Revision Guide

Chemistry - Unit 3
Physical and Inorganic Chemistry

These notes have been authored by experienced teachers and are provided as support to students revising for their GCE A level exams. Though the resources are comprehensive, they may not cover every aspect of the specification and do not represent the depth of knowledge required for each unit of work.

Content

3.1 – Redox and standard electrode potential

Redox reactions

In AS, we saw that in redox reactions, something is oxidised and something else is reduced (remember OILRIG – this deals with loss and gain of electrons). Another way that we can determine if a redox reaction has happened is by using oxidation states or numbers (see AS revision guide pages 2 and 44).

You need to know that: -

- **oxidation** is loss of electrons
- **reduction** is gain of electrons
- an **oxidising agent** is a species that accepts electrons, thereby helping oxidation. It becomes reduced itself in the process.
- a **reducing agent** is a species that donates electrons, thereby helping reduction. It becomes oxidised itself in the process.

You also should remember these rules for assigning oxidation numbers in a compound: -
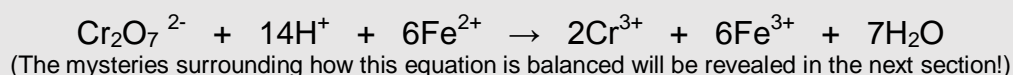
1. All elements have an oxidation number of zero (including diatomic molecules like H_2)
2. Hydrogen is 1 unless it's with a Group 1 metal, then it's -1
3. Oxygen is -2 (unless it's a peroxide when it's -1, or reacted with fluorine, when it's +2).
4. Group 1 and 2 elements are 1 and 2 respectively.
5. Oxidation numbers of elements in a compound or ion must add up to zero or the ion's charge
6. The most electronegative element is given the negative oxidation number.

Changes in oxidation number for an element when it reacts can tell you whether it has been oxidised or reduced: -

If its oxidation number **increases**, the element has been **oxidised** in the reaction.
If its oxidation number **decreases**, the element has been **reduced** in the reaction.

Worked Example

Dichromate ions can be used to oxidise iron(II) ions to iron(III) ions:-

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

(The mysteries surrounding how this equation is balanced will be revealed in the next section!)

Reactants' oxidation numbers:
Cr = +6, O = -2, H = +1, Fe = +2

Products' oxidation numbers:
Cr = +3, O and H unchanged,
Fe = +3

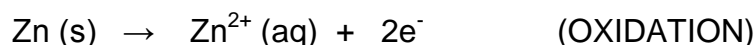*Therefore,* Chromium has been reduced (from +6 down to +3) and Iron has been oxidised (up from +2 to +3).

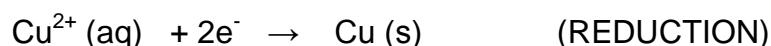## Equations and half-equations for redox reactions

The equation for a redox reaction can be split into two *half-equations*, one showing oxidation and the other one showing reduction. This example of an ionic equation shows the changes that happen when zinc is placed into copper sulphate solution: -

$$Zn\ (s)\ +\ Cu^{2+}\ (aq)\ \rightarrow\ Zn^{2+}\ (aq)\ +\ Cu\ (s)$$
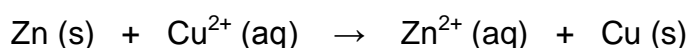
The Zn is converted into a Zn^{2+} (aq) ion. The zinc must have lost two electrons, so we can write the ionic half-equation for this change as follows: -

$$Zn\ (s)\ \rightarrow\ Zn^{2+}\ (aq)\ +\ 2e^{-} \qquad \text{(OXIDATION)}$$

If you're ever confused as to which side to place the electrons, the charges on both sides of the half-equation should balance.

Also, the Cu^{2+} (aq) ion is converted into Cu. The copper ion must have lost two electrons, so the half-equation for this change is: -

$$Cu^{2+}\ (aq)\ +2e^{-}\ \rightarrow\ Cu\ (s) \qquad \text{(REDUCTION)}$$

Electrochemical cells and half-cells

The theory of half equations can be put into practice when the half-equations of a redox reaction are separated. Oxidation happens in one part and reduction in the other. These are called *half-cells* and the half-cells are joined so that a complete circuit is produced. This can be explained better using a diagram: -
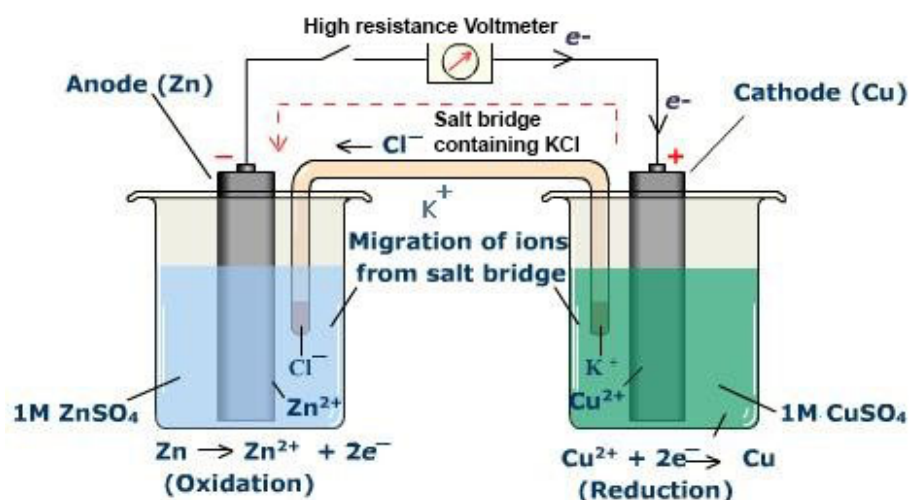
The right-hand beaker has the Cu^{2+}(aq)/Cu(s) reaction taking place in it, whilst the left-hand beaker has the Zn(s)/Zn^{2+} (aq) reaction. A half-cell must contain the reactants and products of the half-equation.

The salt bridge completes the circuit, as ions can move, but the two solutions do not mix.

The electrodes must be able to let electrons flow through the voltmeter.

This set up is called *a cell*.

The high resistance voltmeter measures the EMF produced by the cell. (EMF can be simply described as the voltage produced by any source of electrical energy, in this case, the half-cells producing and accepting electrons).

There are three types of half-cell that you need to know about, the use of each depends on the physical states of the substances in the reaction: -

1 Metal/Metal ion. This is what is seen in the example above. The **solution always has a concentration of 1 mol dm^{-3}** and the metal electrode conducts the electrons. Make sure you're aware of the colour changes that take place.

2 Gas/Non-metal ion solution. These half-cells have no conductor for the electrons produced, so must have an inert platinum electrode in place to do this. The **gas (at 1atm pressure)** is bubbled over the electrode that is dipped into the solution of ions. There is no colour change to be seen.

3 Solution of a metal in two different oxidation states This type of half-cell is usually used for the transition metals, which invariably have several different oxidation states. eg, Fe^{2+}/Fe^{3+}. A platinum electrode must again be used as there is no conducting medium. Make sure you know the colours of the solutions that are formed when oxidation or reduction occurs, eg Fe^{2+} is pale green and Fe^{3+} is a rusty orange colour.

Representing Cells

Cells can be represented using a fully labelled diagram as shown on the previous page, or by using **Cell Diagrams**. If a question asks you for a cell diagram, this is what is expected:-

$$\text{Zn (s)} \mid \text{Zn}^{2+} \text{(aq)} \parallel \text{Cu}^{2+} \text{(aq)} \mid \text{Cu (s)}$$
This is the cell diagram for the cell shown in the labelled diagram on page 2

As you can see, the cell diagram lists the chemicals that are present in the cell, along with some solid vertical lines. These are the conventions that are followed: -
- The conducting metal of the left-hand cell goes first. (It is Zn in this case)
- If there is a change of state (ie, solid, liquid, gas or aqueous solution) between the substances in the half-cell, then a *single vertical line* is used. (Here, Zn^{2+} is aqueous, so a vertical line is required).

- If the substances are in the same physical state, then commas are used instead of vertical lines. (There are none in this example)
- The salt bridge joins the two half cells. This is represented by a **double vertical line.**
- The next half-cell is now represented by the aqueous solution next to the salt bridge and the conducting medium at the other end. If these are in different states, they are separated by a single vertical line.
- Finally, the **more positive electrode is placed on the right-hand side**. (How values are assigned to different electrodes is covered in the next section.)

Standard Electrode Potentials

We know that in a half-cell containing a metal/metal ion solution, a reaction takes place whereby the metal either loses or gains electrons. This process sets up a *potential difference* between the metal and the solution and this is simply defined as the ability of a half-cell to gain or lose electrons.

This potential difference is referred to as the **Electrode Potential.** The electrode potential that you obtain for a half-cell depends on the metal used and the temperature and concentration of the salt solution. So that we can measure standard electrode potentials for different half-cells, temperature and concentration are given a standard value of 298K and 1 moldm^{-3} respectively. You can't measure the potential of a half-cell on its own, but you can measure the potential difference between two electrodes. To obtain the standard electrode potential for any half-cell, it is measured against the standard hydrogen electrode, which is taken to have zero potential difference.

The standard hydrogen electrode

When you see a list of the standard electrode potentials for various half-cells, the measurements have been taken using the **hydrogen electrode** as 0.0 V. The hydrogen electrode is a hydrogen half-cell and it is set up as follows: -


wire to other half-cell

Hydrogen gas
1 atmosphere

platinum

H$^+$ ions
1M
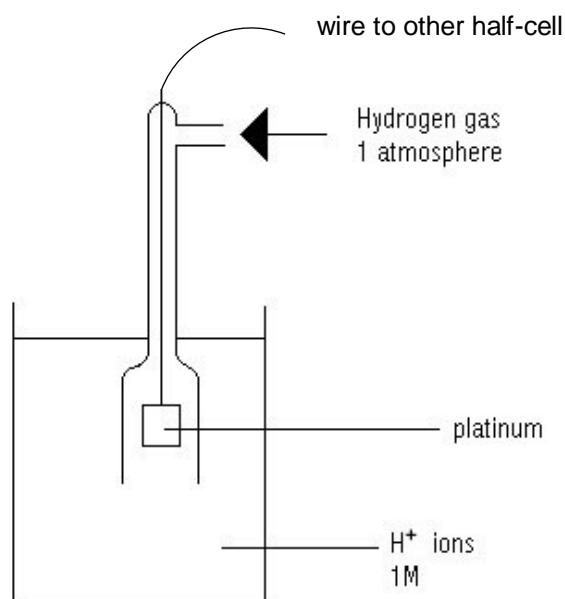
The platinum electrode is black as it is coated with fine platinum grains, which increase surface area. The standard conditions used are: -

1 1 atmosphere pressure for the H$_2$ gas
2 H$^+$ solution has a concentration of 1 mol dm^{-3}. Usually hydrochloric acid.
3 Temperature is 298K

The standard electrode potential (E$^{\theta}$) is the potential difference between the standard hydrogen electrode and any half-cell that fulfils the standard conditions.

