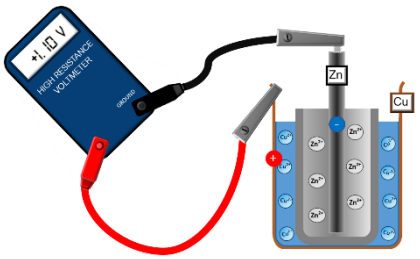
Standard Electrode Potentials, $E^{\ominus}$/V



Introduction

The path to **electrode potentials** began when you were probably 12 or 13 years old, when you first did some simple experiments with metals and solutions of metal compounds.

For example, you may well have added small samples of metal elements to solutions of compounds of other metals. This was probably done in test tubes or a well plates. Indeed, this is how our Year 8 students first observe a range of reactivities in metal elements. They add samples of elemental zinc, magnesium, lead and iron to aqueous solutions of these metal sulfates. They are asked to observe if there is a reaction or not. From this, they can develop a rank order of reactivity assuming that a **more reactive metal will displace a less reactive metal** from its compound. There is no mention of the chemistry behind these reactions. This rank order of metals will have been called the **reactivity series.**

You may have also compared reactivity of metals in water. This is done for metals such as **lithium**, **sodium**, **potassium** and **calcium**. The vigour of fizzing is used to rank the reactivity of the metals. When less reactive metals are placed in water, no fizzing is observed and so is it hard to use the reaction with water to rank metals such as **zinc**, **lead**, **magnesium** and **iron**. However, these metals can be ranked by their reaction with dilute hydrochloric acid. Fizzing is used again to rank these metals. Your teacher may have also explained that metals which react with acid must be more reactive than hydrogen and those that do not react with hydrogen are less reactive that hydrogen. This allows us to include **hydrogen** in the growing reactivity series.

Putting all this together, you have a simple reactivity series.

Reactivity Series
Potassium
Sodium
Lithium
Calcium
Magnesium
Zinc
Iron
Lead
Hydrogen
Tin
Copper

You will have written word (and possibly symbol) equations for the process. But, there will still probably not be a mention of the **REDOX** chemistry involved in these processes.

Fast-forwarding to GCSE, you will have learned about **REDOX** reactions and the fact that OXIDATION can be explained in terms of OXYGEN GAIN (at foundation level) and **ELECTRON LOSS** (the true definition).

Once you have been introduced to the definition, you are then able to appreciate **HALF-EQUATIONS**.

e.g.

$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$ OXIDATION Half-Equation (electron loss)

$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$ REDUCTION Half-Equation (electron loss)

$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$ OVERALL EQUATION (electrons cancelled)

You will have learned about the extraction of metals from their ores and how carbon can be used for metals that are less reactive than **CARBON.** The reaction of the heated metal oxide with carbon is described as SMELTING and is the chemistry involved in the extraction of iron from its ore in the BLAST FURNACE (although, the main **reduction agent** for the reduction of iron oxide is actually carbon monoxide!).

This then allowed **CARBON** to be included in the reactivity series:

Reactivity Series	
Potassium	metals extracted using **electrolysis**
Sodium	
Lithium	
Calcium	
Magnesium	
Zinc	
Carbon	metals extracted using **smelting**
Iron	
Lead	
Hydrogen	
Tin	
Copper	

.

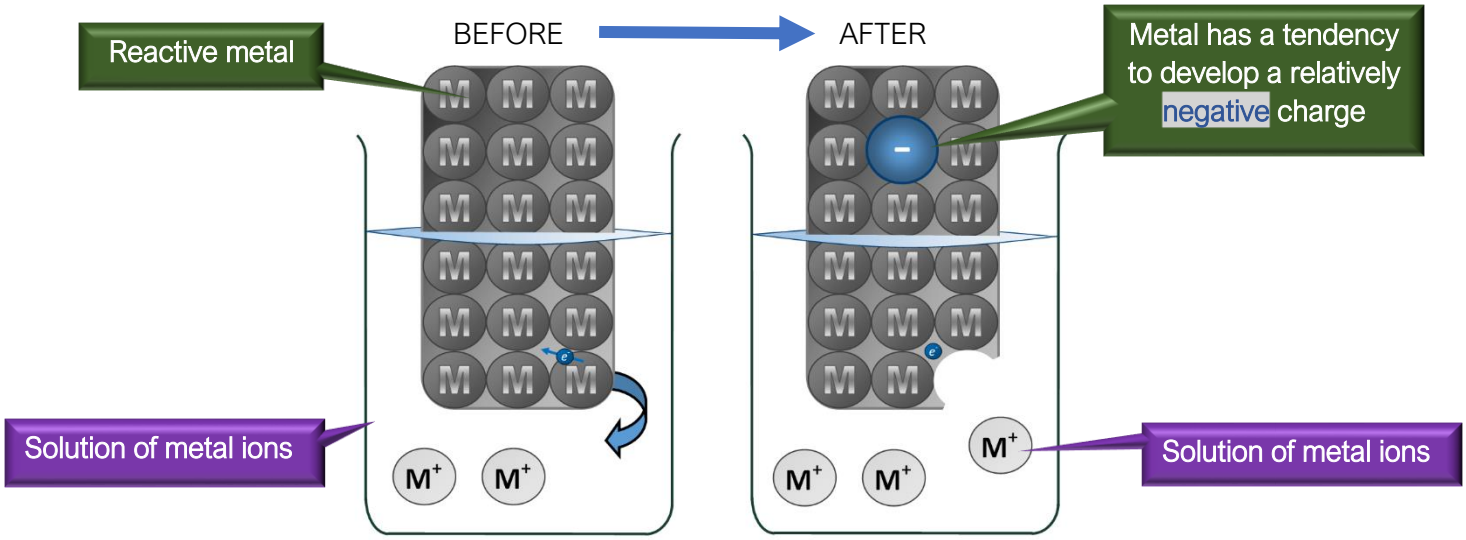
At GCSE some of you may have even been loosely introduced to electrode potentials when you learned that a voltage (potential difference) develops between metals of different reactivity when they are dipped in conducting solutions and that the size of the voltage is indicative for the difference in reactivity (how far apart they are in the reactivity series). Many of you will be familiar with the idea that you can push samples of two different metals into something like a potato, and the difference in potential can be sufficient to drive a current, powering a simply device such as an LCD clock.

By now, you should have been developing a sense that **more reactive metal atoms** have a tendency to **give away electrons** to become ions and **ions of less reactive metals** have a tendency to **gain electrons** to become atoms.

Metals Dipping in Solutions of Their Ions

When we dip a metal into a solution of its ions, there will either be;

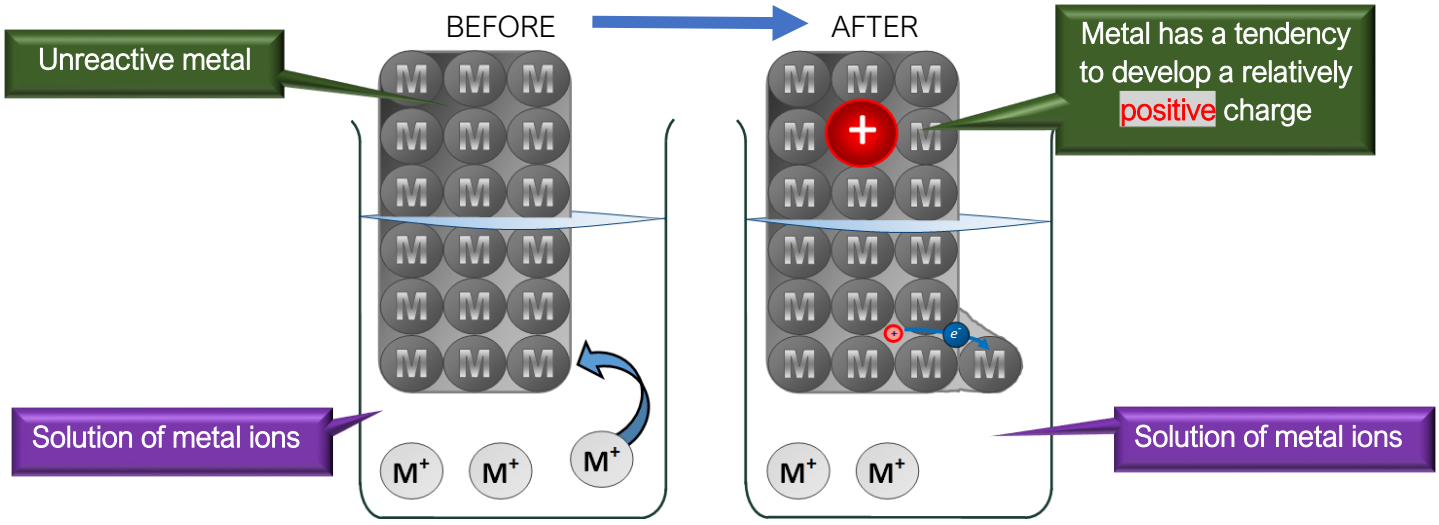
- a tenancy for **atoms** from the piece of metal to be released into the solution to **become hydrated ions**, leaving their electrons behind as part of the '*sea of delocalised electrons*'. This will create an imbalance between the number of electrons in '*sea of delocalised electrons*' and the total positive charge on the piece of metal (from the lattice of ions). The piece of metal will become a little bit negative.



If this process could progress, we would see a process of OXIDATION taking place.

$$M_{(s)} \rightarrow M^{z+}_{(aq)} + z\,e^- \quad \text{OXIDATION}$$

- Or, a tendency for metal **ions** from the solution to **become atoms** of metal by joining the piece of metal. To allow this, electrons from the 'sea of delocalised electrons' must be donated to the ion. This will create an electron deficit and the piece of metal will become a little bit positive.



