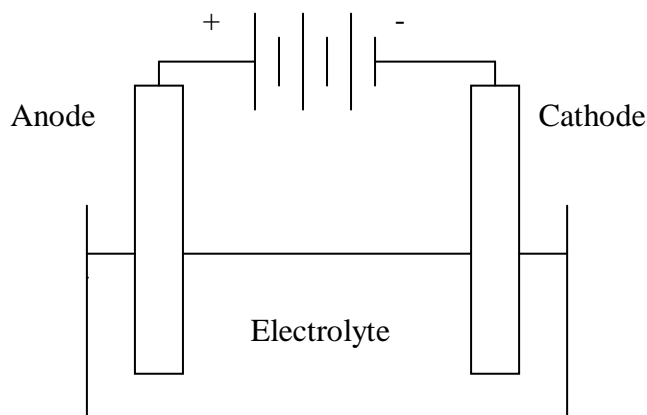
↓ strong reducing agents

# Electrolytic Cells

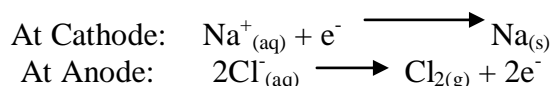
Electrolytic cells are electrochemical cells in which an electrical current is used to drive a non-spontaneous redox reaction. Electrolytic cells are one of the most important industrial processes as they are used in the production and purification of metal, production of chemicals and in electroplating amongst other uses.

In this case the electrolyte is still a conducting liquid however it must be chosen to meet the purpose it is being used for as the products at each electrode will be the components of the electrolyte in most cases

Let us take an example using molten NaCl as the electrolyte. Therefore in the electrolyte we would have  $\text{Na}^+$  and  $\text{Cl}^-$  ions. When the electrolytic cell is turned on the positive  $\text{Na}^+$  ions would be attracted to the cathode where they would gain electrons and the negative  $\text{Cl}^-$  would be attracted to the anode where it would lose electrons.

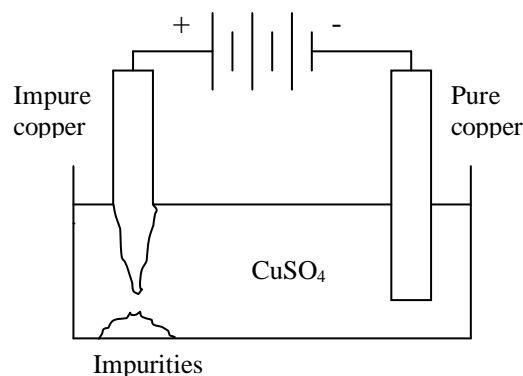


This would give us the production of sodium (Na) metal at the cathode and chlorine ( $\text{Cl}_2$ ) gas at the anode the half reactions are shown below.



This process of electrolysis is such a powerful process that it can be used to extract any metal from any ore although it is not preferred because it uses a lot of energy which is expensive. In this case we used a molten electrolyte as sodium is a very reactive metal and would react with the water as soon as it is formed if it was an aqueous electrolyte. For metals that are less reactive such as copper an aqueous electrolyte can be used.

Electrolysis can also be used in the purification of metals once they have been extracted from the ores. Metals such as copper often have to be extremely pure (>99%) for some uses and electrolysis is the best way of doing this. In this case if the impure copper sample is put on the anode it will be ionised and attracted to the cathode as pure copper whilst the impurities will fall to the bottom of the vessel in which the electrolysis is taking place.



Electrolysis can also be used for the process of electroplating, where one metal is plated on top of another. Like before metals will always collect at the cathode so we want the object being plated there and the plating metal at the anode. This anode will be ionised and broken down where it travels through the electrolyte and is plated onto the object.