This diagram shows how the standard electrode potential for the Zn/Zn^{2+} half-cell is set up.
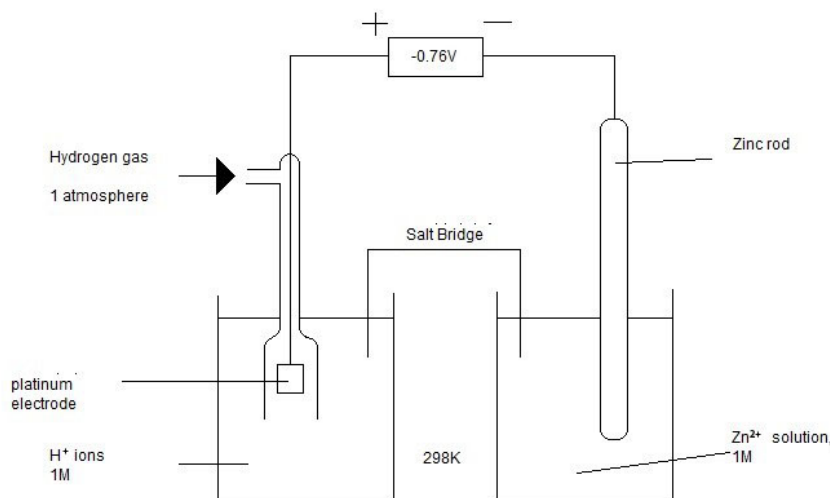
You will see that everything is under standard conditions. The cell diagram for this set up is: -

$$Pt\ (s)\ |\ H_2(g)/H^+(aq)\ ||\ Zn^{2+}\ (aq)\ |\ Zn\ (s)$$
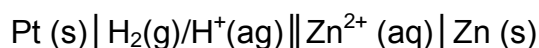
The reading on the high resistance voltmeter is -0.76V, showing that the electrode potential for the zinc half-cell is more negative than that for the standard hydrogen electrode. The flow of electrons goes from zinc to hydrogen, so the hydrogen is the positive electrode and zinc the negative.

Zinc loses electrons more readily than the hydrogen gas, so is easier to oxidise than hydrogen. Zinc is acting as the reducing agent as it is supplying electrons.

Usually, the hydrogen half-cell is drawn on the left.

Using Standard Electrode Potentials

Once you know the standard electrode potentials of various half-cells, you can use them to establish the charge on each electrode in a cell, the direction of electron flow and even whether a reaction is likely to take place.

The **Electrochemical Series** puts the reducing power of different half-cells in order. (Remember that reducing power is the ability of a species to remove electrons from something else.) This order is always shown as the reduction reaction, so you always see atoms or ions *gaining electrons*. We see that the most reactive metals have the most negative E^θ and the least reactive metals/most reactive non-metals have the most positive E^θ.

The diagram below shows some values and the trends that are followed: -

	Half Reaction				Standard Potential (V)
F_2	+	$2e^-$	$\rightleftharpoons$	$2F^-$	+2.87
Pb^{4+}	+	$2e^-$	$\rightleftharpoons$	Pb^{2+}	+1.67
Cl_2	+	$2e^-$	$\rightleftharpoons$	$2Cl^-$	+1.36
$O_2 + 4H^+$	+	$4e-$	$\rightleftharpoons$	$2H_2O$	+1.23
Ag^+	+	e^-	$\rightleftharpoons$	Ag	+0.80
Fe^{3+}	+	e^-	$\rightleftharpoons$	Fe^{2+}	+0.77
Cu^{2+}	+	$2e^-$	$\rightleftharpoons$	Cu	+0.34
$2H^+$	+	$2e^-$	$\rightleftharpoons$	H_2	0.00
Pb^{2+}	+	$2e^-$	$\rightleftharpoons$	Pb	-0.13
Fe^{2+}	+	$2e^-$	$\rightleftharpoons$	Fe	-0.44
Zn^{2+}	+	$2e^-$	$\rightleftharpoons$	Zn	-0.76
Al^{3+}	+	$3e^-$	$\rightleftharpoons$	Al	-1.66
Mg^{2+}	+	$2e^-$	$\rightleftharpoons$	Mg	-2.36
Li^+	+	e^-	$\rightleftharpoons$	Li	-3.05

stronger oxidizing agent

stronger reducing agent

Please note that the electrochemical series can also be written with the most negative E^θ values at the top of the series. If we took out the non-metals, the order would then mirror the Reactivity Series!

NB The significance of the red and blue arrows will be explained on the next page.
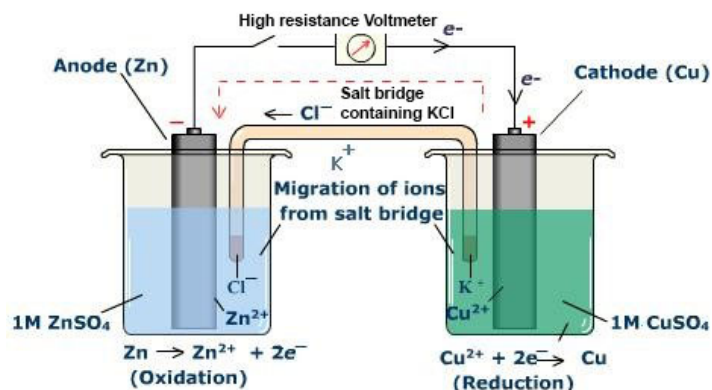
From the information in the electrochemical series, we know that the more negative half-cell is the zinc one, with the more positive one being on the right. The zinc half-

cell will lose electrons more easily than the copper one (oxidation). Electrons are therefore being sent from the zinc reaction towards the copper one, which is indicated on the diagram. Things to note about this type of reaction that can sometimes be confusing: -

- The zinc electrode is negative and the copper one is positive because electrons are being produced in this reaction.
- The zinc metal is being oxidised to zinc ions.
- The copper ions are being reduced to copper atoms.
- Zinc metal is acting as a **reducing agent** because it's supplying electrons.
- Copper ions are acting as an **oxidising agent** because they are accepting electrons.

This is the significance of the red and blue arrows on the diagram on page 5. The red arrow refers to the ions on the left and the blue arrow refers to the reduced species on the right.

Calculating the overall EMF of the cell

EMF values for cells must always be positive. The value of the EMF is shown on the high resistance voltmeter and can be calculated using the standard electrode potentials of the two half-cells. Generally: -

$$E^{\theta}_{cell} \ = \ E^{\theta} \text{ (most positive) } - \ E^{\theta} \text{ (most negative)}$$

So, for the above cell: -

$$E^{\theta} \ = \ +0.34 - (-0.76) \ = \ +1.10V$$

E^{θ} values are positive or negative depending on whether the species has a more positive or negative potential compared to hydrogen, eg

$$Cu^{2+} \text{ (aq) } + \ 2e^{-} \leftrightarrows Cu(s) \qquad E^{\theta} = +0.34V.$$

This means that copper (II) ions will gain electrons more easily than hydrogen ions or hydrogen ions will lose electrons more easily than copper (II) ions. Conversely: -

$$Zn^{2+} \text{ (aq) } + \ 2e^{-} \ \leftrightarrows \ Zn(s) \quad E^{\theta} = -0.76V$$
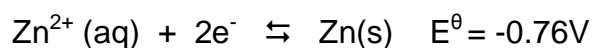
If we compare zinc ions with hydrogen ions, then zinc ions lose electrons more easily than hydrogen ions. They will also lose electrons more easily than copper (II) ions, so the copper ions will gain electrons and form copper metal.

If we go back to the cell we saw on page 2, we can now explain the direction of electron flow and also calculate the overall standard potential of the cell.

## Is the reaction feasible (likely to happen)?

The way in which we can predict whether a redox reaction is likely to occur is by using standard electrode potential values. Before we can do this, we need to remember some key facts: -

- For a reaction to go ahead, its EMF must be positive.
- The oxidation half-reaction is the one with the most negative E^θ value.
- The reduction half-reaction is the one with the most positive E^θ value.
- If you have two negative half-reactions to deal with, the reduction half-reaction is the one that is the least negative of the two.
- When we calculate the EMF of a reaction, we need to work out which half-reaction is the most positive (reduction) and which is the most negative (oxidation).
- We can then use the equation: -
    EMF = E^θ (most positive or reduction) - E^θ (most negative or oxidation)

It is best to use an example so that you can see exactly how this works:-

Suppose you were asked if chloride ions were able to reduce Zn^{2+} ions to zinc metal. You would need to use the E^θ values given on page 5.

The two half-equations that you would need are: -

Cl_2 (aq) + $2e^-$ $\leftrightarrows$ $2Cl^-$ (aq)   +1.36V
Zn^{2+} (aq) + $2e^-$ $\leftrightarrows$ Zn (s)   -0.76V
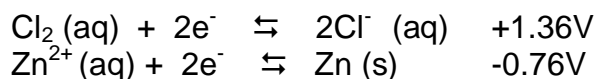
Both are reduction reactions, so we need to work out which would be the oxidation reaction. The question talks about reducing zinc ions to zinc metal, so that must be the reduction reaction. The oxidation reaction must therefore be the chloride reaction.

Substituting into the equation: -

    EMF = -0.76 – 1.36 = -2.12V

The EMF is negative, so the reaction is not feasible.

Worked Example

(i) *(d)* Some standard electrode potentials, $E^{\ominus}$, are given below.

System	$E^{\ominus}/V$
$\frac{1}{2} I_2(s) + e^- \rightleftharpoons I^-(aq)$	+0.54
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$\frac{1}{2} Br_2(l) + e^- \rightleftharpoons Br^-(aq)$	+1.09
$\frac{1}{2} Cl_2(g) + e^- \rightleftharpoons Cl^-(aq)$	+1.36
$Ce^{4+}(aq) + e^- \rightleftharpoons Ce^{3+}(aq)$	+1.45

(i) Using the information from the table, state which of the **halides** will reduce Fe^{3+} to Fe^{2+}. Give a reason for your answer. [2]

(ii) Write the cell diagram of the cell formed by combining the $Fe^{3+}(aq)$, $Fe^{2+}(aq)$ and $Ce^{4+}(aq)$, $Ce^{3+}(aq)$ half cells and calculate the standard e.m.f. of this cell. [2]

The question asks about *halides,* so make sure you ignore anything that isn't! Also, the reduction reaction must be the Fe^{3+} to Fe^{2+}. The halide reaction will therefore be the oxidation reaction. As EMF = E^{θ} (most positive or reduction) - E^{θ} (most negative or oxidation), then the only reaction that will produce a positive EMF is a halide reaction that has E^{θ} of less than +0.77V (the standard electrode potential for the iron(II) reduction reaction). There is only one of these, which is the iodine/iodide reaction.

The correct answer would be **iodide** as the question asks for the halide, not the halogen.

You can also get the second mark for this question by simply showing the correct mathematics for the question: -
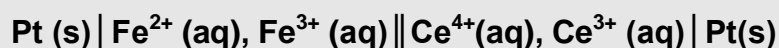
$$EMF = +0.77 - +0.54 = +0.23V$$

Positive EMF, so the reaction is feasible.