If this process was allowed to progress, we would see a process of REDUCTION taking place.

$$M^{z+}_{(aq)} + z\,e^- \rightarrow M_{(s)} \quad \text{REDUCTION}$$

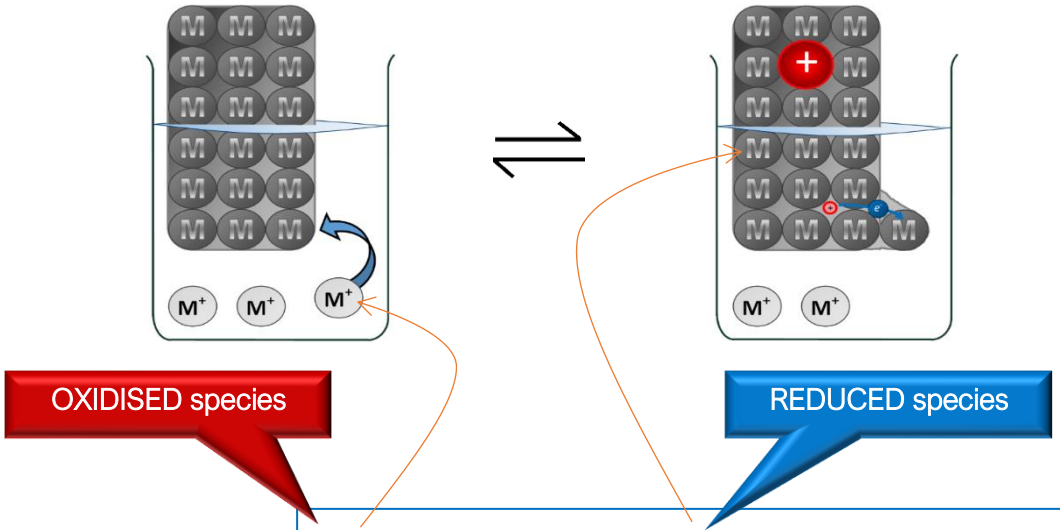
This is a simplified situation. For example, there is no mention of the anions in solution; typically, sulfate or nitrate.

All metals must have a tendency to follow one of either processes shown above, to a greater or less extent.

The more reactive a metal is, the more it shows a tendency to undergo oxidation to produce ions.

The more unreactive a metal is, the more it shows a tendency to undergo reduction of its ions to produce atoms.

These 2 processes can be summarised in one simple equilibrium expression



$M^{z+}_{(aq)} + z\,e^- \rightleftharpoons M_{(s)}$ Written like this, REDUCTION is in the **forwards direction**. This is the convention!

The ***z*** in the equilibrium simply allows the expression to be more general. ***z*** will have values of 1, 2 or 3.

In the equilibrium show above, for **reactive metals** dipped into to a solution of their ions, the equilibrium will lie to the left and the metal will have a tendency to develop a negative charge. **The further to the left, the greater the relative** negative charge.

However, for **unreactive metals** when dipped into to a solution of their ions, the equilibrium will lie to the right and the metal will have a tendency to develop a positive charge. **The further to the right, the greater the relative** positive charge.

Now, this is all rather theoretical.

Firstly, in the set up described so far, these equilibria cannot be fully established as it would lead to a solution that was not electrically neutral and this limits the progression to equilibrium. So far, we have ignored the anions that would be present in the solution. These would typically be **sulfate ions** or **nitrate ions**. There cannot be a situation when the metal cations and anions are significantly imbalanced. If there is going to be a potential **release of metal ions into the solution** OR **removal of metal ions from the solution**, there must be a source of ions that can be added to the solution to maintain the electrical neutrality of the solution. More on how this is done, shortly!

Secondly, the positive or negative charge, created on the piece of metal, needs to be **compared to something** else. We need to say that it has become **positive or negative, relative to something that is standard**. It's rather like describing something as being geographically NORTH. It is meaningless unless you state that it is NORTH of something else, for example, the equator.

A Standard by which we can compare our Metal

In this next section, we will address the 2 issues mentioned above.

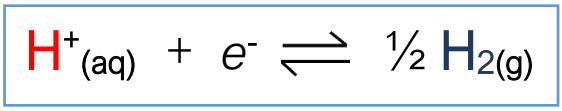
We will introduce a **standard** to compare our metal against. And, we will overcome the issue of electrical neutrality of the solution of ions.

It would seem sensible to compare our metal sample against another system. We could choose another specific metal that is dipped into a solution of its own ions. We could measure a difference in potential between any metal under investigation and that specific metal. Each time we do this, we could compare to the same *'standard metal'*. If our metal is more reactive than the '*standard metal'*, there would be a negative potential difference shown on a voltmeter. If the metal is less reactive, there would be a positive potential difference shown on the voltmeter. Our standard metal would be analogous to our equator in the geographical example offered earlier, where you can describe your position of latitude relative to the equator.

We have settled on one standard combination of element and its ions (a **half-cell**). This **half-cell** may seem a little complicated but there are good reasons for its choice.

- Firstly, it isn't even a metal!
- Secondly, it isn't a solid dipping into a solution.

BUT it has an **oxidised** species in **equilibrium** with the **reduced** species. Here is the equilibrium:



Practically, this equilibrium is a little more complicated to set up. It needs to have **hydrogen gas** and **hydrogen ions** in equilibrium with each other. This is not as difficult as it sounds. It can be done if one has the hydrogen gas and hydrogen ions (from a solution of a strong acid, such as hydrochloric acid) in close contact on the surface of some platinum metal. The unreactive platinum doesn't react, but it does develop the potential created by the equilibrium species.

Standard Conditions

It won't surprise you to hear that we need to have some rules regarding **concentration**, **temperature,** and **pressure** in these 'half-cells'

As these are equilibria, standardising these conditions is essential.

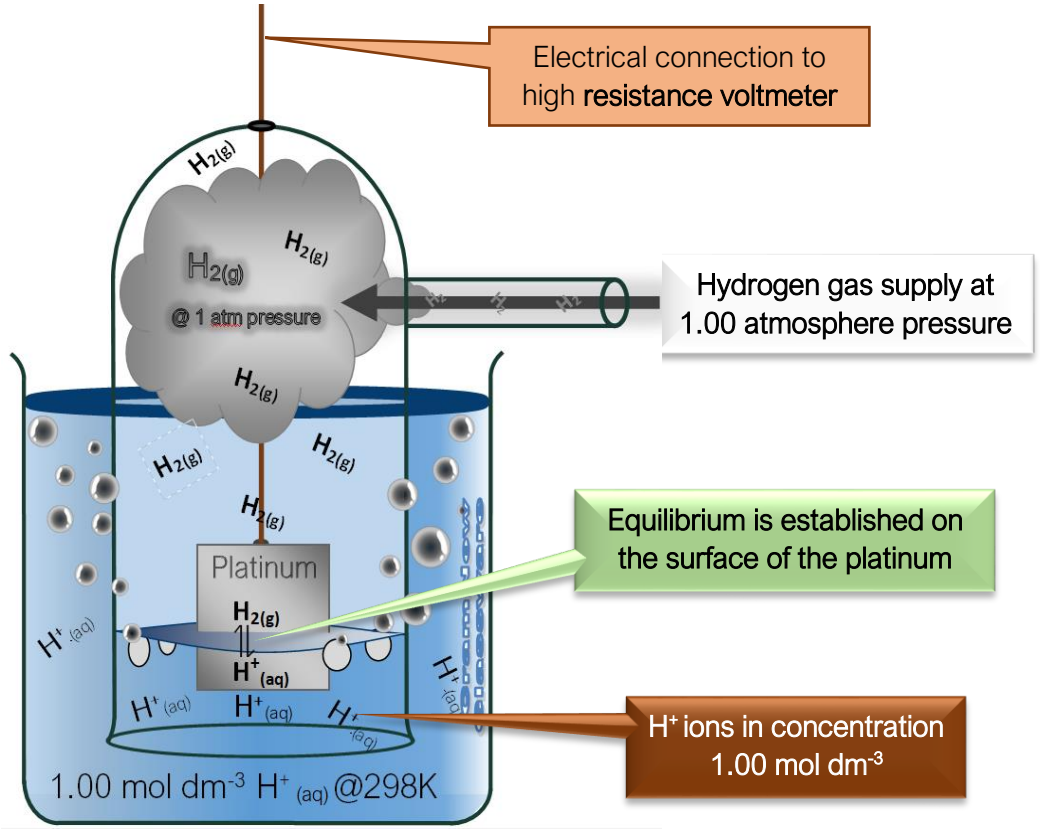
The STANDARD CONDITIONS are:

- **Concentration** must be 1.00 mol dm^{-3}
- **Temperature** must be 298K
- **Pressures** of gases must be 1 atm (100 kPa)

We will use the usual sign, $^{\ominus}$, to show that conditions are standard. None of that should surprise you!

The Standard Hydrogen Electrode (S.H.E.)

An illustration of the standard hydrogen electrode (S.H.E.) is given below.



This hydrogen half-cell is **arbitrarily** taken to have a potential of **0.00V**.

When this is connected to the ground (or COM) of a high resistance voltmeter and the other terminal connected to another half-cell, then the reading on the voltmeter will be the standard electrode potential of that half-cell.

Although the S.H.E. is a bit tricky to set up, it has been adopted as the standard and given the value of **0.00V** arbitrarily. There is some sense in choosing this as hydrogen is placed about halfway down the electrochemical series. We will soon see that standard electrode potentials typically range from around +3V to -3V **compared to hydrogen.**

Function of Salt Bridge

In very simple terms, the salt bridge 'completes the circuit'.

