# Redox and Electrode Potentials

Redox

A **redox** reaction is a reaction where **reduction and oxidation** take place — oxidation is the loss of electrons whereas reduction is the gain of electrons.

The thing being oxidised is known as the **reducing agent** because it transfers electrons to the thing that is being reduced. Likewise, the thing being reduced is known as the **oxidising agent**, because it transfers electrons to the thing that is being oxidised.

When aluminium and oxygen react to form aluminium oxide, aluminium loses electrons to form Al^{3+} while oxygen gains electrons to form O^{2-}. Therefore, aluminium is **oxidised** (and acts as a **reducing agent**) while oxygen is **reduced** (and acts as an **oxidising agent**).

$$4Al + 3O_2 \longrightarrow 2Al_2O_3$$
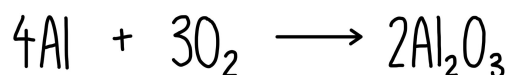
Redox reactions can be shown as two **half equations** – one half equation for the oxidation reaction and the other half equation for the reduction reaction. For example:

$$Al \longrightarrow Al^{3+} + 3e^-$$
$$O_2 + 4e \longrightarrow 2O^{2-}$$
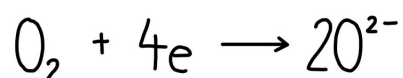
You may be given two half equations and be expected to come up with the **full redox equation**. To do this, **balance the electrons** by multiplying up, **cancel out** the electrons then **add the two half equations together**.

Let's say we have two half equations that show the reduction of copper and the oxidation of silver.

$$Cu \longrightarrow Cu^{2+} + 2e^-$$
$$Ag^+ + e^- \longrightarrow Ag$$
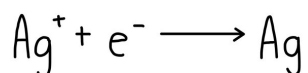
To balance the electrons, we multiply the silver half equation by two. Now we can cancel out the electrons.

$$Cu \longrightarrow Cu^{2+} + \cancel{2e^-}$$
$$2Ag^+ + \cancel{2e^-} \longrightarrow 2Ag$$

$$= Cu + 2Ag^+ \longrightarrow Cu^{2+} + 2Ag$$
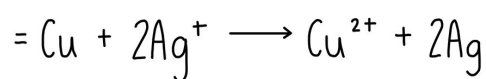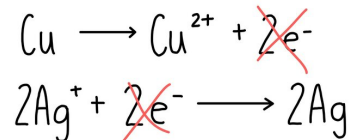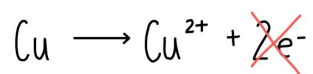
**Writing more complicated redox equations**

You need to know how to balance more complicated half equations, where other species such as H^+ and water are present. If you stick to the rules below, you can't go wrong.

1. Ensure all the **elements** (apart from oxygen and hydrogen) are **balanced**

2. Balance **oxygen** by adding **water** molecules

3. Balance **hydrogen** by adding **hydrogen ions**

4. Balance the **charges** by adding **electrons** – you can check you've done this correctly by looking at the oxidation numbers

Worked example – writing half equations

Dichromate ions, $Cr_2O_7{}^{2-}$, react with iron (II), Fe^{2+} ions, in a redox reaction where $Cr_2O_7{}^{2-}$ is reduced to form Cr^{3+} and Fe^{2+} is oxidised to Fe^{3+}. Write the equation for this redox reaction. We start by writing our **two half equations**. The iron (II) to iron (III) reaction is straightforward:

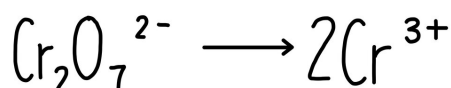$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$
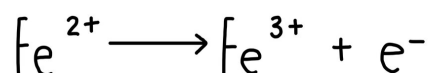
The dichromate one is a little more complicated and we need to follow the rules outlined above.