(ii) If you remember, the more positive half-cell must be placed on the right-hand side. This is the cerium reaction. As it is the more positive half-cell, this means it is the reduction reaction. The left-hand half-cell must be the oxidation reaction, which is when electrons are lost, not gained. We therefore have to reverse the iron(III)/iron(II) equation to show it as the oxidation reaction:

Fe^{3+} (aq) + e$^-$ ⇆ Fe^{2+} (aq) is reversed to become Fe^{2+} (aq) ⇆ Fe^{3+} (aq) + e$^-$
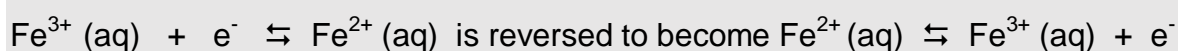
Here is the cell diagram for the reaction: -

Pt (s) $\vert$ Fe^{2+} (aq), Fe^{3+} (aq) $\Vert$ Ce^{4+}(aq), Ce^{3+} (aq) $\vert$ Pt(s)

- single vertical lines separate changes of state
- double vertical lines represent the salt bridge
- the different solutions in the same cell are separated by commas as they are in the same state

$$EMF \text{ of cell} = E^{\theta}(\text{reduction}) - E^{\theta}(\text{oxidation})$$

$$EMF = +1.45 - +0.77 = 0.68V$$

Uses of redox reactions

Redox reactions are extremely common, not only in chemistry, but in biology as well. Respiration and photosynthesis are processes where redox reactions are seen. If you are asked whether a reaction is a redox one, use oxidation numbers to work it out. If there is a change in oxidation numbers, then there is a redox reaction.

Redox in organic chemistry

The organic chemistry that is studied in Unit 4 has several examples of redox reactions. You will see the following: -

- Oxidation of alcohols
- Reduction of nitriles
- Reduction of carboxylic acids, aldehydes and ketones
- Reduction of nitrobenzene

The important thing to learn with these are the reaction conditions and catalysts involved and, of course, the products.

Fuel cells

Fuel cells convert chemical energy stored in the fuel into electrical energy. They release energy far more efficiently than burning fuels in a traditional internal combustion energy, where most of the energy is lost during the different processes that occur.
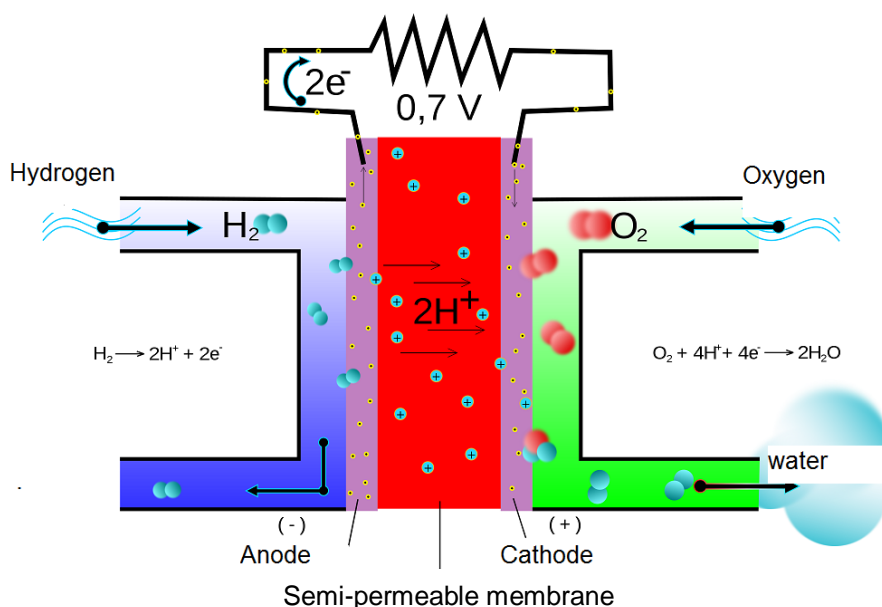
The electrodes are platinum and the fuel (in this case, hydrogen) is passed over it. The platinum also acts as a catalyst. At the anode, electrons are removed from hydrogen: -

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

The H^+ ions then pass through a semi-permeable membrane and reach the cathode, where they receive electrons and react with oxygen to form water: -

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

These cells are being developed particularly for use in cars, as there is no carbon dioxide released.

You are expected to know the advantages and disadvantages of the fuel cell. Make sure you learn them properly as vague answers will not gain credit!

Advantages

- Only produce water, so no CO_2, which is a greenhouse gas, is produced.

- Far less energy is wasted as heat, so they are far more efficient. More energy is used more effectively.

- Hydrogen gas can be produced by the electrolysis of water, therefore is a renewable energy source.

Disadvantages

- Hydrogen gas is highly flammable, with all the associated risks and is therefore difficult to store.

- The usual production method for hydrogen gas is from fossil fuels, so this leads to an overall energy loss.

3.2 Redox Reactions

Constructing and combining ion/electron half-equations

You need to be able to learn how to construct electron half-equations for oxidation and reduction processes within a redox reaction and then learn how to combine them to give the overall ionic equation for that reaction.

Example 1

Chlorine gas oxidises iron(II) ions to iron(III) ions. In the process, the chlorine is reduced to chloride ions. Construct electron half-equations for both processes and then combine them to write the overall ionic equation for this reaction.

Constructing half-equations

Step 1 – write down what you know for each of the half equations: -

If we start with chlorine, we know that chlorine gas is reduced to chloride ions. Chlorine gas is Cl_2: -

$$Cl_2 \rightarrow 2Cl^-$$
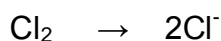
We balanced the atoms on each side by showing that there were two chloride ions.

ALWAYS make sure the atoms balance before you start or you will never get the right answer.

Step 2 – add things to the half-equation so that it balances completely. **The only things that you can add are: -**

- **electrons**
- **water**
- **hydrogen ions**

The only thing that's wrong with the chlorine reaction is that the charges don't balance. All we have to do is add electrons so that there are two negative charges on each side of the equation: -

$$Cl_2 + 2e^- \rightarrow 2Cl^-$$
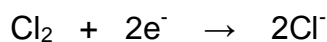
This has to be repeated for the second iron ion reaction. We know from the question that iron (II) is oxidised to iron (III), so we write this down: -

$$Fe^{2+} \rightarrow Fe^{3+}$$
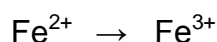
We don't have to change the number of atoms as they balance, but the charges don't, so we have to add something to the equation in order to make them balance. There are two positive charges on one side and three on the other. We need to add one electron on the side with three positives in order to make the charges balance.

$$Fe^{2+} \quad \rightarrow \quad Fe^{3+} + e^-$$
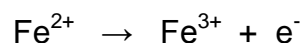
Now we have to combine the two half-equations to make the full equation for the reaction.

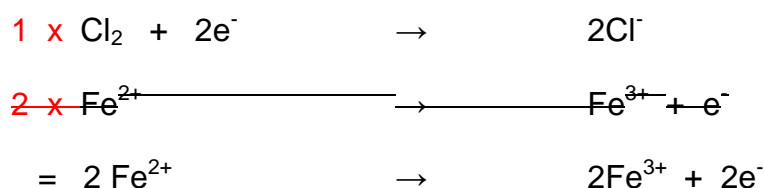## Combining half-equations to make the equation for the reaction

Step 1 – Write down the two half equations under each other so that the arrows are aligned: -

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

$$Fe^{2+} \quad \rightarrow \quad Fe^{3+} + e^-$$
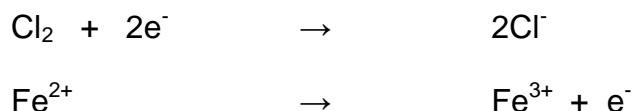
The first reaction needs two electrons for it to occur and the second only needs one.

Step 2 – Multiply both equations with a number so that the number of electrons are the same in each equation.

This example is fairly straightforward as you only have to multiply the first equation by one and the second equation by 2: -

$$1 \times Cl_2 + 2e^- \quad \rightarrow \quad 2Cl^-$$

$$2 \times Fe^{2+} \quad \rightarrow \quad Fe^{3+} + e^-$$

$$= \; 2\,Fe^{2+} \quad \rightarrow \quad 2Fe^{3+} + 2e^-$$

Add together: $Cl_2 + 2Fe^{2+} + 2e^- \rightarrow 2Cl^- + 2Fe^{3+} + 2e^-$

The electrons cancel each other out, as you would expect, so the final ionic equation is as written without them.

Example 2

Manganate (VII) ions, MnO₄-, can oxidise hydrogen peroxide, H_2O_2, to oxygen gas. The hydrogen peroxide solution is acidified with dilute sulfuric acid and during the reaction the manganate (VII) ions are reduced to manganese (II) ions.

If we start with the hydrogen peroxide half-equation: -

Steps 1 and 2 – write down what you know about the half-equation and then add things to it so that it is balanced: -

$$H_2O_2 \quad \rightarrow \quad O_2$$
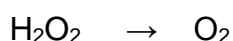
The oxygen is already balanced, but what about the hydrogen? There are no hydrogens on the right-hand side, so how can we add any more? Remember that the only things we can add are electrons, water and hydrogen ions, so what can we do? If you add water, then this will also add more oxygen, so will mess things up, so we should therefore add some H^+ ions: -
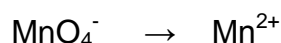
$$H_2O_2 \quad \rightarrow \quad O_2 \ + \ 2H^+$$
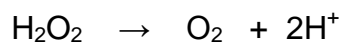
Now we have to balance the charges. The right-hand side needs negative charges in order to balance out the positive charges. We add two electrons and then this half-equation is complete.

$$H_2O_2 \quad \rightarrow \quad O_2 \ + \ 2H^+ \ + \ 2e^-$$
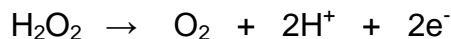
We will now deal with the manganate (VII) half-equation: -

Manganate (VII) ions reduce to manganese (II) ions as follows: -

$$MnO_4^- \quad \rightarrow \quad Mn^{2+}$$

The manganese balances, but the oxygen doesn't, so we have to think of a way of adding more oxygen on the right-hand side. We have to use water:-

$$MnO_4^- \quad \rightarrow \quad Mn^{2+} \ + \ 4H_2O$$

We now have to balance the hydrogens that we have introduced and for this we can add H^+ : -

$$MnO_4^- \ + \ 8H^+ \quad \rightarrow \quad Mn^{2+} \ + \ 4H_2O$$
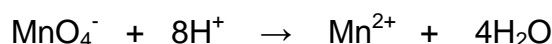
Now balance the charges by adding some electrons to the left hand side as there is a charge of 5+ too many on this side: -

$$MnO_4^- \ + \ 8H^+ \ + \ 5e^- \quad \rightarrow \quad Mn^{2+} \ + \ 4H_2O$$
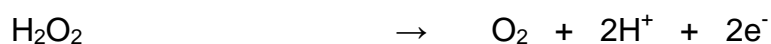
This half-equation is now balanced and complete.