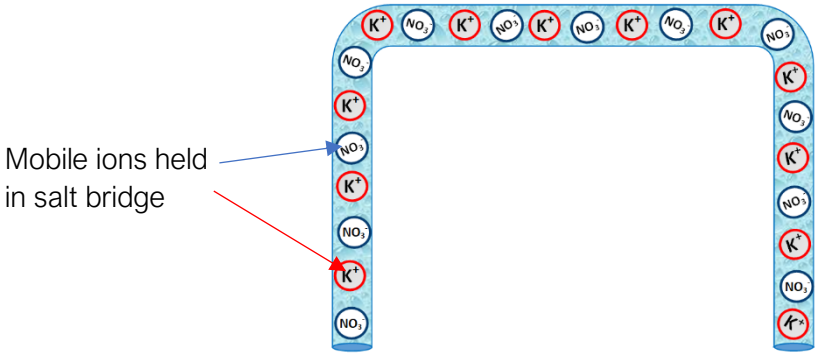
It is worth explaining how the salt bridge does this.

Each half-cell can't reach it's potential when the metal is simply dipped into the solution of its ions because it would involve a change to the balance of anions and cations in solution. If the metal were to release some cations into the solution, these would need to be balanced by the addition of anions to the solution so that electrical neutrality would be maintained. Likewise, if metal cations were converted to metal atoms then there would be a shortage of cations in solution. This would require a source of cations to replace them.

In essence, the salt bridge is a reservoir of inert ions than can be released on demand into the solutions in half-cells. This allows the solutions to maintain electrical neutrality.

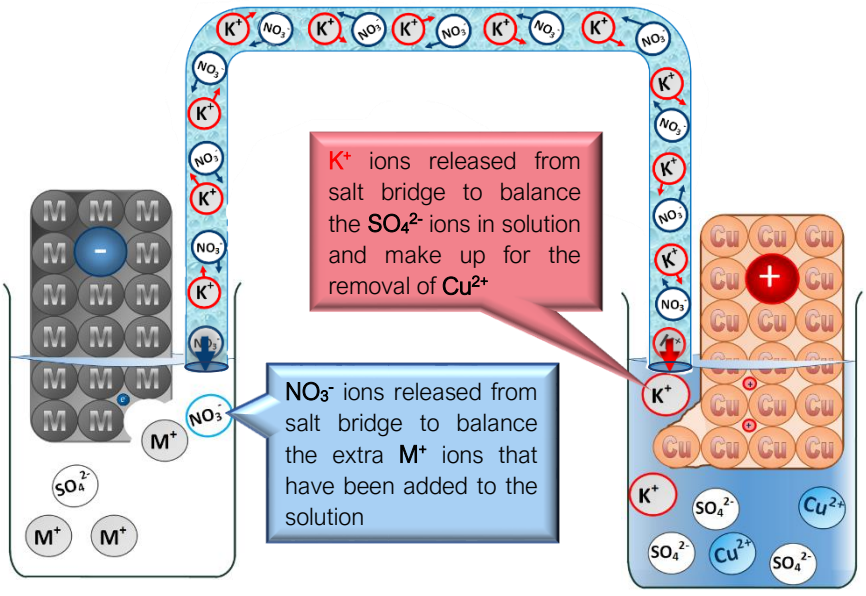
A salt bridge can be is simple as a strip of filter paper, soaked in saturated potassium nitrate solution. Each end is then dipped in each half-cell.

A more sophisticated arrangement is a glass tube containing the potassium nitrate in a gel. In each case, the bridge is capable of delivering cations and anions.

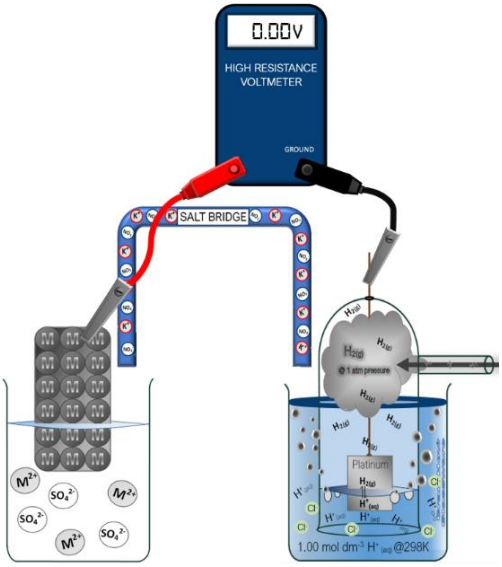


- In one half-cell, reduction of ions in solution will be taking place (creating atoms in the electrode. This requires extra cations to allow equilibrium to be attained, K^+ ions flow from the bridge.

- In the other half-cell, oxidation of atoms in solution will be taking place (creating cations in the solution) This requires extra anions to allow equilibrium to be attained, NO_3^- ions flow from the bridge



Before the salt bridge is inserted into the circuit, each electrode is incapable of reaching its true potential.



Upon addition of salt bridge, equilibrium can establish itself in both half-cells and a potential difference can be measured between the half-cells. In this case, one of the half-cells is the standard hydrogen electrode. This is connected to the ground (or common, COM) of the voltmeter. The reading on the voltmeter is therefore the standard electrode potential in the other half-cell. Remember, the standard hydrogen electrode is been decided **arbitrarily** to be **0.00V**!

One of two processes can then take place.

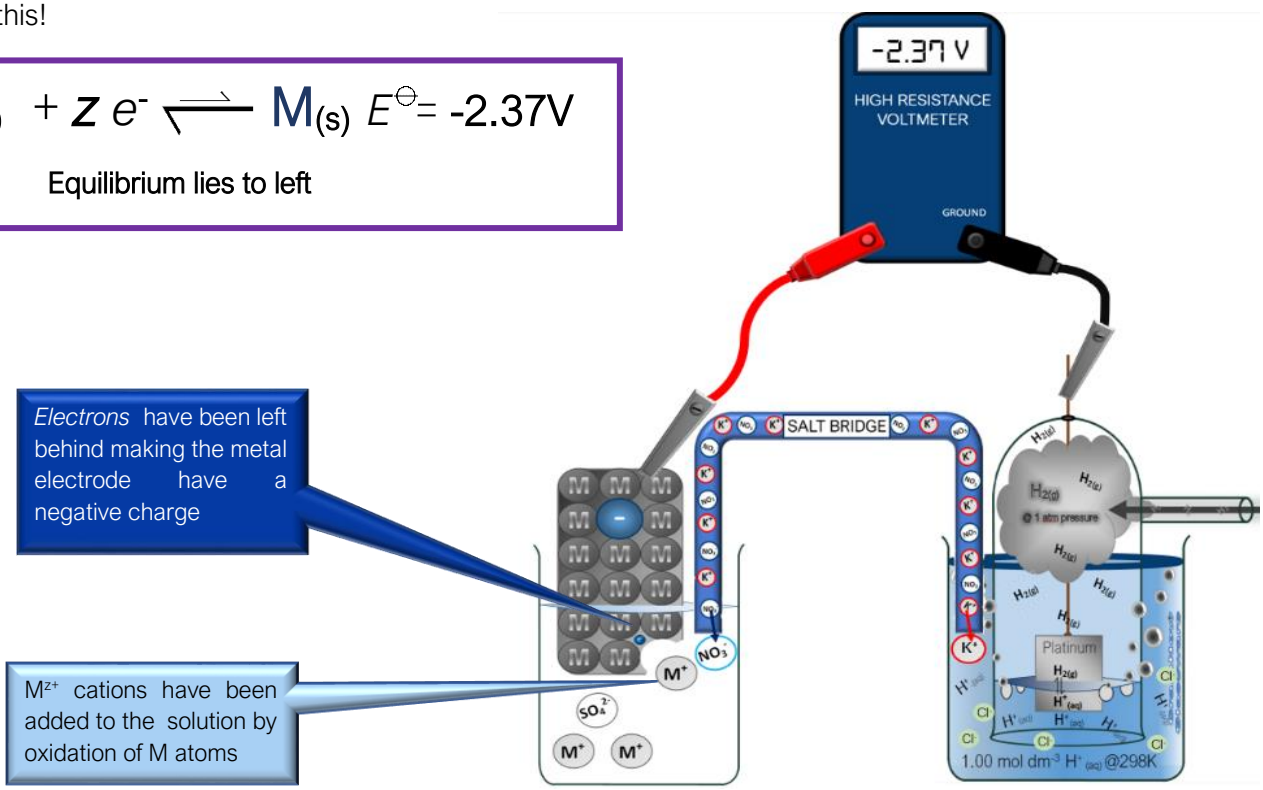
For a **metal that is more reactive than hydrogen**, there is a tendency for atoms of the metal electrode to undergo oxidation and metal atoms from the electrode dissolve in the solution leaving the electrode **negative**, relative to hydrogen. This would be typical for a metal such as magnesium.

Oxidation **takes place at this electrode and so we define this electrode as the ANODE**.

Sadly, at GCSE you may have been led to assume that cathodes are always negative. This is true in the process of **electrolysis** but not in the case of **spontaneous processes taking place in cells**! Make sure that you understand this!