So far we know that dichromate is converted into chromium (III) ions:

$$Cr_2O_7{}^{2-} \longrightarrow Cr^{3+}$$
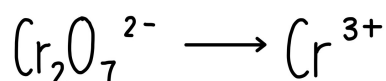
We're going to start by making sure everything other than hydrogen and oxygen are **balanced**. In this case, that's just chromium.

$$Cr_2O_7{}^{2-} \longrightarrow 2Cr^{3+}$$

Now we **balance the oxygens** by adding **water** molecules. I have 7 oxygens on the left so need 7 lots of water on the right.

$$Cr_2O_7{}^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$
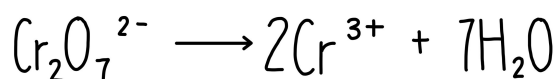
Then **balance the hydrogens** by adding **hydrogen ions**. I have 14 hydrogens on the right so need to add 14 hydrogen ions on the right.

$$Cr_2O_7{}^{2-} + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O$$
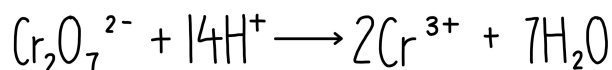
Then **balance the charges** by adding **electrons**. I have a charge of +12 on the left and +6 on the right so I need to add 6 electrons (6x negative charges) to get both sides equal.

$$Cr_2O_7{}^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$
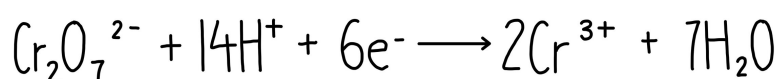
Done! If you look at the **oxidation numbers** of chromium, we can see that we've added the correct number of electrons.

- Cr in $Cr_2O_7^{2-}$ = +6
- Cr in Cr^{3+} = +3

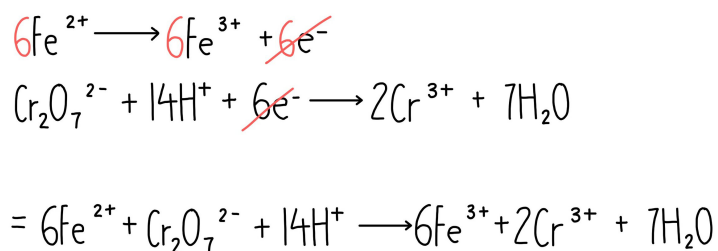Three electrons are gained by Cr to be converted from dichromate to chromium (III) ions. Because there are 2x Cr, that is a total of 6 electrons gained.

The last step is to **put these two half equations together** by balancing the electrons, cancelling out and merging.

$$6Fe^{2+} \longrightarrow 6Fe^{3+} + \cancel{6e^-}$$
$$Cr_2O_7^{2-} + 14H^+ + \cancel{6e^-} \longrightarrow 2Cr^{3+} + 7H_2O$$

$$= 6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

As well as cancelling out electrons, you may also have to **cancel any protons or water molecules** if they are on opposite sides of the two half equations. In this case, it wasn't necessary, but it is worth bearing in mind.
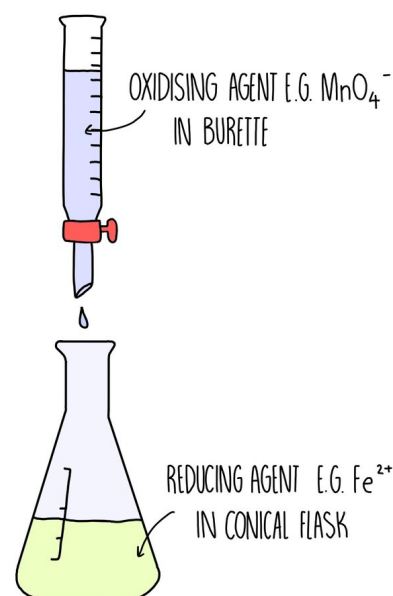
Redox titrations

Acid-base titrations are used to work out the volume of acid needed to neutralise a base (or vice versa) to work out its concentration. **Redox titrations** are basically the same thing except it's used to work out the volume of **oxidising agent** needed to react with a **reducing agent** (or vice versa) and from the volume, we can work out its concentration. It's the same set-up as acid-base titrations except indicator dyes aren't used.

Transition metals are used as the oxidising or reducing agent because they can exist in multiple oxidation states – so they are good at being oxidised or reduced. They also change colour when they gain or lose electrons, which tells us when the reaction is complete.