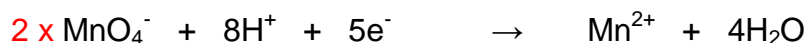For these more complex reactions, these are the steps that have to be followed: -

- Balance atoms apart from hydrogen and oxygen
- Balance the oxygens using water
- Balance the hydrogens using H^+ ions
- Balance the charges using electrons

We now combine the half equations: -

$$H_2O_2 \qquad\qquad\qquad \rightarrow \quad O_2 \ + \ 2H^+ \ + \ 2e^-$$

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

Next, balance the electrons. The first half-equation needs 2 electrons and the second needs 5. We must therefore multiply each equation by the number of electrons required for the opposing equation so that they will cancel each other out: -

$$5 \text{ x } H_2O_2 \qquad\qquad\qquad \rightarrow \quad O_2 \ + \ 2H^+ \ + \ 2e^-$$

16

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

giving:
$$5H_2O_2 \rightarrow 5O_2 + 10H^+ + 10e^-$$

$$2MnO_4^- + 16H^+ + 10e^- \rightarrow 2Mn^{2+} + 8H_2O$$

The electrons cancel each other out automatically and we can also cancel out some H^+ ions, leaving just 6 on the left-hand side.

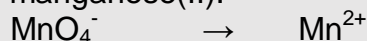$$5H_2O_2 + 2MnO_4^- + 6H^+ \rightarrow 5O_2 + 2Mn^{2+} + 8H_2O$$
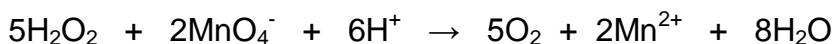
This question has been slightly modified from the WJEC Question Bank. Part (i) is 1 mark and there would be a maximum of 3 for the second part. Make sure you know how to do these and can do them quickly!
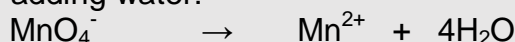
Worked example

(i) Write an ion/electron half-equation for the reduction of acidified manganate(VII) ions, MnO_4^-
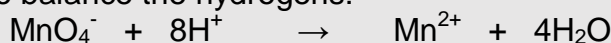
Manganate(VII) is reduced to manganese(II): -
$$MnO_4^- \rightarrow Mn^{2+}$$
Atoms balance, so no further step for this
Balance the oxygens by adding water: -
$$MnO_4^- \rightarrow Mn^{2+} + 4H_2O$$
Add hydrogen ions to balance the hydrogens: -
$$MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$$
Balance the charges using electrons: -
$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$
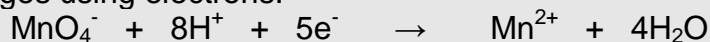
(ii) Ethanedioate ions, $C_2O_4^{2-}$, are oxidised to CO_2 when they react with manganate(VII) ions. write the ion/electron half-equation for the oxidation and then write the equation for the reaction.
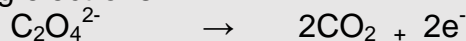
Ethanedioate is oxidised to CO_2: -
$$C_2O_4^{2-} \rightarrow CO_2$$
Balance the carbon atoms: -
$$C_2O_4^{2-} \rightarrow 2CO_2$$
The oxygens are balanced, so no water.
No hydrogen ions needed.
Balance the charges using electrons: -
$$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$$
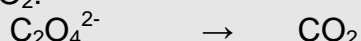
Balance the number of electrons in the two half-equations by multiplying: -

$$2 \times MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$
$$5 \times C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$$

$$2MnO_4^- + 16H^+ + 10e^- \rightarrow 2Mn^{2+} + 8H_2O$$
$$5C_2O_4^{2-} \rightarrow 10CO_2 + 10e^-$$
$$\mathbf{2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 8H_2O + 10CO_2}$$
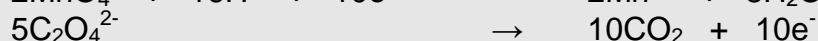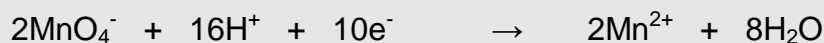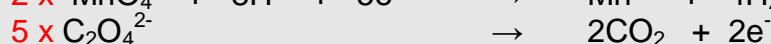
Redox titrations

Redox titrations follow the same procedure as acid-base titrations, the only difference being the type of reaction that takes place. As one of the reactants in a redox titration invariably changes colour, then there is no need for an indicator.

You are expected to carry out a simple redox titration as a specified practical task. As there are several to choose from using a range of oxidising and reducing agents, this section will outline the two reagents mentioned in the specification for WJEC, the colour changes expected and how to perform any calculations.

Oxidation of iron(II) ions by acidified manganate(VII), MnO_4^-

Reaction equation: -

$$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$$
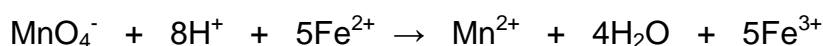
Colour change: -

Purple   Pink (due to some purple colour remaining)
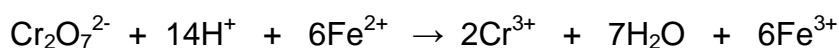
Calculations: -

Use N^o of moles = Concentration x volume in dm^3 (ie, $cm^3 \div 1000$)

Then use the stoichiometric ratio of $1MnO_4^- \equiv 5Fe^{2+}$

Oxidation of iron(II) ions by acidified dichromate(VI), $Cr_2O_7^{2-}$

Reaction equation: -

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

Colour change:-

Orange   Green

Calculation: -

Stoichiometric ratio is $1Cr_2O_7^{2-} \equiv 6Fe^{2+}$

Worked example of a simple redox titration
Four samples of 25cm³ of an ethanedioate ($C_2O_4^{2-}$) solution were titrated against acidified potassium manganate(VII) solution of concentration 0.0200 mol dm⁻³. The volumes of manganate(VII) solution required for the reaction are as follows: -

	1	2	3	4
Volume of KMnO₄(aq)/cm³	*28.80*	*27.95*	*28.00*	*27.80*

Use the information given to calculate the concentration of the ethanedioate ($C_2O_4^{2-}$) solution.

We did the first part of this question on the previous page, so we have the equation: -

$$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 8H_2O + 10CO_2$$

The ratio of manganate(VII) to ethanedioate is 2 : 5.

Mean titre for the manganate(VII) first: - $\dfrac{27.95 + 28.00 + 27.80}{3}$ = 27.92 cm^3

Moles of manganate(VII) = 0.0200 x 0.02792 = 0.0005584 or 5.584 x 10^{-4} mol

Ratio of manganate(VII) to ethanedioate is 2 : 5

Moles of ethanedioate = $\dfrac{5.584 \times 10^{-4}}{2}$ x 5   =   1.396 x 10^{-3} mol

Concentration of ethanedioate = moles ÷ volume in dm^3

= 1.396 x 10^{-3} ÷ 0.025 = 0.0558 mol dm^{-3}

Redox titration to determine the concentration of copper(II) ions

It isn't possible to find out the concentration of Cu^{2+} ions directly, so we have to use a secondary reaction to discover it. If iodide ions are added to a blue solution of Cu^{2+}, a white solid of CuI and a brown solution of iodine is formed: -

$$2Cu^{2+} (aq) + 4I^- (aq) \rightarrow 2CuI_2 (s) + I_2 (aq)$$
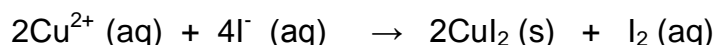
We see that 2 moles of Cu^{2+} ions form 1 mole of aqueous I_2 molecules.

The white copper iodide formed stays as a solid in the bottom of the conical flask, so it is possible to use a solution of sodium thiosulfate to discover how much iodine has been formed. Thiosulfate ions ($S_2O_3^{2-}$) reduce iodine molecules to iodide ions, becoming oxidised to $S_4O_6^{2-}$ ions in the process. Here is the overall equation for the reaction (it may be useful if you can work out how the equation is constructed): -

$$2S_2O_3^{2-} (aq) + I_2 (aq) \rightarrow S_4O_6^{2-} (aq) + 4I^- (aq)$$
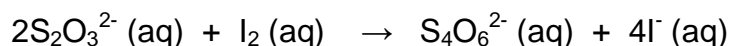
From this, we see that 1 mole of I_2 molecules reacts with 2 moles of $S_2O_3^{2-}$.

Combining the two statements in bold gives us: -

$$2Cu^{2+} \equiv I_2 \equiv 2S_2O_3^{2-}, \text{ so } 1Cu^{2+} \equiv 1S_2O_3^{2-}$$
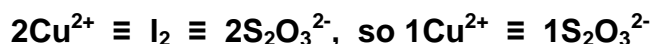
Worked example
KI solution was added in excess to 25cm^3 of a solution containing copper(II) ions. The iodine that was formed was titrated with sodium thiosulfate solution and needed 30.25cm^3 of the solution to convert the iodine to iodide ions. The concentration of the thiosulfate solution was 0.250 mol dm^{-3}. Calculate the concentration of the copper(II) solution.

$$1Cu^{2+} \equiv 1S_2O_3^{2-}$$
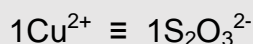
Number of moles of thiosulfate needed to react with iodine = concentration x volume/1000

= 0.250 x 0.03025
= 0.0075625 moles

There are therefore 0.0075625 moles of Cu^{2+} ions in 25cm^3 of solution.

Concentration of Cu^{2+} solution = number of moles ÷ volume/1000

$$= 0.0075625 ÷ 0.025$$
$$= 0.303 \text{ mol dm}^{-3}$$

This is part of a question from a WJEC paper: -

The percentage of copper in a sample from a spoil heap was found by a titration using ethylenediaminetetra-acetic acid (EDTA).
19.20 cm^3 of an EDTA solution of concentration 0.010 mol dm^{-3} reacted with 50.00 cm^3 of a solution containing copper(II) ions.
EDTA reacts with copper(II) ions in a 1:1 mole ratio.

(i)   Calculate the number of moles of EDTA solution used in the titration.   [1]

Number of moles = concentration x volume in dm^3

$$= 0.010 \text{ x } 0.0192$$
$$= 0.000192 \text{ moles of EDTA}$$

(ii)   State the number of moles of copper(II) ions present in 50.00 cm^3 of the copper-containing solution.   [1]

Number of moles of copper = number of moles of EDTA = 0.000192 moles

(iii) Calculate the concentration of copper in the solution in g dm^{-3}.   [2]

Concentration = number of moles ÷ volume in dm^3

$$= 0.000192 ÷ 0.05 = 0.00384 \text{ mol dm}^{-3}$$

Concentration in g dm^{-3} = moles x M_r = 0.00384 x 63.5 = 0.244 g dm^{-3}

The mass of the copper-containing sample was 11.56 g. All the copper in this sample was present in a solution of volume 1.00 dm^3.
Calculate the percentage of copper in the sample.   [1]

% of copper in the sample = (0.244 ÷ 11.56) x 100 = 2.11%

3.3 – Chemistry of the p-block

Introduction

p-block elements are so called as they have their outermost electrons in p-subshells, ie those elements in Groups 3 to 0 in the Periodic Table. Remember that group number corresponds to the number of outer shell electrons an element has, so Group 3 elements have two electrons in an s-orbital and one electron in a p-orbital, Group 4 elements have two in an s-orbital and two in a p-orbital and so on.
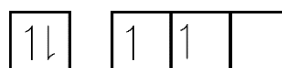
Group 3 – ns^2, np^1 Group 4 – ns^2, np^2

The 'n' in the configurations above represents the period number, so if your Group 3 element was in period 3, you'd write $3s^2 3p^1$.