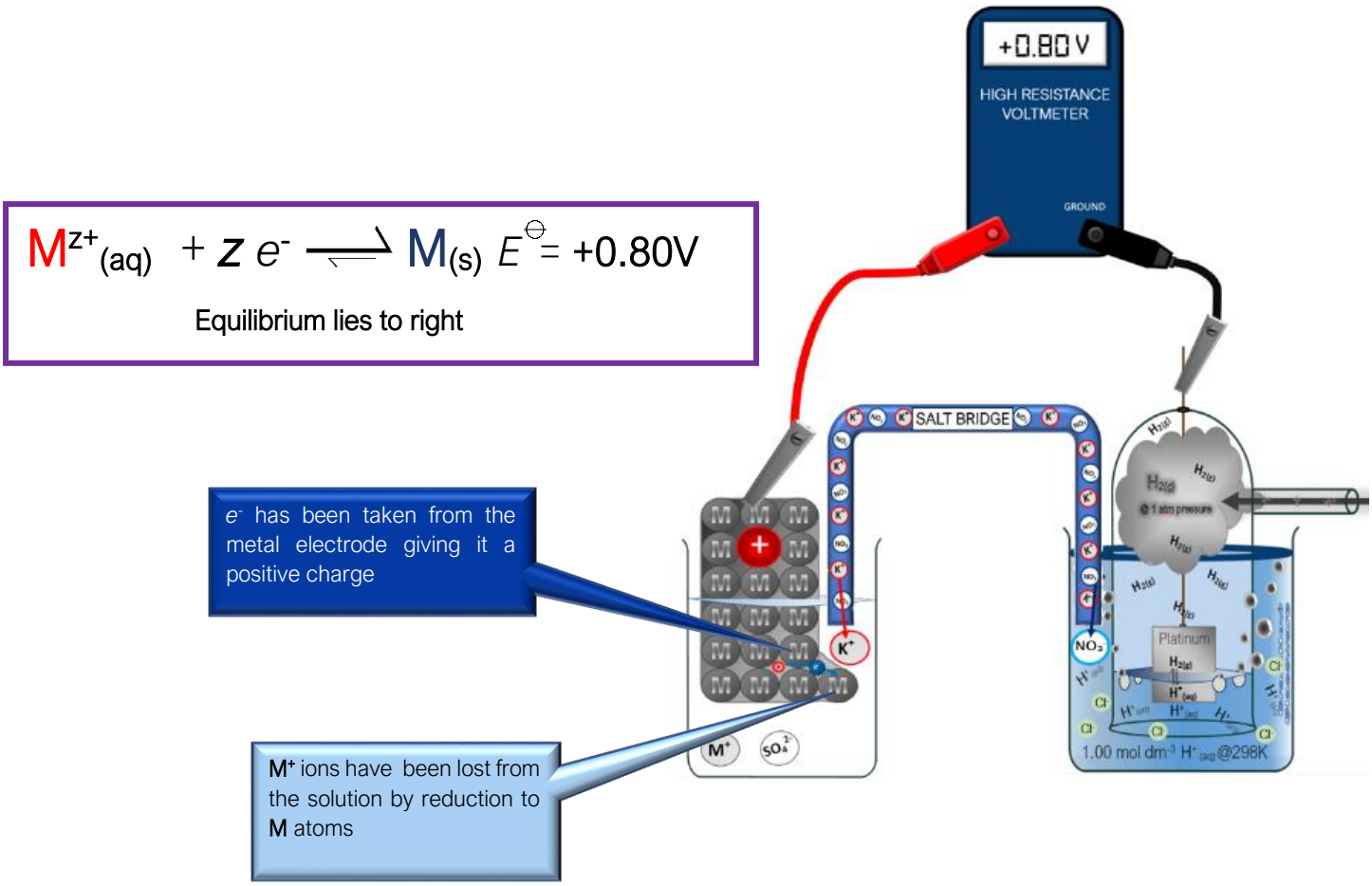
$$M^{z+}_{(aq)} + z\,e^- \rightleftharpoons M_{(s)} \quad E^{\ominus} = -2.37V$$

Equilibrium lies to left



For a **metal that is less reactive than hydrogen**, there is a tendency for ions of the metal solution to undergo reduction and the ions leave solution and become part of the electrode making the electrode **positive**, relative to hydrogen. This would be typical for a metal such as silver. In this case, M is Silver.

REDUCTION takes place at this electrode and so we define this electrode as the CATHODE.



$$M^{z+}_{(aq)} + z\,e^- \rightleftharpoons M_{(s)} \quad E^{\ominus} = +0.80V$$

Equilibrium lies to right

By repeating the process with different half-cells, a list of standard electrode potentials $E^{\ominus}/V$ has been created (The Electrochemical Series).

The list shows the equilibria with **reduction in the forward direction**. This is the convention.

Traditionally, the **more negative values are placed at the top**. These are for equilibria where the position of equilibrium lies to the left, *i.e.* towards the oxidised form. Be careful though; some sources list these electrode potentials with the more positive ones at the top! A selection of **Standard Electrode Potentials** is shown on the following page.

We can conclude that **the more positive an electrode potential value**, the **further to the right the equilibrium lies**.

The **high resistance voltmeter** is essential to ensure that virtually no current flows in the circuit. We are only trying to measure a potential. If current could flow through the voltmeter, the half-cells would not be in equilibrium and chemical processes would progress to take place and run to completion. Electrons building up on the anode would be allowed to flow to the cathode where they would reduce metal ions. Neither the anodic nor cathodic processes would be closed systems due to addition or loss of electrons, therefore not in equilibrium! Think about Le Chatelier's Principle.

Here is an analogy. Consider the point where two professional boxers face each other, the day before a boxing match. This is similar in the way that, **no fighting must take place** at this point. However, those wishing to gamble on the outcome can get a feeling for the potential of each boxer. The fighters need to be close but kept apart so that no fighting takes place. Of course, this sometimes goes spectacularly wrong and they start fighting. I do not promote boxing or gambling!

A Selection of Standard Electrode Potentials, $E^{\ominus}$/ V

	Electrode Potentials, $E^{\ominus}$			
	OXIDISED FORM	⇌	REDUCED FORM	$E^{\ominus}$/ V
1	$Li^+_{(aq)} + e^-$	⇌	$Li_{(s)}$	-3.03
2	$K^+_{(aq)} + e^-$	⇌	$K_{(s)}$	-2.92
3	$Na^+_{(aq)} + e^-$	⇌	$Na_{(s)}$	-2.71
4	$Mg^{2+}_{(aq)} + 2e^-$	⇌	$Mg_{(s)}$	-2.37
5	$ZnO_{(s)} + H_2O_{(l)} + 2e^-$	⇌	$Zn_{(s)} + 2OH^-_{(aq)}$	-1.28
6	$2H_2O_{(l)} + 2e^-$	⇌	$2OH^-_{(aq)} + H_{2(g)}$ (alkaline conditions)	-0.83
7	$2Cd(OH)_{2(s)} + 2e^-$	⇌	$Cd_{(aq)} + 2OH^-_{(aq)}$	-0.81
8	$Zn^{2+}_{(aq)} + 2e^-$	⇌	$Zn_{(s)}$	-0.76
9	$Fe^{2+}_{(aq)} + 2e^-$	⇌	$Fe_{(s)}$	-0.44
10	$PbSO_{4(s)} + 2e^-$	⇌	$Pb_{(s)} + SO_4^{2-}{}_{(aq)}$	-0.36
11	$V^{3+}_{(aq)} + e^-$	⇌	$V^{2+}_{(aq)}$	-0.26
12	$Sn^{2+}_{(aq)} + 2e^-$	⇌	$Sn_{(s)}$	-0.14
13	$H^+_{(aq)} + e^-$	⇌	$\frac{1}{2}H_{2(g)}$ (acidic conditions)	0.00
14	$S_4O_6{}^{2-}_{(aq)} + 2e^-$	⇌	$2\ S_2O_3{}^{2-}_{(aq)}$	+0.09
15	$Cu^{2+}_{(aq)} + e^-$	⇌	$Cu^+_{(aq)}$	+0.15
16	$2MnO_{2(s)} + H_2O_{(l)} + 2e^-$	⇌	$Mn_2O_{3(s)} + 2OH^-_{(aq)}$	+0.15
17	$Cu^{2+}_{(aq)} + 2e^-$	⇌	$Cu_{(s)}$	+0.34
18	$VO^{2+}_{(aq)} + 2H^+_{(aq)} + e^-$	⇌	$V^{3+}_{(aq)} + H_2O_{(l)}$	+0.34
19	$O_{2(g)} + 2H_2O_{(l)} + 2e^-$	⇌	$4OH^-_{(aq)}$ (alkaline conditions)	+0.40
20	$2NiOOH_{(s)} + 2H_2O + 2e^-$	⇌	$2Ni(OH)_{2(s)} + 2OH^-_{(aq)}$	+0.49
21	$Cu^+_{(aq)} + e^-$	⇌	$Cu_{(s)}$	+0.52
22	$\frac{1}{2}I_{2(aq)} + e^-$	⇌	$I^-_{(aq)}$	+0.54
23	$O_{2(g)} + 2H^+_{(aq)} + 2e^-$	⇌	$H_2O_{2(aq)}$	+0.68
24	$2MnO_{2(s)} + 2NH_4^+{}_{(aq)} + 2e^-$	⇌	$Mn_2O_{3(s)} + 2NH_{3(aq)} + H_2O_{(l)}$	+0.75
25	$Fe^{3+}_{(aq)} + e^-$	⇌	$Fe^{2+}_{(aq)}$	+0.77
26	$Ag^+_{(aq)} + e^-$	⇌	$Ag_{(s)}$	+0.80
27	$NO_3^-{}_{(aq)} + 2H^+_{(aq)} + e^-$	⇌	$\frac{1}{2}N_2O_{4(aq)} + H_2O_{(l)}$	+0.80
28	$VO_2^+{}_{(aq)} + 2H^+_{(aq)} + e^-$	⇌	$VO^{2+}_{(aq)} + H_2O_{(l)}$	+1.00
29	$\frac{1}{2}Br_{2(l)} + e^-$	⇌	$Br^-_{(aq)}$	+1.09
30	$O_{2(g)} + 4H^+_{(aq)} + 4e^-$	⇌	$2H_2O_{(l)}$ (acidic conditions)	+1.23
31	$Cr_2O_7^{2-}{}_{(aq)} + 14H^+_{(aq)} + 6e^-$	⇌	$2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$	+1.33
32	$\frac{1}{2}Cl_{2(g)} + e^-$	⇌	$Cl^-_{(aq)}$	+1.36
33	$MnO_4^-{}_{(aq)} + 8H^+_{(aq)} + 5e^-$	⇌	$Mn^{2+}_{(aq)} + 4H_2O_{(l)}$	+1.51
34	$PbO_{2(s)} + SO_4^{2-}{}_{(aq)} + 4H_{(aq)} + 2e^-$	⇌	$PbSO_{4(s)} + 2H_2O_{(l)}$	+1.69
35	$H_2O_{2(aq)} + 2H^+_{(aq)} + 2e^-$	⇌	$2H_2O_{(l)}$	+1.77
36	$\frac{1}{2}F_{2(g)} + e^-$	⇌	$F^-_{(aq)}$	+2.87