Here's the **method** for carrying out a redox titration:

1. Measure a certain volume or the **reducing agent** (e.g. Fe^{2+} solution) using a **pipette** and transfer to a **conical flask**

2. Add an **excess** of **dilute sulfuric acid** to the conical flask.

3. Add a solution of **oxidising agent** (e.g. MnO_4^-) to a **burette**. Record the initial volume.

4. Open the tap, **slowly adding the oxidising agent** to the conical flask. Swirl to mix.

5. When the solution **changes colour**, close the tap on the burette and record the **final volume**. Placing a white tile underneath the conical flask makes this easier to spot.

6. Calculate the **titre volume** (initial volume – final volume).

7. Repeat to get **concordant titres** and calculate a **mean**.

8. Remember that this can be carried out the other way – with the oxidising agent in the conical flask and the reducing agent in the burette.

OXIDISING AGENT E.G. MnO_4^- IN BURETTE

REDUCING AGENT E.G. Fe^{2+} IN CONICAL FLASK

Worked example – redox titration calculations

Ethanedioic acid, (COOH)$_2$, is present in rhubarb leaves. A student carries out a redox titration using aqueous cerium (IV) sulfate, Ce(SO$_4$)$_2$ (aq), to determine the percentage, by mass, of ethanedioic acid in rhubarb leaves.

In the titration, Ce^{4+} (aq) ions oxidise ethanedioic acid in hot acid conditions:

$$2Ce^{4+}_{(aq)} + (COOH)_2{}_{(aq)} \longrightarrow 2Ce^{3+}{}_{(aq)} + 2CO_2{}_{(g)} + 2H^+{}_{(aq)}$$
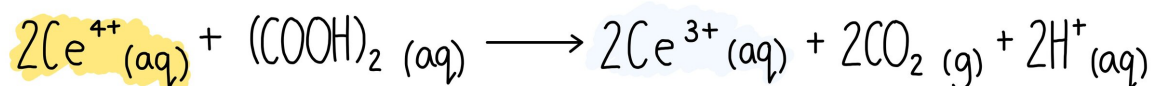
Ce^{4+}(aq) ions have a yellow colour. Ce^{3+}(aq) ions are colourless.

The student weighs 82.68 g of rhubarb leaves and extracts ethanedioic acid from the leaves. The ethanedioic acid is added to dilute sulfuric acid to form a colourless solution which is made up to 250.0 cm^3 with distilled water. The student heats 25.00 cm^3 of this solution to

70°C and titrates this volume with 0.0500 moldm^{-3} Ce(SO$_4$)$_2$ from the burette. The student repeats the titration to obtain concordant (consistent) titres.

- *Titration 1 = 23.25 cm^3*
- *Titration 2 = 23.50 cm^3*
- *Titration 3 = 23.15 cm^3*

Calculate the percentage, by mass, of ethanedioic acid in the rhubarb leaves.

- Only titrations 1 and 3 are concordant so we discard titration 2 before calculating a mean. Concordant titres are within 0.1 cm3 of each other.
- Mean titre = 23.20 cm^3
- Moles = volume in dm^3 x concentration
- Moles of Ce^{4+} = (23.20/1000) x 0.05 = 1.16 x 10^{-3}
- There is a 2:1 ratio between Ce^{4+} and (COOH)$_2$
- Moles of (COOH)$_2$ in 25 cm^3 = 1.16 x 10^{-3} / 2 = 5.8 x 10^{-4}
- Moles of (COOH)$_2$ in 250 cm^3 = 5.8 x 10^{-4} x 10 = 5.8 x 10^{-3}
- Mass = moles x Mr
- Mass of ethanedioic acid = 5.8 x 10^{-3} x 90 = 0.522
- Percentage mass in rhubarb = 0.522 / 82.68 x 100 = 0.631 %

Iodine-thiosulfate titrations

Iodine-sodium thiosulfate titrations are a type of titration that can be used to work out the **concentration** of an **oxidising agent**. To carry out an iodine-sodium thiosulfate titration, carry out the procedure below:

1. Use a **measuring cylinder** to measure out a certain volume (e.g. 25 cm^3) of **oxidising agent** e.g. potassium iodate (V) solution, KIO$_3$.
2. Add this to a beaker containing an **excess of acidified potassium iodide solution**, KI. The iodate ions (IO$_3^-$) will oxidise the iodide ions to **iodine**.