You need to understand and recall the following chemistry of Groups 3, 4 and 7 (Group 7 was studied in AS).

Oxidation States

Unlike those of the s-block, p-block elements usually show two oxidation states – the higher one is the group number and a lower one that is usually two less. So, we see that:

- Group 3 elements have oxidation states of 3 and 1
- Group 4 elements have oxidation states of 4 and 2
- Group 5 elements have oxidation states of 5 and 3

Which one is the more stable oxidation state of the two depends on the group and the position of the element within it, eg in groups 3 and 4, the higher oxidation state is more stable at the top of the group and the lower oxidation state is more stable at the bottom. There are two things that determine which is the more stable of the two oxidation states; **octet expansion** and the **inert pair effect**.

Octet Expansion

If we look at the elements that are in period 2 of the p-block, we will see that the maximum number of electrons that can surround the atoms is eight (the *octet*). This is because they only have s- and p-orbitals. When we move down the groups into periods 3 and lower, we find that atoms are able to form several bonds, with each electron in the outer shell being able to form a covalent bond. This is due to the presence of the d-orbitals, which are able to accommodate any spare electrons. We call this *expansion of the octet*, where more than eight electrons are able to be present in the outer shell. Examples include: -

- Group 5 – Phosphorus can form 5 covalent bonds, eg PCl_5
- Group 6 – Sulfur can form 6 covalent bonds, eg SF_6, H_2SO_4
- Group 7 – Chlorine can form 7 covalent bonds, eg ClO_4^-

You also need to show examples of period 2 compounds, eg NCl_3 (compared to PCl_5).

Definition of octet expansion: - the ability of atoms to use their d-orbitals so that they can have more than 8 electrons in their outer shell.

Inert Pair Effect

The lower oxidation states are more stable the lower down the group you go, as stated above. This is due to the inert pair effect in groups 3, 4 and 5.

Definition

The tendency of the s^2 electrons in the outer shell to stay paired, which leads to a lower oxidation state.

Eg, $SnCl_4$ is more stable than $SnCl_2$ because the s^2 electrons in tin are not able to take part in bonding and they are called an inert pair.

$$ns^2 \qquad np^2$$
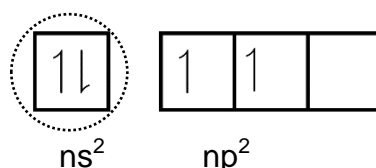
The chemistry behind this is that one of the s-electrons needs energy to promote it to a p-orbital and if the energy 'paid-back' by the formation of covalent bonds is less than the energy required for the promotion, then it won't happen. As you go down the group, the covalent bonds formed get weaker, so there isn't enough energy being formed.

Change from non-metallic to metallic properties down the groups

Elements at the top of each group in the p-block are non-metals, whilst there are metals at the bottom of groups 3 – 6. This change in property is the reason for the zig-zag line separating metals from non-metals that you learn in KS3 Science. This region of change leads to some interesting effects on the way that p-block compounds bond and their consequential properties.

This change from non-metal to metal concerns the ionisation energies of the elements. As the IE decreases going down the group, it's easier to form positive ions, which is a characteristic of metals.

Amphoteric character

Definition

Amphoteric - means something that reacts with both acids and bases.

Several p-block elements that are close to the zig-zag line form oxides that are **amphoteric,** ie they react with both acids and bases. Examples of these are aluminium, zinc and lead: -

Reactions as a base	Reactions as an acid
$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$	$Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2Na[Al(OH)_4]$
$ZnO + 2HNO_3 \rightarrow Zn(NO_3)_2 + H_2O$	$ZnO + 2NaOH + H_2O \rightarrow Na_2[Zn(OH)_4]$
$PbO + 2HNO_3 \rightarrow Pb(NO3)2 + H2O$	$PbO + 2NaOH + H_2O \rightarrow Na_2[Pb(OH)_4]$

Note that the zinc and lead reactions mirror each other as far as valency is concerned as they are both 2^+ ions.

The reaction of **sodium hydroxide** with amphoteric metal solutions can now be explained. The metal solution forms a precipitate of the hydroxide, which is then able to redissolve in excess sodium hydroxide. This is one of the tests that is used to determine unknown metal compounds, if they redissolve in excess sodium hydroxide, then they are amphoteric.

Group 3 – Boron and Aluminium

When group 3 elements form covalent compounds, they only form 3 covalent bonds (giving only 6 electrons in the outer shell), which causes **electron deficiency**. This is because the usual octet of electrons is not attained. We will look at **boron trifluoride, boron trichloride** and **aluminium chloride**.

All three compounds form three covalent bonds with the halogen involved. Because they are electron deficient, they will form **co-ordinate bonds** (with a **lone pair of electrons** from another atom) in order to gain the extra electron pairs that they need – they are called **electron acceptors.**

Aluminium chloride dimer
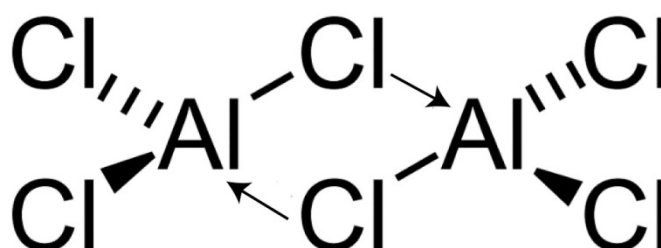
The arrows denote a lone pair being transferred from a chlorine atom to the aluminium atoms to form two co-ordinate bonds

The two $AlCl_3$ monomers form a **dimer** of Al_2Cl_6.

Aluminium chloride can also form the tetrachloroaluminate ion, $AlCl_4^-$.

Definitions

Electron deficient – a species that has less than eight electrons in its outer shell, so it's not full
Co-ordinate bond – covalent bond in which both electrons come from one atom as a lone pair
Lone pair of electrons – electron pair in the outer shell that's not involved in bonding
Dimer – created when two molecules join together.

Donor-acceptor compounds, eg BF_3NH_3
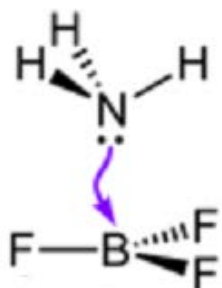
As the name implies, these are compounds where a lone pair is donated by one compound and another accepts it, thereby forming a co-ordinate bond.

If we look at the diagram, we see boron trifluoride accepting a lone electron pair from the nitrogen in ammonia.

The compound formed is no longer electron deficient as both the boron and nitrogen atoms now have a complete octet of electrons.
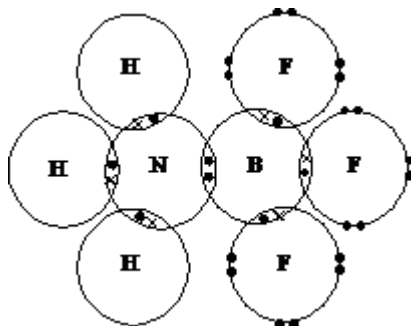
Boron Nitride

If you look at the number of electrons in boron + nitrogen and carbon + carbon, you will see that they have the same number, 12. This is known as **isoelectronic**. You will also need to know that boron nitride forms similar structure to graphite, diamond and nanotubes, which are allotropes of carbon.
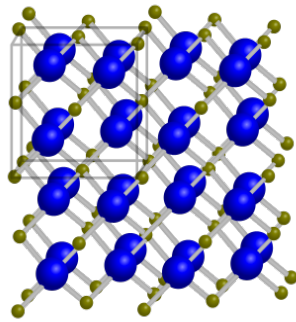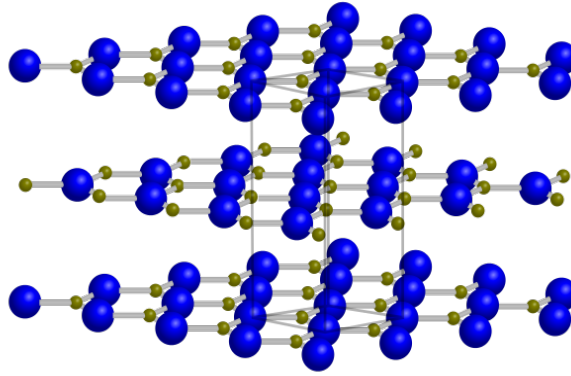
kubisches BN   **hexagonales BN**

You need to be able to quote similarities and differences between the two forms of boron nitride and their corresponding forms of carbon. Graphite and hexagonal boron nitride have more extensive uses.

Diamond and Cubic BN

- Extremely strong and high melting point due to strong covalent bonds between the atoms.
- BN used as a wear-resistant coating or as an industrial abrasive.

Graphite and Hexagonal BN

- Layers in BN are directly above each other with no delocalised electrons. Layers in graphite don't have atoms directly above each other.
- No delocalised electrons in BN, whilst there are in graphite, so BN cannot conduct electricity. BN is used as an electrical insulator.
- Forces between layers in both is weak, so layers can slide over one another, making both useful as a lubricant.

BN hexagonal nanotubes
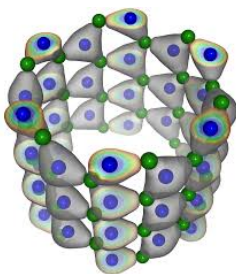

- These can be wrapped around a carbon nanotube and act as an insulating layer, thereby ensuring that the electrical current cannot escape.

Group 4

This group exhibits the greatest change from top to bottom of all the groups of the Periodic Table. Carbon and silicon are the non-metals on the top and tin and lead are the metals on the bottom. You need to remember the change from non-metallic to metallic properties, as well as the inert pair effect as you go down the group.