The colour pairs are well known ½ cell pairings in common cells and redox titrations

is the Daniell Cell

is the typical non-rechargeable storage cell (Leclanché)

is the rechargeable lead/acid cell

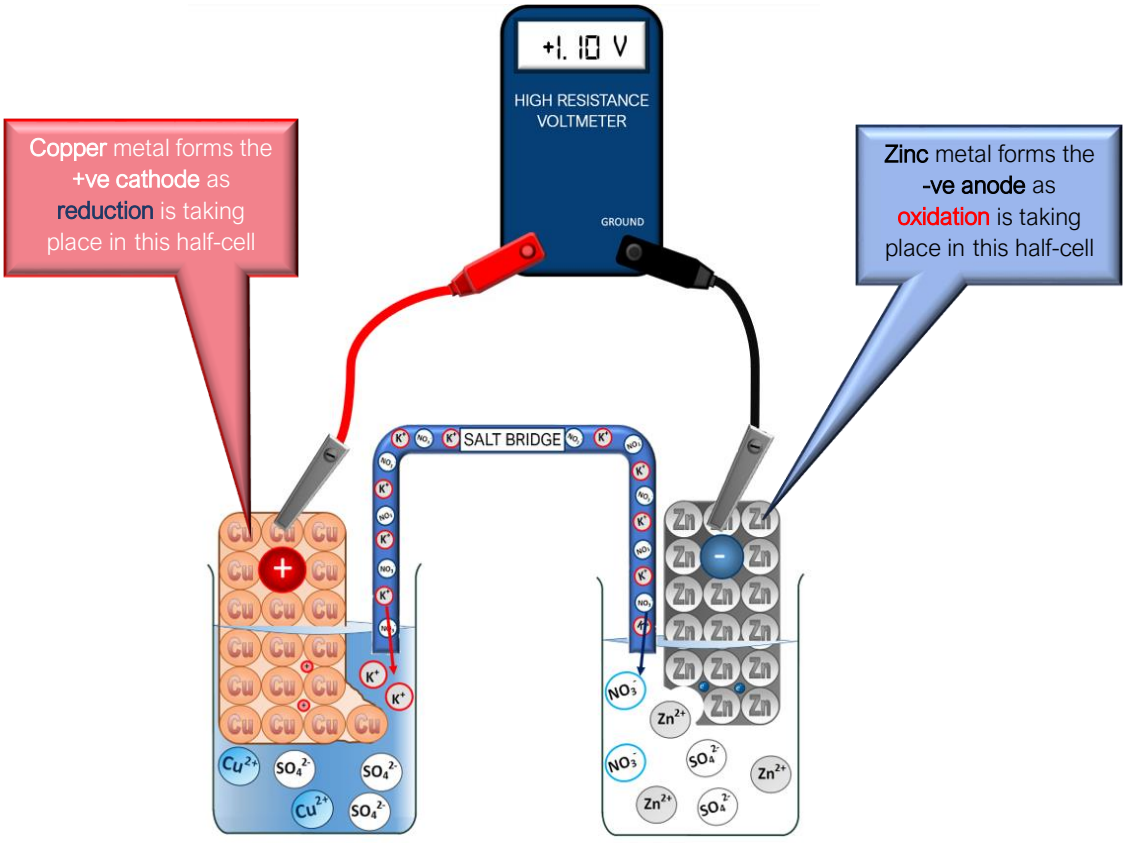
is the rechargeable NiCd cell

is the hydrogen fuel cell (acidic conditions)

is the hydrogen fuel cell (alkaline conditions)

Copper/Zinc Cell - 'The Daniell Cell'

		Electrode Potentials, $E^{\ominus}$			
		OXIDISED FORM	⇌	REDUCED FORM	$E^{\ominus}$/ V
	8	$Zn^{2+}_{(aq)} + 2e^-$	⇌	$Zn_{(s)}$	-0.76
	17	$Cu^{2+}_{(aq)} + 2e^-$	⇌	$Cu_{(s)}$	+0.34



$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$

Equilibrium pushes to right in REDUCTION DIRECTION

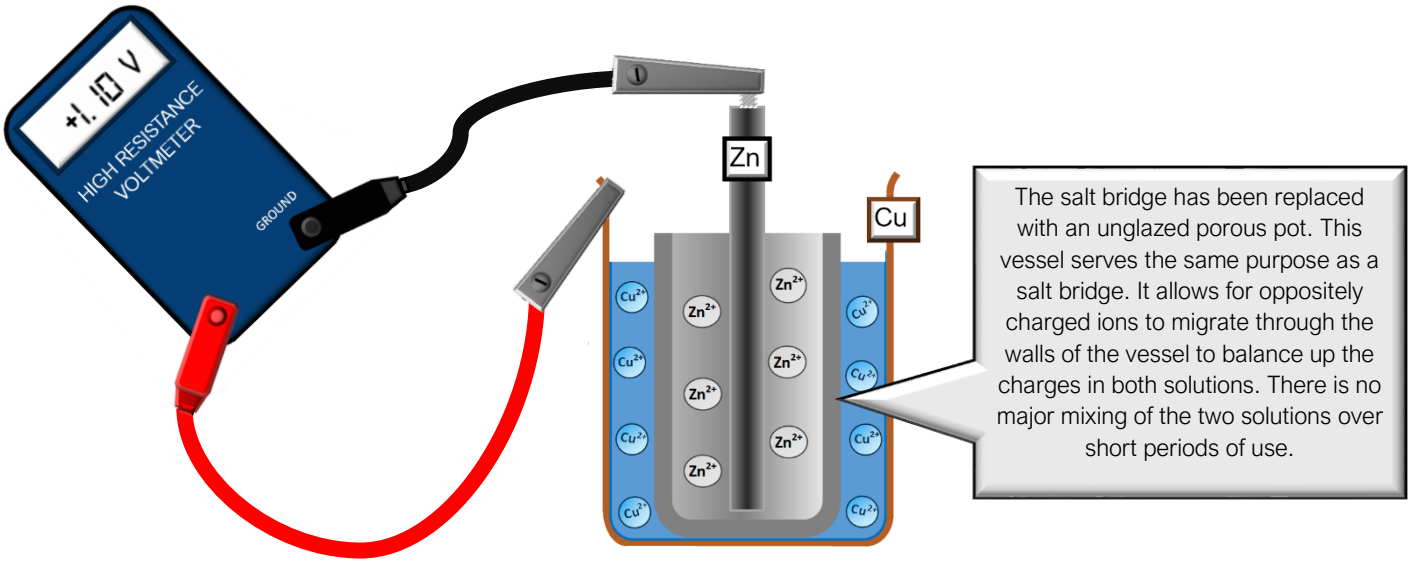
$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)}$

Equilibrium pushes to left in OXIDATION DIRECTION

In the case of this cell, the copper half-cell is more positive (by **1.10V**) than the zinc half-cell and so the Zn/Zn^{2+} equilibrium **pushes to the left-hand side** (OXIDATION DIRECTION). The Cu/Cu^{2+} equilibrium **pushes to the right-hand side** (REDUCTION DIRECTION)

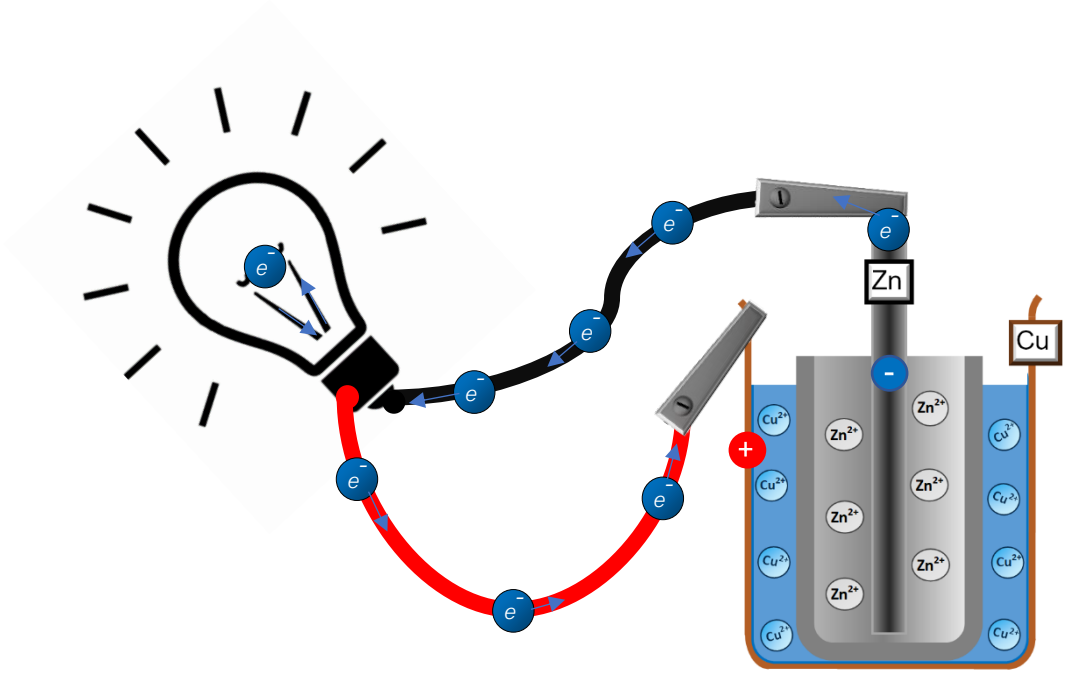
We can see again that **the more positive an electrode potential value**, the **further to the right the equilibrium lies**.