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$$
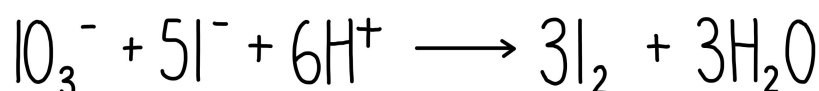
3. Add a solution of **sodium thiosulfate**, Na$_2$S$_2$O$_3$, of **known concentration** to a burette.

4. Transfer the iodine solution to a conical flask and **slowly add the thiosulfate** from the burette into the conical flask.

5. When the iodine turns pale yellow, you are close to the end point. Add **starch** to the mixture to serve as an **indicator**. A **blue** colour tells you that there is still iodine present.

6. Keep adding the sodium thiosulfate drop by drop until the **blue colour disappear**s. You have reached the **end point** as all the iodine has reacted.

7. Record the **titre volume** for the sodium thiosulfate required for complete oxidation. Use this to calculate the concentration of the iodine solution.

The equation for the titration is:

$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$$
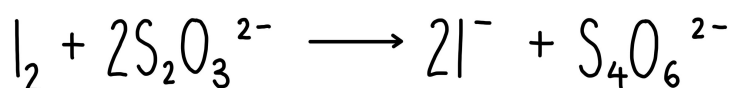
Worked example – thiosulfate titrations

In an experiment, iodide ions from potassium iodide react with iodate(V) ions and hydrogen ions from hydrochloric acid according to the ionic equation:

$$IO_3^-{}_{(aq)} + 5I^-{}_{(aq)} + 6H^+{}_{(aq)} \longrightarrow 3I_2{}_{(aq)} + 3H_2O_{(l)}$$
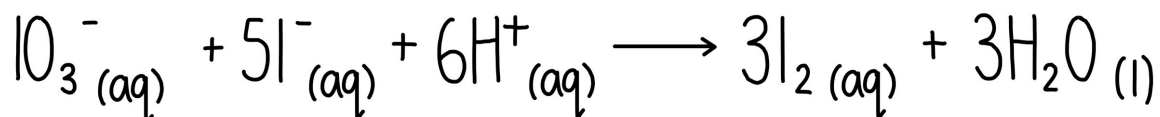
The amount of iodine formed can be determined by titration with sodium thiosulfate solution of known concentration. The equation for this reaction is:

$$I_2{}_{(aq)} + 2S_2O_3^{2-}{}_{(aq)} \longrightarrow 2I^-{}_{(aq)} + S_4O_6^{2-}{}_{(aq)}$$
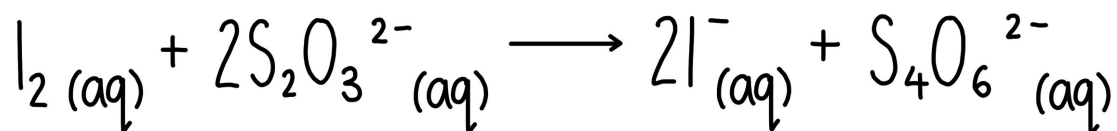
30.0 cm^3 of a solution of hydrochloric acid was added to an excess of potassium iodate(V) and potassium iodide solutions in a conical flask. The iodine formed in the conical flask was titrated with sodium thiosulfate solution of concentration 0.100 mol dm^{-3}. The mean titre was 45.00 cm^3 . Calculate the concentration of hydrochloric acid in mol dm^{-3}.

- Moles of thiosulfate = (45/1000) x 0.1 = 4.5 x 10^{-3} mol
- There is a 2:1 ratio between thiosulfate : iodine

- Moles of iodine = 4.5 x 10^{-3} / 2 = 2.25 x 10^{-3} mol
- There is a 3:6 ratio between iodine : hydrogen ions
- Moles of H$^+$ = 4.5 x 10^{-3}
- Concentration of HCl = 4.5 x 10^{-3} / (30/1000) = 0.15 mol dm^{-3}

Electrochemical cells

Electrochemical cells are cells that use **redox reactions** to **generate electricity**. Oxidation happens in one half cell and electrons move through a wire to the other half cell, where reduction takes place.