The oxides of carbon and lead

We need to think of the reactions of these compounds in two categories: -

1 **Redox**

Oxidation states in group 4 are +2 and +4, with the stability of the +2 states increasing as you go down the group due to the inert pair effect. Lead's most stable oxidation state is +2, with +4 being the stablest state for the rest of the elements in the group. We can see this if we look at the redox reactions of both oxides of carbon and lead: -

|	Carbon monoxide CO	Lead (II) Oxide PbO	Carbon Dioxide CO_2	Lead (IV) Oxide PbO_2
Oxidation state of element	+2	+2	+4	+4
Stability of oxide	Unstable	Stable	Stable	Unstable
Redox change in unstable oxides	From +2 to +4, so oxidation	No change	No change	From +4 to +2, so reduction
Type of reagent	Reducing agent			Oxidising agent

We see carbon monoxide acting as a reducing agent in the blast furnace as it reduces iron(III) oxide to iron.

$$Fe_2O_3 \text{ (s)} + 3CO \text{ (s)} \rightarrow 2Fe \text{ (l)} + 3CO_2 \text{ (g)}$$
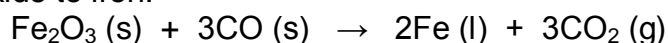
2 **Acid-Base**
- Carbon dioxide is an *acidic oxide* as it will only react with bases, eg sodium hydroxide, to produce carbonates or hydrogencarbonates.
$$CO_2 \text{ (g)} + 2NaOH \text{ (aq)} \rightarrow Na_2CO_3 \text{ (aq)} + H_2O \text{ (l)}$$
- Lead oxide is *amphoteric*. It will react with acids and bases.
$$PbO \text{ (s)} + 2HNO_3 \text{ (aq)} \rightarrow Pb(NO_3)_2 \text{ (aq)} + H_2O \text{ (l)}$$
lead nitrate is one of only two soluble lead salts
$$PbO \text{ (s)} + 2NaOH \text{ (aq)} + 2H_2O \text{ (l)} \rightarrow Na_2[Pb(OH)_4] \text{ (aq)}$$
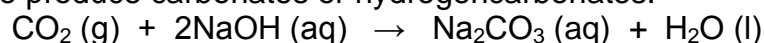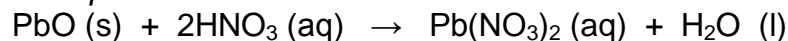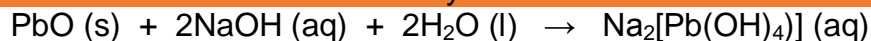
The chlorides of carbon, silicon and lead

Carbon and silicon chloride form the tetrachlorides using covalent bonding, so they are liquids. Lead (II) chloride bonds ionically and is an ionic solid, which is insoluble in water.

Reactions of CCl_4 and $SiCl_4$ with water

Carbon tetrachloride doesn't react with water, it simply forms a separate liquid layer.

Silicon tetrachloride reacts quickly and quite violently with water, forming a white solid of silicon dioxide (SiO_2) and cloudy fumes of HCl: -

$$SiCl_4 \text{ (l)} + 2H_2O \text{ (l)} \rightarrow SiO_2 \text{ (s)} + 4HCl \text{ (g)}$$
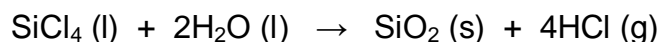
Silicon tetrachloride is able to react due to the availability of d-orbitals in the silicon atom. They allow a lone pair from oxygen to bond with the $SiCl_4$ in order to start the reaction. These d-orbitals don't exist in the carbon atom, so it cannot react in the same way.

Reactions of Pb^{2+} ions in solution

There are only two soluble lead salts, lead (II) nitrate, $Pb(NO_3)_2$ and lead (II) ethanoate, $Pb(CH_3COO)_2$. When a solution of one of these salts is added to different anions, you will therefore get a precipitate of an insoluble lead compound formed: -

| Ions added	Observation	Precipitate formed
OH^- (aq)	White precipitate formed	$Pb(OH)_2$ – Lead (II) hydroxide
excess OH^- (aq)	White precipitate dissolves to form a colourless solution	No precipitate, instead $[Pb(OH)_4]^{2-}$ - tetrahydroxyplumbate ions formed
Cl^-	Heavy white precipitate formed	$PbCl_2$ – Lead (II) chloride
I^-	Heavy bright yellow precipitate formed	PbI_2 – Lead (II) iodide

(The formation of a bright yellow precipitate with iodide ions (usually KI) is a good starting point when you want to identify lead (II) ions)

Group 7

You studied group 7 at AS level, so you will be familiar with the physical states and appearance of the elements and the identification of chloride, bromide and iodide using silver nitrate.

Reactivity of the halogens in terms of oxidising power

The relative strength of the halogens was seen in GCSE, when we saw that chlorine could displace bromide and iodide ions from their solutions. This can now be explained in terms of the oxidising power of the halogens, which decreases down the group.

(Remember oxidation is loss of electrons, so a good oxidising agent will gain electrons easily.)

The table below shows the standard electrode potentials for the three halogens studied: -

Reaction	E^θ/V
Cl_2 (g) + 2e⁻ ⇆ 2Cl⁻ (aq)	+1.36
Br_2 (g) + 2e⁻ ⇆ 2Br⁻ (aq)	+1.09
I_2 (g) + 2e⁻ ⇆ 2I⁻ (aq)	+0.54

The reaction for chlorine occurs most readily as this has the highest E^θ value. This value also shows that it is most difficult to convert chloride ions back into chlorine molecules. Conversely, the iodide ions will convert most readily into iodine molecules.

We can therefore make the following statements – **make sure you understand the difference between them as these terms can be confusing**: -

Chlorine is the strongest oxidising agent, whilst iodine is the weakest oxidising agent of the three.
Conversely, it is easier to oxidise iodide ions into iodine than it is to oxidise chloride ions into chlorine, so iodide ions are a stronger reducing agent that chloride ions.

Explaining displacement reactions using electrode potentials

A more reactive halogen oxidises the ions of a less reactive one, which we can see below: -

$$Br_2 \text{ (aq)} + 2I^- \text{ (aq)} \rightarrow 2Br^- \text{ (aq)} + I_2 \text{ (aq)}$$
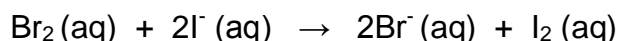
If we look at the E^θ values, that for bromine is more positive than that for iodine, so bromine is the stronger oxidising agent and it will oxidise iodide to iodine.

Make sure that when you are comparing E^θ values that you use the terms more positive or less negative. If you use the terms larger or smaller, then this can become confusing when you're talking about negative numbers.

Reaction of sodium halides with conc H_2SO_4

Concentrated sulfuric acid is an oxidising agent as well as a strong acid. This means that it reacts differently with halide ions depending on the ease of oxidation of the ions. If we look at the table on the previous page, we see that chloride ions are the most difficult to oxidise, whilst iodide are the easiest ions to oxidise back to the corresponding element.

Stage 1: -
All of the ions react with sulfuric acid to form the sodium hydrogensulfate and steamy fumes of HHal gas (where Hal = Cl, Br or I): -

$$NaHal \text{ (s)} + H_2SO_4 \text{ (conc)} \rightarrow NaHSO_4 \text{ (aq)} + HHal \text{ (g)}$$
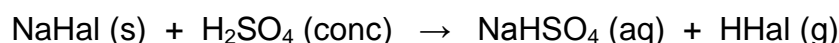
This is where the reaction with sodium chloride ends as chloride ions cannot be oxidised by the sulfuric acid due to its E^θ value being the most positive at +1.36V. The other two halide ions react further as follows: -

Stage 2: -
The sulfuric acid can oxidise bromide ions in HBr to form brown fumes of Br_2: -

$$HBr\ (s)\ +\ H_2SO_4\ (conc)\ \rightarrow\ SO_2\ (g)\ +\ Br_2\ (g)\ +\ H_2O\ (l)$$
Oxidation numbers: -   -1   +6   +4   0

Sulfur is therefore reduced and bromine is oxidised.

The reaction can go one stage further with HI: -

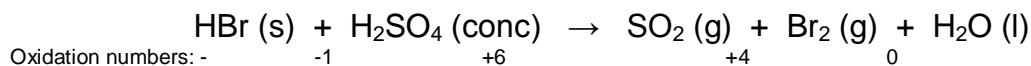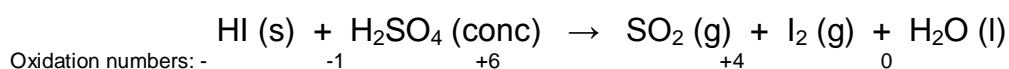$$HI\ (s)\ +\ H_2SO_4\ (conc)\ \rightarrow\ SO_2\ (g)\ +\ I_2\ (g)\ +\ H_2O\ (l)$$
Oxidation numbers: -   -1   +6   +4   0

Sulfur is therefore reduced and iodine is oxidised.

The sulphuric acid can be reduced further to S (oxidation number 0) and H_2S (oxidation number   -2) by the iodide ions as they can act as a better reducing agent than Br^- or Cl^- ions). You may therefore see the following products in the reaction between iodide ions and conc sulfuric acid: -

Steamy fumes of HI, purple fumes of I_2 or a black/brown solution, smell of rotten eggs with H_2S or the yellow solid sulfur.

Reaction of chlorine with NaOH

Definition –

Disproportionation happens during a reaction where atoms of the same element become oxidised and reduced to form different products.

Depending on the temperature of the reaction, chlorine can react with dilute sodium hydroxide in one of two ways. **In the cold** they form sodium chloride and sodium chlorate(I). This is known as a **disproportionation** reaction and you can see the oxidation states below the equation: -

$$Cl_2\ (g)\ +\ 2NaOH\ (aq)\ \rightarrow\ NaCl\ (aq)\ +\ NaOCl\ (aq)\ +\ H_2O\ (l)$$
Oxidation States   0   -1   +1
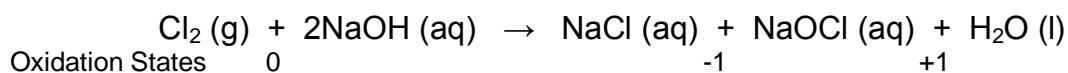
Chlorine has been oxidised to +1 in sodium chlorate(I) and reduced to -1 in sodium chloride.

When **heated**, sodium chloride and sodium chlorate(V) are formed. Again, this is a disproportionation reaction: -

$$3Cl_2\ (g)\ +\ 6NaOH\ (aq)\ \rightarrow\ 5NaCl\ +\ NaClO_3\ (aq)\ +\ 3H_2O\ (l)$$
Oxidation states   0   -1   +5
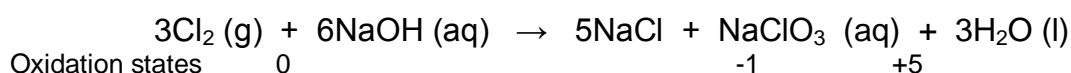
Chlorine has been oxidised to +5 in sodium chlorate(V) and reduced to -1 in sodium chloride

Uses of chlorine and chlorate(I) ions

Chorine and chlorate(I) ions are more stable as the chloride ion, which means they want to gain electrons to become more stable. This gain of electrons means that they are excellent oxidising agents, helping another species to lose their electrons. Chlorine and chlorate(I) will gain electrons in the process and become reduced.

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

$$ClO^- + 2H^+ + 2e^- \rightarrow Cl^- + H_2O$$
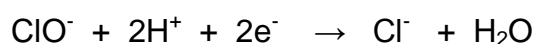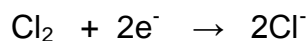
Chlorine is used in water supplies and works as a disinfectant by killing bacteria. It does this by oxidising the DNA of the bacteria so that it can no longer control the cell.

Chlorate(I) ions are used in bleach (as sodium chlorate). They kill bacteria in the same way as chlorine. The other property shown by bleach is, of course, its ability to decolourise or *bleach*. This happens when dyes are oxidised to form colourless compounds.

This bleach is for sale in the USA and it uses chemistry in its name!