A more useful way of setting up the *Daniell cell* is as follows.



A cell, set up like this, is actually capable of delivering a small current when the voltmeter is replaced with a load, such as a light bulb.

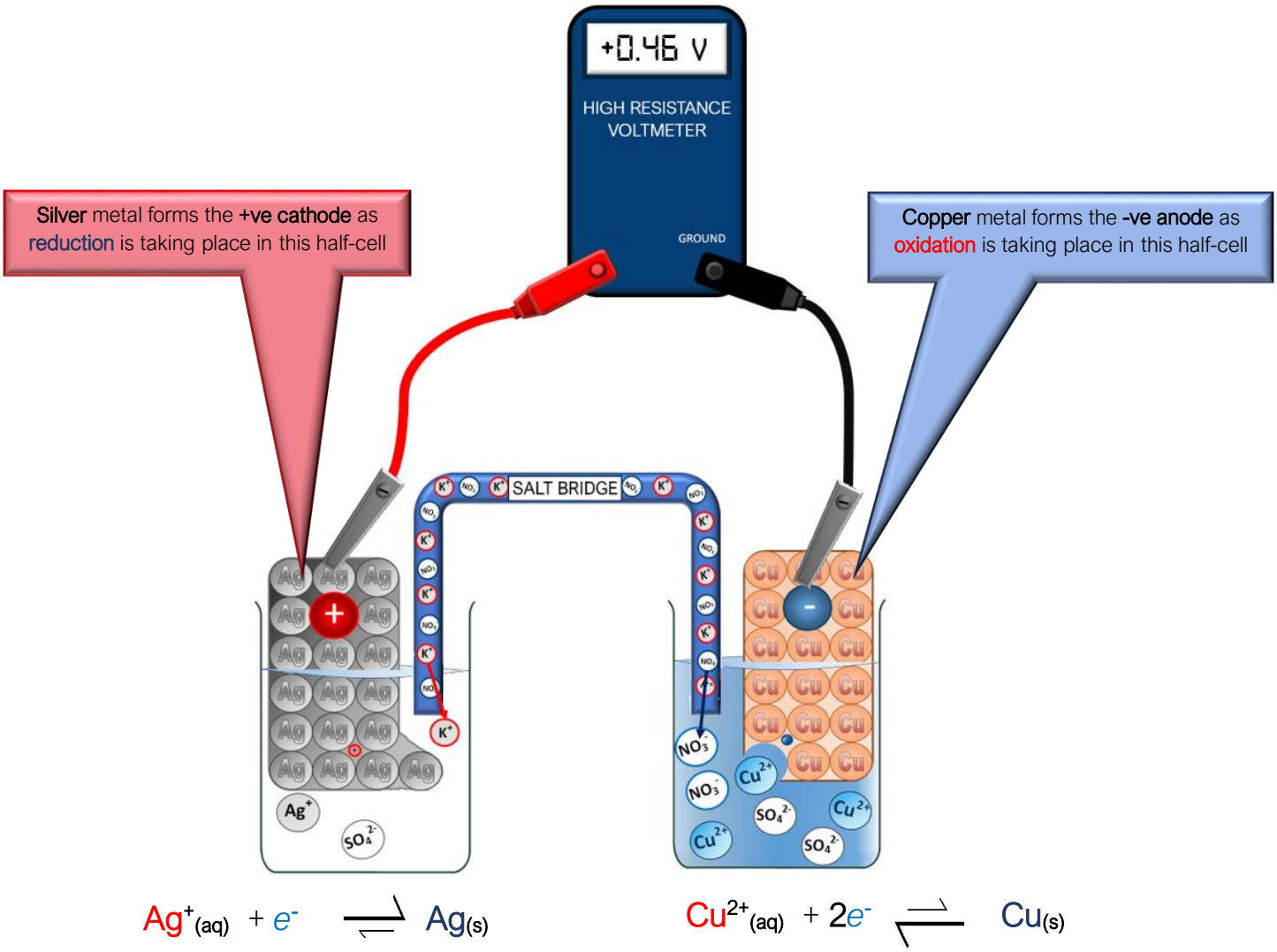
Electrons flow from the **zinc anode** to the **copper cathode**. Energy is released in the bulb.



Daniell cells were used in the first electric telegraph machines developed by inventors such as Edward Davy in the late 1830s.

Copper/Silver Cell

Electrode Potentials, E ⊖			
OXIDISED FORM	⇌	REDUCED FORM	$E^{\ominus}$/ V
$Cu^{2+}_{(aq)} + 2e^-$	⇌	$Cu_{(s)}$	+0.34
$Ag^{+}_{(aq)} + e^-$	⇌	$Ag_{(s)}$	+0.80



$Ag^{+}_{(aq)} + e^- \rightleftharpoons Ag_{(s)}$

Equilibrium pushes right- in the REDUCTION DIRECTION

$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$

Equilibrium pushes left- in the OXIDATION DIRECTION

In the case of this cell, the silver electrode is more positive (by **+0.80V**) than the copper electrode and so the Ag/Ag^+ equilibrium **pushes to the right-hand side** (REDUCTION DIRECTION). This time, the Cu/Cu^{2+} equilibrium **pushes to the left-hand side** (OXIDATION DIRECTION)

We can see again that **the more positive an electrode potential value**, the **further to the right the equilibrium lies**.

The following is well worth remembering

> Equilibria with more positive electrode potentials (the cathode) will push forwards driving the equilibrium with the less positive electrode potential backwards (the anode)

What about all those equilibria that aren't simply a metal dipping into a solution of its ions?

From a practical perspective, having a metal dipping into a solution of its ions is pretty easy to work with. There is a solid lump of metal that one can attach a crocodile clip to and a solution into which a salt bridge can be added.

However, most of the equilibria in the electrochemical series don't involve solid metals. Indeed, many don't involve metals at all!

Let's deal with **gas/solution equilibria** first.

We have already seen how this can be done in the standard hydrogen electrode. The gas (at 1 atm) is exposed to the ions in solution **in the presence of platinum**. The same can be used for chlorine/chloride, for example.

$$\tfrac{1}{2}\,Cl_{2\,(g)} + e^- \rightleftharpoons Cl^-_{(s)} \qquad E^{\ominus} = +1.36\ V$$

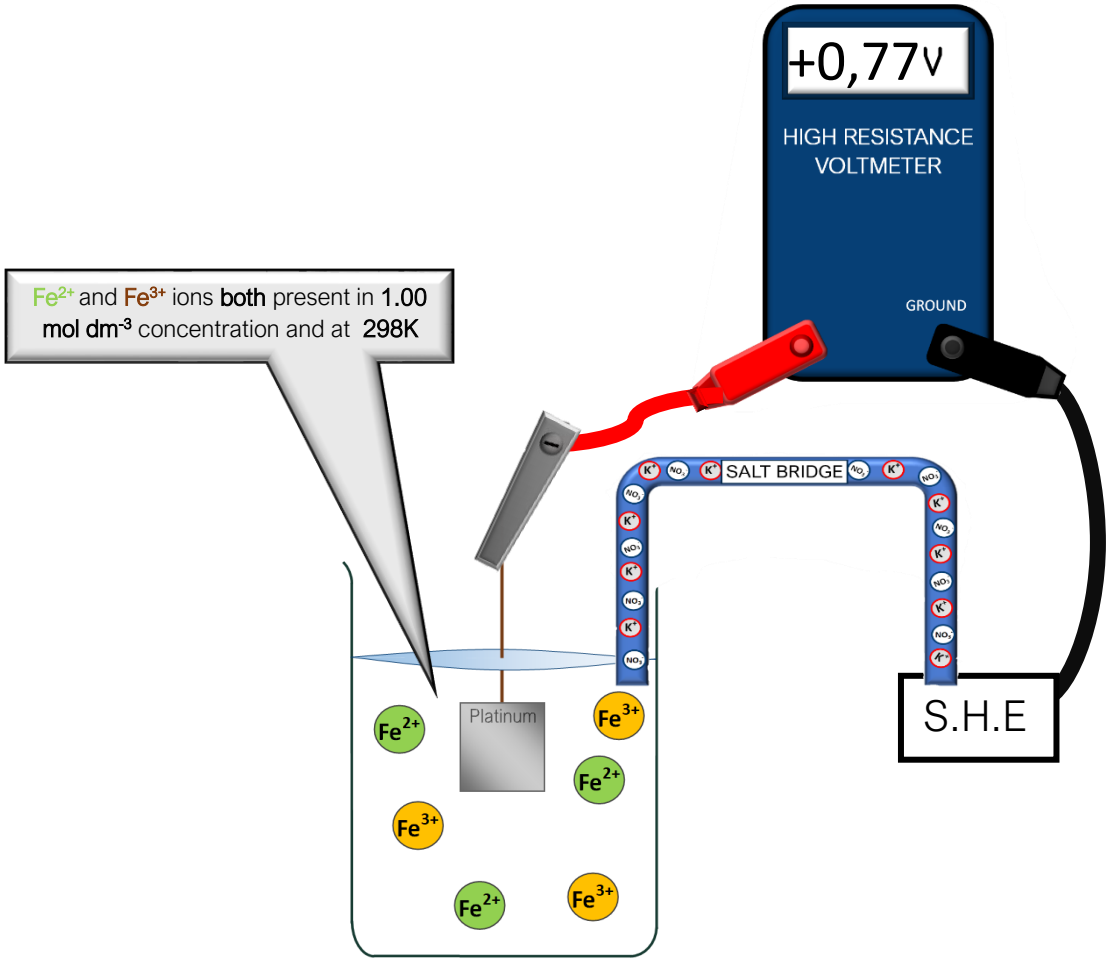
This suggests that this equilibrium tends to push to the right, in the reduction direction. This makes sense when you think about the reactivity of elemental chlorine and the relative inertness of chloride ions.