For example, an electrochemical cell consisting of copper and zinc half cells will work like this:

Zinc is oxidised since it loses electrons more readily than copper. Electrons are lost from zinc which **travel through the wire** to the copper half-cell. The zinc atoms move into solution when they are converted into aqueous ions, so the zinc electrode will **lose mass** and get smaller.

$$Zn \longrightarrow Zn^{2+} + 2e^-$$
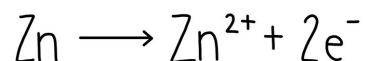
Copper ions are reduced to form copper atoms. The aqueous ions are converted into solid copper atoms which are deposited on the electrode, so the copper electrode will **gain mass** and get bigger.

$$Cu^{2+} + 2e^- \longrightarrow Cu$$
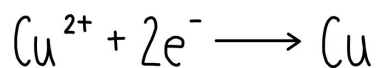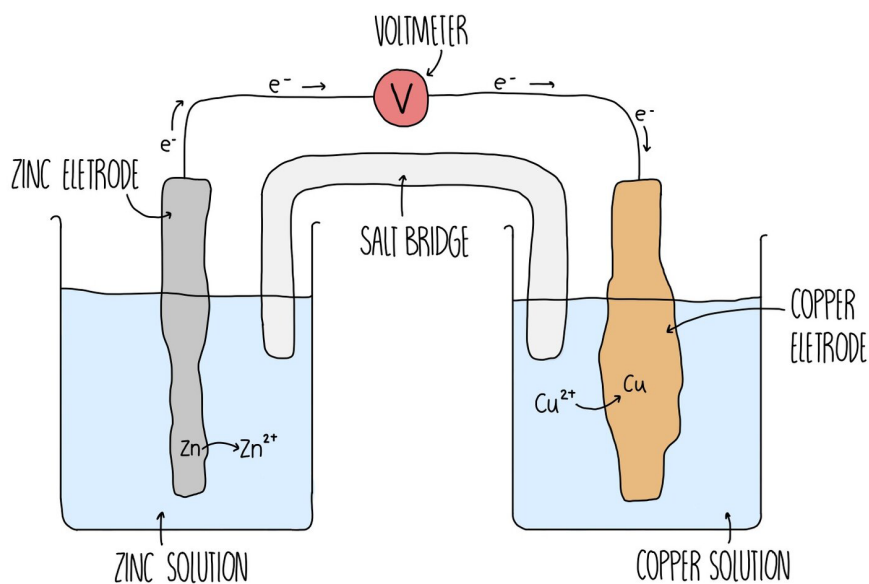
You may be given information on the **electrode potential** of a half cell. This value tells you **how easily a metal is oxidised**. The **more negative** the electrode potential, the more likely the metal is to be **oxidised**. The **more positive**, the more likely it is to be **reduced**. Here are the electrode potentials for the zinc and copper half cells:

HALF CELL	ELECTRODE POTENTIAL, $E^{\ominus}$ (V)
$Zn^{2+} + 2e^- \longrightarrow Zn$	-0.76
$Cu^{2+} + 2e^- \longrightarrow Cu$	+0.34

Zinc has the **more negative** electrode potential so we know it is more likely to be **oxidised**. We need to reverse the direction of the arrow for the reduction reaction, to show that the **reverse reaction** is taking place.

When drawing half-cells, it's the rule that the half-cell with the **more negative electrode potential** (the oxidised half-cell) goes on the **left**.

The **potential** of the **whole cell** is calculated by subtracting the more negative (oxidised) potential from the more positive (reduction) potential. In other words, the electrode potential

from the right-hand side half-cell minus the electrode potential from the left-hand side half-cell.

$$E^{\ominus} \text{ CELL} = \underset{\text{(MORE +VE)}}{E^{\ominus} \text{ REDUCTION}} - \underset{\text{(MORE -VE)}}{E^{\ominus} \text{ OXIDATION}}$$

Using the data for the zinc/copper electrochemical cell given above, the electrode potential would be 0.34 - -0.76 = 1.1. Remember that the cell potential will **always be positive** because the more negative value is being subtracted from a more positive value.