3.4 Chemistry of the d-block transition elements

Elements of the d-block have their outer electrons in d-orbitals, whereas transition elements have partially filled d-orbitals. If we concentrate of the first row of the d-block, we see that zinc is the last element to occupy a position. Although zinc is part of the d-block, it is not a transition element as it does not have a partially filled d-orbital. Copper has a full set of d-orbitals as a metal but is a transition element because the Cu^{2+} ion has a partially filled d-orbital.

19 K 39.098	20 Ca 40.078	21 Sc 44.956	22 Ti 47.88	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80

s-block	d-block containing transition elements (NOT Zn)	p-block

These are the properties of the elements that you need to know and explain: -

- They have different oxidation states
- They form (usually) coloured complexes by co-ordinate bonding
- There are several catalysts found amongst the metals and their compounds

Electronic configuration

The order of filling the orbitals of the d-block elements was covered at AS. The following points are important to note in relation to d-block elements: -

- once the 3p orbitals are filled, the 4s orbital is filled next
- the 3d orbitals can then be filled
- there are two exceptions to this, chromium and copper, who only have 1 electron in the 4s orbital and either half-full or complete d-orbitals

The following diagram shows the outer shell orbitals for a manganese atom – its
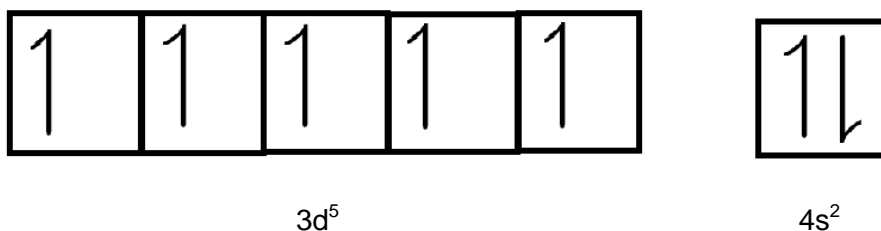
$3d^5$ $4s^2$

electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$

Transition metal ions lose their 4s electrons before the 3d electrons. When you write or draw the electronic configuration of any transition metal ion, they always have an **empty 4s orbital**.

Oxidation states

Transition metals can form different oxidation states as the energies of the 4s and 3d orbitals are very similar, so energy required for electron removal is similar. This means that the energy required to achieve higher oxidation states is very small, so many are possible. The oxidation state that occurs depends on many different factors, eg the oxidising power of the other atoms in the compound.

You need to learn the common oxidation states of the following metals: -

- **chromium** +3 and +6
- **manganese** +2, +4 and +7
- **iron** +2 and +3
- **cobalt** +2 and +3
- **copper** +1 and +2

Transition metal complexes

Definitions

Ligand – a small molecule with a lone pair that can bond to a transition metal ion
Complex – ligands joined to a transition metal ion using co-ordinate bonds
Monodentate – ligand that has one atom that can bond to the metal ion
Bidentate – ligand that has two atoms that can bond to the metal ion

Transition metal ions have many orbitals that are available for bonding, which are often empty. Ligands form co-ordinate bonds with the empty orbitals on the transition metal ion.

Examples of ligands are water, ammonia, chloride ion and cyanide ion.

Types of complex
There are two, the most common being the **octahedral** shape, which has six ligands (B) surrounding the central ion (A). The other type is the **tetrahedral** shape, which has four ligands surrounding the central ion.

Tetrahedral – 4 ligands around central metal ion	Octahedral – 6 ligands around central metal ion (MOST COMMON)
Examples	**Examples**
$[CuCl_4]^{2-}$ - yellow-green coloured complex $[CoCl_4]^{2-}$ - blue coloured complex	$[Fe(H_2O)_6]^{2+}$ - pale green complex $[Fe(H_2O)_6]^{3+}$ - yellow complex $[Cu(H_2O)_6]^{2+}$ - blue complex $[Cr(H_2O)_6]^{3+}$ - dark green complex $[Co(H_2O)_6]^{2+}$ - pink complex

Colours of transition metal ions you need to know: -

Cr^{3+} - green	CrO_4^{2-} - yellow
$Cr_2O_7^{2-}$ - orange	MnO_4^{-} - purple
Co^{2+} - pink	Fe^{2+} - pale green
Fe^{3+} - red-brown	Cu^{2+} - pale blue

Both shapes can be seen with the same transition metal ion, but with different ligands. The shape found is dependant on the metal, its oxidation state and the ligands themselves.
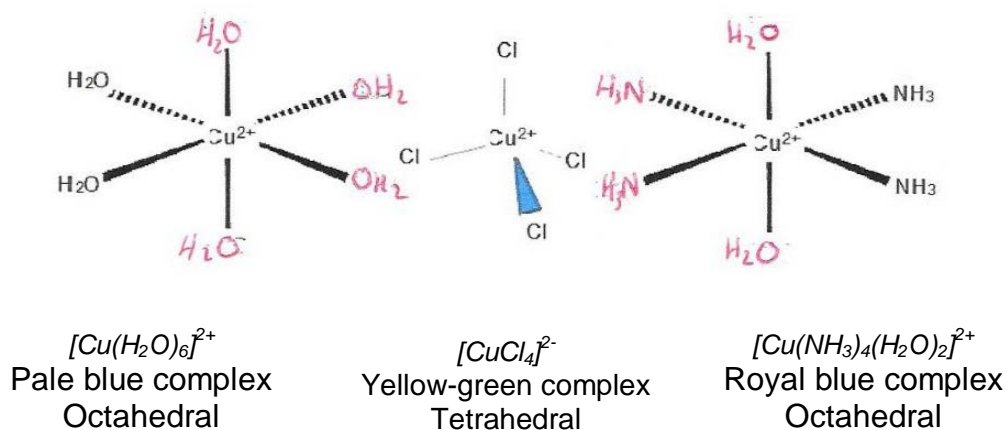

$[Cu(H_2O)_6]^{2+}$
Pale blue complex
Octahedral

$[CuCl_4]^{2-}$
Yellow-green complex
Tetrahedral

$[Cu(NH_3)_4(H_2O)_2]^{2+}$
Royal blue complex
Octahedral

The first complex is formed when any copper(II) compound is dissolved in water and the water molecules act as ligands. The oxygen atom provides the lone pair. In the second complex, concentrated hydrochloric acid has been added in order to provide the Cl⁻ ions. The third complex has had ammonia solution added to the first one.

NB If you add hydrochloric acid to the octahedral pink complex of $[Co(H_2O)_6]^{2+}$, then the blue tetrahedral complex of $[CoCl_4]^{2-}$ is formed.

Why we get coloured complexes

Have you ever wondered why anhydrous copper sulphate is white, but it turns the characteristic blue in solution? It's because transition metal ions are only coloured when they form complexes. The copper(II) ion forms a complex with water ions as the ligands when it is in solution, hence the blue colour.

The reason for this is that the d-orbitals are all at the same level (degenerate) in the transition metal ion, but when it forms a complex, the d-orbitals split into two sets, 3 of lower energy and 2 of higher energy: -

2 orbitals

5 degenerate d-orbitals

ΔE

3 orbitals
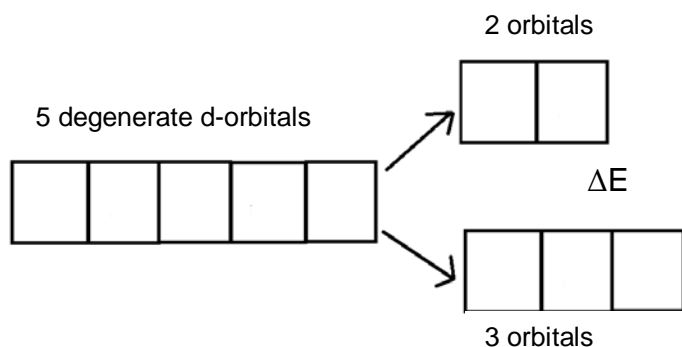
If electrons are to move from the lower to the higher energy level, then they must absorb ΔE of energy. Because $\Delta E = hf$, then this must correspond to a specific frequency of light. The colour you see is made up of the light frequencies that *are not absorbed*. Different ligands cause different splitting, so different ΔEs, different frequencies are absorbed and different colours produced.

Not all complexes are coloured, however, eg Cu^+, Sc^{3+}, Ti^{4+}. These ions have either completely full or completely empty d-orbitals, so electrons cannot move from lower to higher orbitals.

Use of transition metals as catalysts

Examples of transition metals and their compounds used as catalysts (**learn these!**):-
- **Iron** in the **Haber Process**
- **Nickel** to make **margarine from the hydrogenation of vegetable oils**
- **Vanadium(V) Oxide** in the **Contact Process**
- **Manganese(IV) Oxide** in the **catalytic decomposition of hydrogen peroxide**

Definitions:

Homogenous catalyst - catalyst in same physical state as reactants
Heterogenous catalyst – catalyst in a different physical state to reactants

Homogenous catalysts work by having partially filled d-orbitals and the ability to achieve variable oxidation states. The reactant molecules can be bonded into the d-orbitals which can increase the reactivity of the reactants as well as bringing them closer together. Variable oxidation states make transition metal catalysts very useful

in redox reactions as the catalyst can oxidise or reduce one of the reactants and then be converted back into its original state by another molecule.

Heterogenous catalysts have the above advantages as well as being a solid surface on which reactants can be adsorbed and brought closer together for more opportunity to react. It is this latter property that is most often used by heterogenous catalysts.

Reactions of transition metal ions with hydroxide ions

If you add sodium hydroxide solution to most transition metal ions, you will get a coloured precipitate. If the precipitate formed is amphoteric (as in chromium(III) hydroxide), then this precipitate will dissolve on further addition of excess sodium hydroxide solution. Here is a table of the reactions you need to know: -

Ion	Colour of Solution	Observation when NaOH (aq) added	Observation when excess NaOH (aq) added
Cr^{3+}, Chromium(III)	Green	Green-grey precipitate	Precipitate dissolves to produce green solution
Fe^{2+}, Iron(II)	Pale green	Dark green precipitate	No change seen
Fe^{3+}, Iron(III)	Yellow	Rusty, red-brown precipitate	No change seen
Cu^{2+}, Copper(II)	Blue	Pale blue precipitate	No change seen

The ionic equations for the 2+ ions follow this pattern, where M is the metal ion: -

$$M^{2+} \text{ (aq)} + 2OH^- \text{ (aq)} \rightarrow M(OH)_2 \text{ (s)}$$
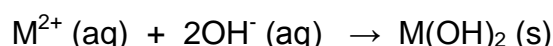
The ionic equations for the 3+ ions follow a similar pattern, according to the oxidation state of the OH^- ion: -

$$M^{3+} \text{ (aq)} + 3OH^- \rightarrow M(OH)_3 \text{ (s)}$$
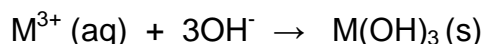
There is one other equation for you to be aware of and that is the equation of the chromium(III) hydroxide precipitate and the excess sodium hydroxide: -

$$Cr(OH)_3 \text{ (s)} + 3OH^- \text{ (aq)} \rightarrow [Cr(OH)_6]^{3-} \text{ (aq)}$$
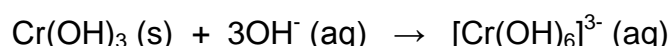
3.5 – Chemical Kinetics

Measuring rates of chemical reactions

You will have encountered the methods for measuring how quickly a chemical reaction proceeds at GCSE by measuring one factor in the reaction as it changes over a certain period of time. Some methods that may be used are: -

- **Measuring gas volume** (at constant pressure) using a **gas syringe.** Obviously can only be used when a gas is produced in a reaction.
- **Measuring gas pressure** (at constant volume) – used when both reactants and products are gases and the pressure changes as the number of gas molecules changes.
- **Measurement of change in mass** – used when a dense gas is produced during a reaction.
- **Colorimetry** – used when something with colour is produced or used up during a reaction.
- **Sampling and quenching** – this is used when all other methods aren't suitable. It involves removing small samples of the reaction mixture at regular time intervals. These are placed in ice water to lower the concentration of the reactants and to stop the reaction continuing. This is known as *quenching*. The samples can then be tested by other techniques like titration.