There are homogeneous aqueous equilibria. For example,

$$Fe^{3+}_{(aq)} + e^- \rightleftharpoons Fe^{2+}_{(aq)} \qquad E^{\ominus} = +0.77\ V$$

This is practically rather easy to set up.

The two solutions need to be mixed together so that the **final concentrations** of each ion is 1.00 **mol dm^{-3}**



Calculating a cell potential (emf).

This is a simple equation to remember in chemistry,

$$E^{\ominus}_{cell} = E^{\ominus}_{\text{more positive half-cell}} - E^{\ominus}_{\text{less positive half-cell}}$$

$$E^{\ominus}_{cell} = E^{\ominus}_{\text{cathode}} - E^{\ominus}_{\text{anode}}$$

If you are not an OCR A level chemistry student, you will have learned how to express the chemical processes taking place in a cell in the form of a '*Cell Diagram*' or '*Cell Notation*'.

In this case, you can also write the equation in the box above as;

$$E^{\ominus}_{cell} = E^{\ominus}_{\text{right-hand side}} - E^{\ominus}_{\text{left-hand side}}$$

How is the Cell Potential Affected by Non-Standard Conditions?

When it comes to predicting the change in $E^{\ominus}_{cell}$, when the **concentrations of solution are changed**, we can simply apply Le Chatelier's principle (L.C.P).

Consider a simple zinc and copper cell (the *Daniell cell*).

If both solutions are in **1.00 mol dm^{-3}** concentration and the temperature is **298K**, there should be a potential difference of **1.10V** between the zinc anode and copper cathode.

$$E^{\ominus}_{cell} = E^{\ominus}_{\text{more positive half-cell}} - E^{\ominus}_{\text{less positive half-cell}}$$

OR

$$E^{\ominus}_{cell} = E^{\ominus}_{\text{cathode}} - E^{\ominus}_{\text{anode}}$$

$$E^{\ominus}_{cell} = +0.34\text{V} - (-0.76\text{V}) = +1.10\text{V}$$

Electrode Potentials, $E^{\ominus}$			
OXIDISED FORM	⇌	REDUCED FORM	$E^{\ominus}$/ V
$Zn^{2+}_{(aq)} + 2e^-$	⇌	$Zn_{(s)}$	-0.76
$Cu^{2+}_{(aq)} + 2e^-$	⇌	$Cu_{(s)}$	+0.34

Let's consider raising the concentration of the **copper sulfate solution to 2.00 mol dm^{-3}** .

If you think about the effect on the equilibrium containing the **Cu/Cu^{2+}**, the equilibrium position will shift further to the right, **removing more electrons from the electrode**. The potential in that half-cell will become **more positive** than it was under standard conditions. This will make E_{cell} larger than it was before, i.e. >1.10V

$$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$$

Now let's consider raising the concentration of the **zinc sulfate solution to 2.00 mol dm^{-3}** .

If you think about the effect on the equilibrium containing the **Zn/Zn^{2+}**, the equilibrium position will also shift further to the right, **removing more electrons from the electrode**. The potential in that half-cell will become **more positive (**or **less negative)** than it was under standard conditions. This will make E_{cell} smaller than it was before, i.e. <1.10V

$$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)}$$

The opposite would occur for concentrations **less than standard**. Simply apply **LCP** and see whether electrons are being used up (so more positive electrode potential at that electrode) OR being created (so less positive electrode potential at the electrode)

Determining Whether one Species can React with Another in a REDOX Reaction

Let's consider a typical question such as,

"Will zinc metal displace copper from a solution?"

Reworded, this is "Will zinc atoms be oxidised to zinc ions by copper ions that get reduced copper atoms"

Will the following reaction occur (spontaneously)?

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Cu_{(s)} + Zn^{2+}_{(aq)}$$

We can inspect the electrochemical series to answer the question!

The first thing to do is find the reactants. They are highlighted below, in yellow.

Electrode Potentials, $E^{\ominus}$			
OXIDISED FORM	⇌	REDUCED FORM	$E^{\ominus}$ / V
$Zn^{2+}_{(aq)} + 2e^-$	⇌	$Zn_{(s)}$	-0.76
$Cu^{2+}_{(aq)} + 2e^-$	⇌	$Cu_{(s)}$	+0.34

Now we ask ourselves, will the equilibrium involving copper species go in a forwards direction allowing (or making) the equilibrium containing the zinc species, to go backwards. If the answer is yes, then the reaction will proceed spontaneously.

We have already established to following:

Equilibria with more positive electrode potentials (the cathode) will push forwards driving the equilibrium with the less positive electrode potential backwards (the anode)

So, this can happen spontaneously when the zinc metal is added to copper sulfate solution. The zinc atoms reduce the copper ions to copper metal.

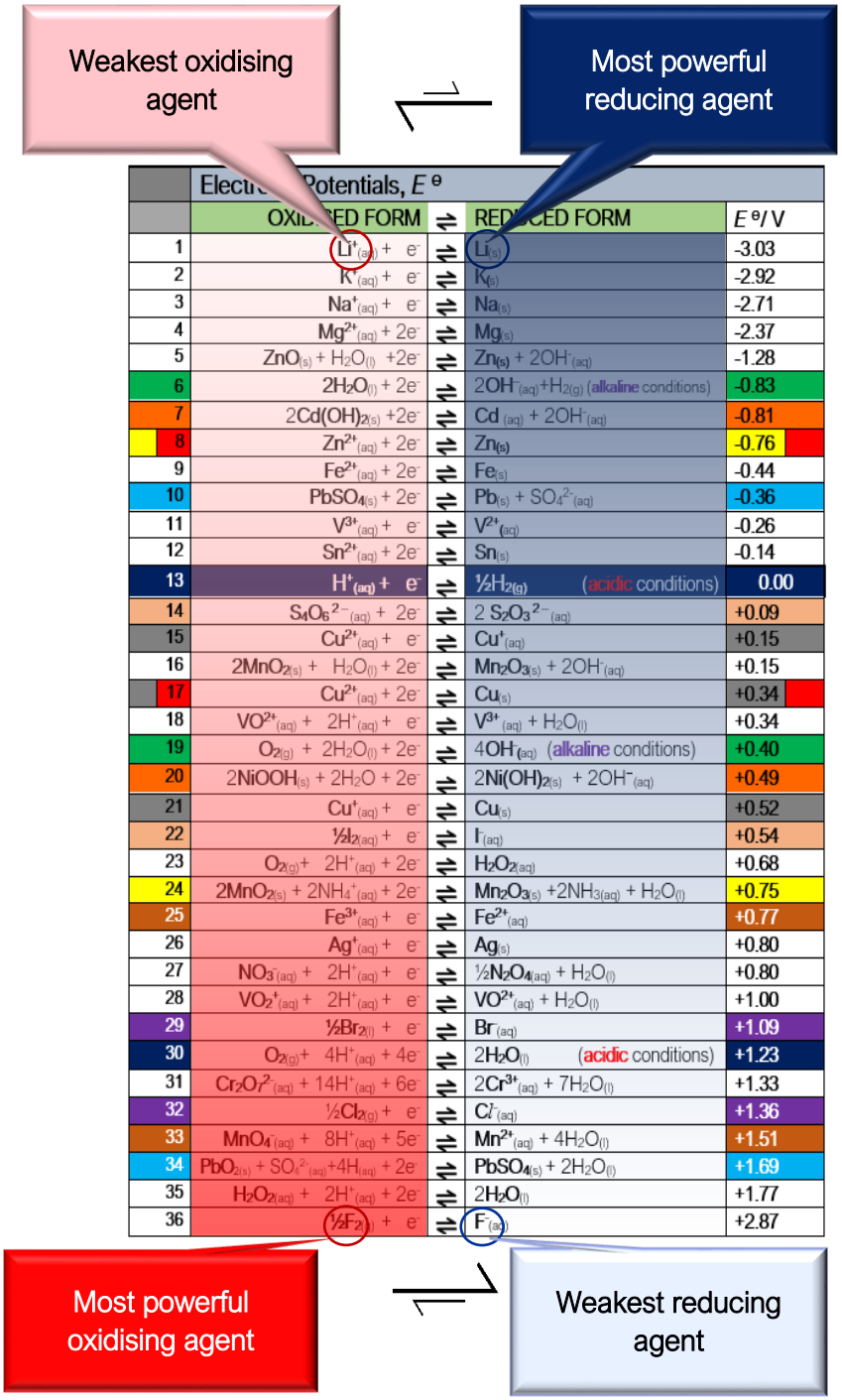
Let's consider another question

"Will silver metal displace copper from a solution of copper sulphate?"

Electrode Potentials, $E^{\ominus}$			
OXIDISED FORM	⇌	REDUCED FORM	$E^{\ominus}$ / V
$Cu^{2+}_{(aq)} + 2e^-$	⇌	$Cu_{(s)}$	+0.34
$Ag^{+}_{(aq)} + e^-$	⇌	$Ag_{(s)}$	+0.80

So, this can't happen spontaneously when the silver metal is added to copper sulfate solution. The silver atoms can't reduce the copper ions to copper metal. The copper equilibrium can't go forwards as the value of its E / V is less positive than that for the silver equilibrium.