You can also have a half cell made up of the **same element in two different oxidation states** e.g. Fe^{2+} / Fe^{3+}. In this case, a **platinum electrode** is used. Some electrochemical cells involve gases, which are bubbled over a platinum electrode in a solution of its aqueous ions.

The **standard electrode potential** is the electrode potential of a half cell when measured against a **standard hydrogen electrode**. The official definition is:

- **Standard electrode potential** = the voltage of a half-cell when connected to a standard hydrogen electrode and measured under standard conditions (1 mol dm^{-3} concentrations, 298 K and 100 kPa).

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It is important to measure electrode potentials at **standard conditions**, as variations in temperature, pressure and concentration can affect the position of equilibrium of the redox reactions, therefore changing the cell potential.

The electrochemical series

We've already seen that the **more negative** the electrode potential, the **more readily a metal will lose electrons** to form positive metal ions. This means that a half cell with a more negative potential is **more reactive** than one with a less negative potential.

For **non-metals**, which gain electrons when they react to form negative ions, the **more positive** the electrode potential the more likely they are to **gain electrons** and become reduced. This means that a non-metal half-cell with a more positive potential is **more reactive** than one with a less positive potential.

Just like the reactivity series, standard electrode potentials can be placed in order from the most negative to the most positive – this is called the **electrochemical series**. The half-reactions at the top of the series show the half cells that are most likely to be **reduced** and the ones at the bottom show the half cells that are most likely to be **oxidised**.

HALF CELL	ELECTRODE POTENTIAL, $E^{\ominus}$ (V)
$Mg^{2+} + 2e^- \longrightarrow Mg$	-2.36
$Zn^{2+} + 2e^- \longrightarrow Zn$	-0.76
$2H^+ + 2e^- \longrightarrow H_2$	0.00
$Cu^{2+} + 2e^- \longrightarrow Cu$	+0.34
$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	+0.77
$Ag^+ + e^- \longrightarrow Ag$	+0.80
$Cl_2 + 2e^- \longrightarrow 2Cl^-$	+1.36

MORE -VE ELECTRODE POTENTIAL: SUBSTANCES ON THE RIGHT ARE MORE EASILY OXIDISED

MORE +VE ELECTRODE POTENTIAL: SUBSTANCES ON THE LEFT ARE MORE EASILY REDUCED

You can use the electrochemical series to work out **whether a reaction will happen**. For instance, whether magnesium will react with iron (III) ions, Fe^{3+}. If we pick out the electrode potentials for the two relevant half equations, we can see that magnesium has the more negative value, so it will lose electrons and the reaction will occur in the backwards direction.

$$Mg \longrightarrow Mg^{2+} + 2e^-$$

The iron half equation has a more positive value so it will occur in the forwards direction, with Fe^{3+} being reduced into Fe^{2+}.

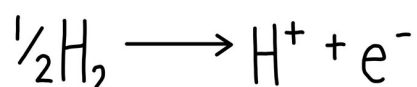$$Fe^{3+} + e^- \longrightarrow Fe^{2+}$$
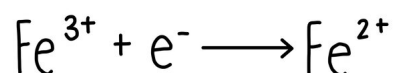
Putting those two half equations gives us:

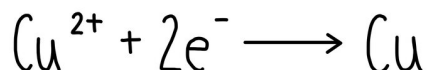$$Mg + 2Fe^{3+} \longrightarrow Mg^{2+} + 2Fe^{2+}$$
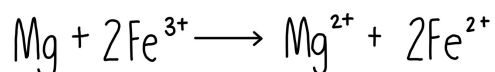
We can see that the reaction will take place.

Now let's see whether hydrogen ions (i.e. an acid solution) will react with solid copper. The hydrogen half equation is the most negative, so we need to rewrite it in the backwards direction.

$$\frac{1}{2}H_2 \longrightarrow H^+ + e^-$$

The copper half equation is more positive, so it is written in the forward direction.

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

Cancelling out the electrons and putting these two half equations together gives us:

$$H_2 + Cu^{2+} \longrightarrow 2H^+ + Cu$$
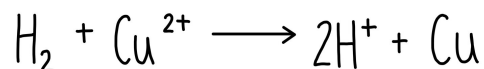
This tells us that copper won't react with hydrogen ions – it's the copper ions which react with hydrogen gas.