Understanding the Oxidising and Reducing Power in terms of Position in the Electrochemical Series



	Electrode Potentials, $E^\ominus$			
	OXIDISED FORM	⇌	REDUCED FORM	$E^\ominus$/ V
1	$Li^+_{(aq)} + e^-$	⇌	$Li_{(s)}$	-3.03
2	$K^+_{(aq)} + e^-$	⇌	$K_{(s)}$	-2.92
3	$Na^+_{(aq)} + e^-$	⇌	$Na_{(s)}$	-2.71
4	$Mg^{2+}_{(aq)} + 2e^-$	⇌	$Mg_{(s)}$	-2.37
5	$ZnO_{(s)} + H_2O_{(l)} + 2e^-$	⇌	$Zn_{(s)} + 2OH^-_{(aq)}$	-1.28
6	$2H_2O_{(l)} + 2e^-$	⇌	$2OH^-_{(aq)} + H_{2(g)}$ (alkaline conditions)	-0.83
7	$2Cd(OH)_{2(s)} + 2e^-$	⇌	$Cd_{(aq)} + 2OH^-_{(aq)}$	-0.81
8	$Zn^{2+}_{(aq)} + 2e^-$	⇌	$Zn_{(s)}$	-0.76
9	$Fe^{2+}_{(aq)} + 2e^-$	⇌	$Fe_{(s)}$	-0.44
10	$PbSO_{4(s)} + 2e^-$	⇌	$Pb_{(s)} + SO_4^{2-}{}_{(aq)}$	-0.36
11	$V^{3+}_{(aq)} + e^-$	⇌	$V^{2+}_{(aq)}$	-0.26
12	$Sn^{2+}_{(aq)} + 2e^-$	⇌	$Sn_{(s)}$	-0.14
13	$H^+_{(aq)} + e^-$	⇌	$\frac{1}{2}H_{2(g)}$ (acidic conditions)	0.00
14	$S_4O_6^{2-}{}_{(aq)} + 2e^-$	⇌	$2\,S_2O_3^{2-}{}_{(aq)}$	+0.09
15	$Cu^{2+}_{(aq)} + e^-$	⇌	$Cu^+_{(aq)}$	+0.15
16	$2MnO_{2(s)} + H_2O_{(l)} + 2e^-$	⇌	$Mn_2O_{3(s)} + 2OH^-_{(aq)}$	+0.15
17	$Cu^{2+}_{(aq)} + 2e^-$	⇌	$Cu_{(s)}$	+0.34
18	$VO^{2+}_{(aq)} + 2H^+_{(aq)} + e^-$	⇌	$V^{3+}_{(aq)} + H_2O_{(l)}$	+0.34
19	$O_{2(g)} + 2H_2O_{(l)} + 2e^-$	⇌	$4OH^-_{(aq)}$ (alkaline conditions)	+0.40
20	$2NiOOH_{(s)} + 2H_2O + 2e^-$	⇌	$2Ni(OH)_{2(s)} + 2OH^-_{(aq)}$	+0.49
21	$Cu^+_{(aq)} + e^-$	⇌	$Cu_{(s)}$	+0.52
22	$\frac{1}{2}I_{2(aq)} + e^-$	⇌	$I^-_{(aq)}$	+0.54
23	$O_{2(g)} + 2H^+_{(aq)} + 2e^-$	⇌	$H_2O_{2(aq)}$	+0.68
24	$2MnO_{2(s)} + 2NH_4^+{}_{(aq)} + 2e^-$	⇌	$Mn_2O_{3(s)} + 2NH_{3(aq)} + H_2O_{(l)}$	+0.75
25	$Fe^{3+}_{(aq)} + e^-$	⇌	$Fe^{2+}_{(aq)}$	+0.77
26	$Ag^+_{(aq)} + e^-$	⇌	$Ag_{(s)}$	+0.80
27	$NO_3^-{}_{(aq)} + 2H^+_{(aq)} + e^-$	⇌	$\frac{1}{2}N_2O_{4(aq)} + H_2O_{(l)}$	+0.80
28	$VO_2^+{}_{(aq)} + 2H^+_{(aq)} + e^-$	⇌	$VO^{2+}_{(aq)} + H_2O_{(l)}$	+1.00
29	$\frac{1}{2}Br_{2(l)} + e^-$	⇌	$Br^-_{(aq)}$	+1.09
30	$O_{2(g)} + 4H^+_{(aq)} + 4e^-$	⇌	$2H_2O_{(l)}$ (acidic conditions)	+1.23
31	$Cr_2O_7^{2-}{}_{(aq)} + 14H^+_{(aq)} + 6e^-$	⇌	$2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$	+1.33
32	$\frac{1}{2}Cl_{2(g)} + e^-$	⇌	$Cl^-_{(aq)}$	+1.36
33	$MnO_4^-{}_{(aq)} + 8H^+_{(aq)} + 5e^-$	⇌	$Mn^{2+}_{(aq)} + 4H_2O_{(l)}$	+1.51
34	$PbO_{2(s)} + SO_4^{2-}{}_{(aq)} + 4H_{(aq)} + 2e^-$	⇌	$PbSO_{4(s)} + 2H_2O_{(l)}$	+1.69
35	$H_2O_{2(aq)} + 2H^+_{(aq)} + 2e^-$	⇌	$2H_2O_{(l)}$	+1.77
36	$\frac{1}{2}F_{2(g)} + e^-$	⇌	$F^-_{(aq)}$	+2.87

If the electrochemical series is presented with the **most negative values at the top**, then you can apply a simple **anti-clockwise rule** to predict whether a reaction will take place spontaneously between any two species.

Consider the question, can hydrogen peroxide, $H_2O_{2(aq)}$ oxidise $V^{3+}_{(aq)}$ to $V^{2+}_{(aq)}$

OXIDISED FORM	⇌	REDUCED FORM	$E^\ominus$/ V
$V^{3+}_{(aq)} + e^-$	⇌	$V^{2+}_{(aq)}$	-0.26
$H_2O_{2(aq)} + 2H^+_{(aq)} + 2e^-$	⇌	$2H_2O_{(l)}$	+1.77

These two processes taken together abide by the anticlockwise rule and therefore we can conclude that $H_2O_{2(aq)}$ will oxidise $V^{3+}_{(aq)}$ to $V^{2+}_{(aq)}$ if they were mixed together (in the presence of acid)

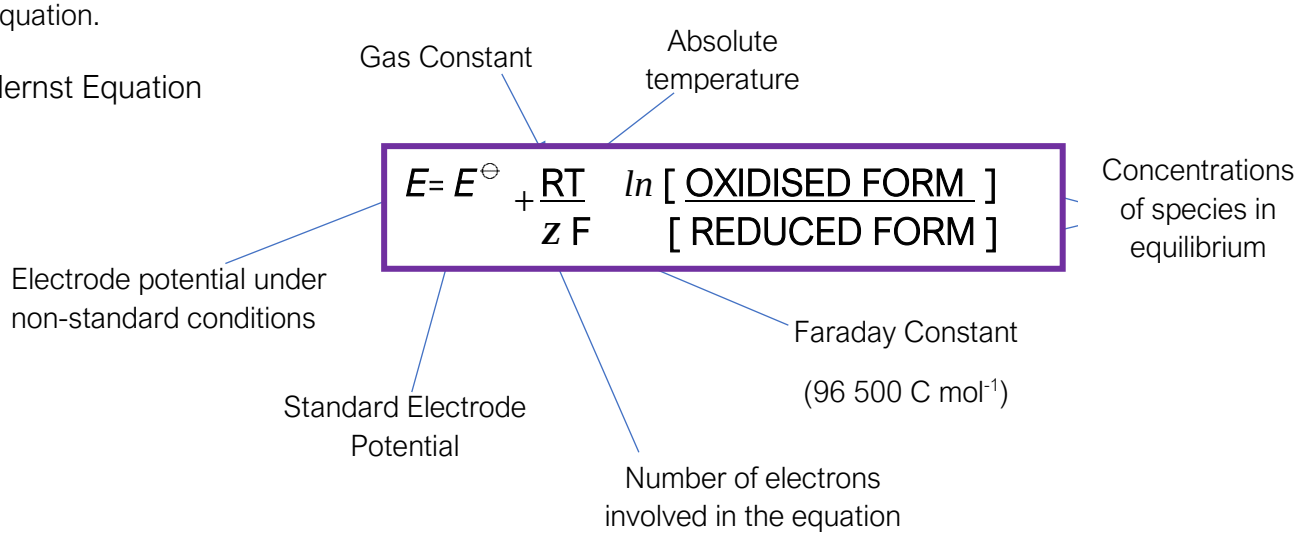
So , $H_2O_{2(aq)} + 2H^+_{(aq)} + 2V^{2+}_{(aq)} \rightarrow 2V^{3+}_{(aq)} + 2H_2O_{(l)}$

The Effect of Concentration and Temperature on E_{cell}

This material is not required in most A Level Chemistry courses.
We have seen that we can use a simple application of Le Chatelier's Principle to predict the effect of concentration changes on the value of E/V in half-cells and therefore on E_{cell}.

However, the accurate value of E/V can be calculated under non-standard conditions using the Nernst Equation.

Nernst Equation



Let's apply this to the familiar example of $Cu_{(s)}/Cu^{2+}_{(aq)}$.

$$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)} \quad E^{\ominus} = +0.34\ V$$

We can work out the new potential under non-standard conditions of 2.00 mol dm^{-3} $Cu^{2+}_{(aq)}$.

Let's assume a standard temperature of 298K

Using the Nernst equation:

The concentration of the $Cu_{(s)}$ is taken as 1(unity) because it is a solid.

$$E = +0.34V + \left\{\frac{8.314 \times 298}{2 \times 96500} \times \ln 2.00\right\} = +0.35V$$

The value is **more positive** at a higher concentration $Cu^{2+}_{(aq)}$. This fits with what we would have predicted using Le Chatelier's Principle.

If we combine the Nernst equations for copper and zinc then we arrive at a useful equation that can be applied to the Daniell Cell. We also need to remember that :

$$E^{\ominus}_{cell} = E^{\ominus}_{\text{more positive half-cell}} - E^{\ominus}_{\text{less positive half-cell}}$$

Then we have,

$$E_{cell} = E^{\ominus}_{cell} - \frac{RT}{2F} \ln \frac{[Cu^{2+}]}{[Zn^{2+}]}$$

There are some quizzes on this topic on *CramNow* Module 5 (Physical Chemistry).