That's not to say that certain reactions will never happen, only that they won't happen under **standard conditions**. If you change the concentration, pressure, or temperature, this will shift the position of equilibrium in the reversible reaction and change the value of the electrode potential, meaning that certain reactions that won't occur at standard conditions may be possible once the conditions have changed.

Even reactions which are possible according to their electrode potentials may not happen due to a **high activation energy** or an extremely **slow reaction rate**.

Storage and fuel cells

Electrochemical cells are used in **batteries**, also known **as energy storage cells**, using the electrons released in redox reactions to generate electricity. You might be given two half-equations that are occurring in an energy storage cell and be asked to write the **overall reaction** and calculate the **voltage of the battery**. You'd do this in the same way as we saw for other electrochemical cells, as shown below.

For example, suppose we have a nickel/cadmium battery and are given the following half-equations:

| HALF CELL	ELECTRODE POTENTIAL, $E^{\ominus}$ (V)
$Cd(OH)_2 + 2e^- \longrightarrow Cd + 2OH^-$	-0.88
$NiO(OH) + H_2O + e^- \longrightarrow Ni(OH)_2 + OH^-$	$+0.52$

The first thing we do is identify the half-cell with the **more negative potential** and **reverse the equation**.

$$Cd + 2OH^- \longrightarrow Cd(OH)_2 + 2e^-$$
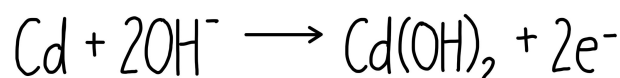
Then **multiply** the equations if necessary, so that the **electrons are equal**.

$$Cd + 2OH^- \longrightarrow Cd(OH)_2 + 2e^-$$
$$2NiO(OH) + 2H_2O + 2e^- \longrightarrow 2Ni(OH)_2 + 2OH^-$$
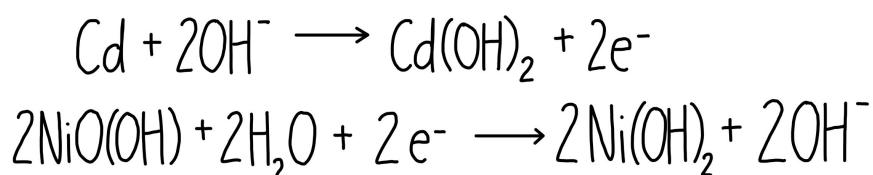
Now **cancel out** anything that is the same and put the equations together.

$$Cd + 2NiO(OH) + 2H_2O \longrightarrow Cd(OH)_2 + 2Ni(OH)_2$$
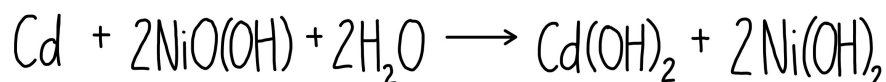
To calculate the cell voltage, we use the formula: **cell voltage = reduction reaction – oxidation reaction**, or more positive potential – more negative potential.

For the nickel/cadmium battery, this is 0.52 - -0.88 = 1.4 V. Remember that the overall cell voltage will always be positive.

A **fuel cell** is a bit different to an energy storage cell – it produces electricity by **reacting fuel with an oxidant**. In hydrogen fuel cells, **hydrogen** is reacted with **oxygen**.

- **Hydrogen is oxidised at the anode**. It loses electrons to form **hydrogen ions**.

- The anode and cathode are separated by a **polymer electrolyte membrane (PEM)** which is only permeable to the hydrogen ions. The **electrons** must move **around the circuit** in the opposite direction.

- The movement of electrons around the circuit towards the cathode generates an **electric current**.

- At the cathode, **oxygen gains electrons** (it is reduced) and combines with hydrogen ions to produce **water**.

One advantage of hydrogen fuel cells is that they **only form water as a waste product** — they don't generate any polluting gases. Electrochemical cells are also **more efficient** than combustion engines because energy is not wasted as heat. However, **toxic chemicals** are used which need to be carefully disposed of once batteries have run out and these chemicals are highly **flammable**, posing a fire risk.