Calculating rates of reaction

The rate of a reaction can be calculated from either numerical results or from curves drawn from such results. Whichever method is used, we should know that: -

$$\text{Rate of reaction} = \frac{\text{change in concentration}}{\text{time}}$$

If you have numerical values, it's easy to extract information in order to place values in the equation. If you have a curve, you have to draw a tangent to it and calculate its gradient in order to work out the rate: -

You can calculate rates at different times by drawing tangents at different places on the curve. Concentration can be that of reactants or products. The graph obviously shows the concentration of the products increasing as time goes on. The curve
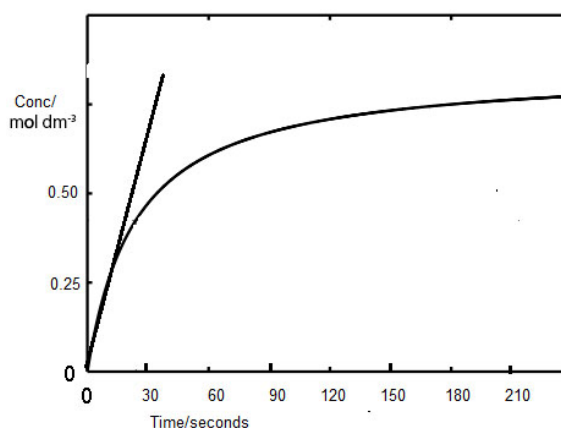
would be going down if it were concentration of reactants.

Rate = change in concentration
                    time

With the tangent drawn at time = 0 seconds

Rate = 0.5-0.0
                30   =   0.0167 mol dm^{-3} s^{-1}

(Please note that the values extracted from the graph are approximate due to inaccuracy in reading the diagram)

Order of Reactions

This sometimes confusing topic of reaction order is better understood if you know the reason why they are calculated. Orders of reac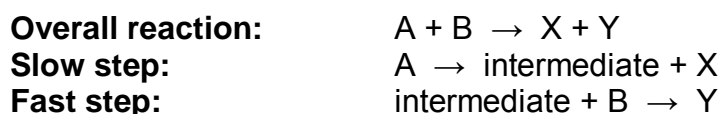tion are **calculated** (fairly simply) **from reaction data that you will be given** and are **used by chemists to work out the mechanism for a reaction**. (Look back at your AS organic work if you can't remember what a reaction mechanism is.)

Effect of concentration on reaction rates

When we consider the effect of increasing concentration on the rate of a reaction, we must think about how the reaction may be taking place as changing the concentration of some reactants may make no difference.
Most reactions take place in more than one step, with some steps being very fast and others being very slow. (This is what is found out by calculating the order of the reaction.) The rate of a reaction depends on the speed of the **slowest** step as it has to be achieved before the rest of the reaction can happen. Here is an example: -

This reaction takes place in two steps: -

Overall reaction:	A + B $\rightarrow$ X + Y
Slow step:	A $\rightarrow$ intermediate + X
Fast step:	intermediate + B $\rightarrow$ Y

If we increase the concentration of A, then there are more molecules that can potentially decompose, so the overall reaction will be faster. If we increase the concentration of B, then the reaction rate will not change because it is also a very fast reaction, so making it faster would make no difference anyway! So, we can say that changing the concentration of A affects the rate of the reaction, but changing the concentration of B does not.

Explaining orders of reaction using the rate equation

Definitions

Rate – the rate of change of the concentration or amount of a particular reactant or product

Rate constant – the constant in the rate equation. Constant for a given reaction at a **given temperature**, but is not changed by changing the concentration of reactants.

Order of reaction – with respect to a particular reactant it is the power to which the concentration is raised in the rate equation. The **overall** order of reaction is the individual orders for the different reactants added together.

If you have a chemical reaction as follows: -

$$xA + yB + zC \rightarrow \text{products}$$

and you find out by carrying out experiments that the rate of this reaction is related to the concentrations of the reactant by the following equation: -

$$\text{Rate} = k[A]^a[B]^b[C]^c$$

This is known as the **rate equation**, with k being the **rate constant if the temperature remains constant.** Its unit equation as you will see when we do some calculations u

Note that the orders have no relationship to the stoichiometry of the reaction (numbers in the equation). Orders can only be discovered by carrying out experiments.

Also: - a is the order of reaction with respect to A
b is the order of reaction with respect to B
c is the order of reaction with respect to C

The overall order of this reaction is a + b + c

Orders of reaction are small numbers and the ones that you will deal with are orders of 0, 1 & 2.

Zero order - This means that the concentration of the particular reactant that has this order will not affect the rate of reaction. This reactant will not appear in the rate equation.

First order – This means that whatever you do to the concentration of this reactant, exactly the same thing will happen to the rate, eg if you double the concentration, you double the rate; if you triple the concentration, you triple the rate and so on. It will be written into the rate equation as Rate = k[A] (no numbers are required as 1 isn't necessary here).

Second order – Whatever you do to the concentration of this reactant, the rate will be the **square** of that, eg if you double the concentration, the rate increases by four times (2^2), if you triple the concentration, the rate increases by 9 times (3^2). It will be written into the equation as Rate = $k[A]^2$.

Example
Say you have a reaction with the following equation: -

$$2A + B + 3C \rightarrow 2D + E$$

and you found out by experiment that doubling the concentration of: -

A doubled the rate of the reaction

B had no effect of the rate of reaction

C increased the rate of reaction four times

The reaction is   first order with respect to A
                       zero order with respect to B
                       second order with respect to C

The rate equation is therefore Rate = $k[A][C]^2$

and the overall order of the reaction is 3 (because the sum of the individual orders is 1 + 0 + 2)

Finding orders of reaction from experiments

A series of experiments is carried out in which the concentrations of the reactants are changed individually, but everything else stays the same. The rate is measured by measuring the loss of a reactant or the formation of a product. You should be given the results for at least four of these experiments: Here's an example: -

Experiment	Concentrations (mol dm^{-3})			Rate of loss of A/mol dm^{-3} s^{-1}
	A	B	C	
1	0.1	0.1	0.1	2.0×10^{-4}
2	0.2	0.1	0.1	4.0×10^{-4}
3	0.2	0.2	0.1	1.6×10^{-3}
4	0.1	0.1	0.2	2.0×10^{-4}

Look for two experiments where the concentration of A has changed, but B and C has stayed the same: -

Experiments 1 and 2   concentration of A has doubled and so has the rate. so, we have **first order** with respect to A

For B: -

Experiments 2 and 3   concentration of B has doubled, and the rate has quadrupled. We have **second order** with respect to B

For C: -

Experiments 1 and 4   concentration of [C] has stayed the [same]... with respect to C.

> There is no [C] in the rate equation as its order is zero.

Now we write the **rate equation**: -

Rate = $k[A][B]^2$

As we have a series of concentrations and rates in the table, we can calculate the value of the rate constant, k. We rearrange the rate equation and use the values for **one** experiment: -

$$k = \frac{\text{Rate}}{[A][B]^2}$$

If we use the values for the first experiment: -

$$k = \frac{2.0 \times 10^{-4}}{(0.1) \times (0.1)^2} = 0.2 \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$$

-1-1

How do we work out the units for k?

Instead of putting numbers into the equation for k, put in units for the various terms and then cancel them out as you would if you had ordinary fractions. When you've done that, tidy up to make sure they're on the same line.

$$k = \frac{\text{Rate}}{[A][B]^2}$$

$$= \frac{\text{mol dm}^{-3} \text{ s}^{-1}}{(\text{mol dm}^{-3})(\text{mol dm}^{-3})^2}$$

Cancel out the single mol dm^{-3} on the top and the bottom of the line. This leaves you with: -

$$k = \frac{\text{s}^{-1}}{(\text{mol dm}^{-3})^2}$$

$$= \frac{\text{s}^{-1}}{\text{mol}^2 \text{ dm}^{-6}}$$

Now bring the bottom line up to the top (this **reverses the sign of the indices**)

$$k = \underline{\text{mol}^{-2} \text{ dm}^6 \text{ s}^{-1}}$$

Another example:-
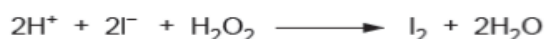
$$k = \frac{\text{Rate}}{[A][B][C]^2}$$

$$= \frac{\text{mol dm}^{-3} \text{ s}^{-1}}{(\text{mol dm}^{-3})(\text{mol dm}^{-3})(\text{mol dm}^{-3})^2}$$

$$= \underline{\text{mol}^{-3} \text{ dm}^9 \text{ s}^{-1}}$$

(e) Hydrogen peroxide reacts with acidified potassium iodide according to the equation below.

$$2H^+ + 2I^- + H_2O_2 \longrightarrow I_2 + 2H_2O$$

(i) This reaction was studied using an iodine clock reaction. Describe the principles of how the rate of a clock reaction is determined. Experimental details are not required. [2]

(ii) The rate of this reaction was studied by a different method for a range of concentrations of $H_2O_2(aq)$ and $I^-(aq)$ and pH values. These are listed in the table below.

Experiment number	Initial concentration of $H_2O_2(aq)$/mol dm^{-3}	Initial concentration of $I^-(aq)$/mol dm^{-3}	pH	Initial rate/ mol dm^{-3} s^{-1}
1	0.0010	0.10	1	2.8×10^{-6}
2	0.0020	0.10	1	5.6×10^{-6}
3	0.0020	0.10	2	5.6×10^{-6}
4	0.0010	0.40	1	11.2×10^{-6}

I. Some experiments were undertaken at pH 1 and some at pH 2. Give the difference in the concentrations of H$^+$ ions in these two solutions. [1]

II. Use the data in the table to deduce the rate equation for this reaction, giving your reasoning. [3]

III. Calculate the value of the rate constant, k, giving its units. [2]

(i)

Rate is measured by measuring the time taken for the sudden change in colour.
Then rate is calculated by the equation: - Rate = 1÷Time

(ii)

I pH 1 is ten times more concentrated that pH 2

II For H₂O₂, use experiments 1 and 2: - conc doubles whilst rate doubles, so order with respect to hydrogen peroxide is 1.

For I⁻ use experiments 1 and 4: - conc goes up by four and rate goes up by four, so order with respect to iodide is 1.

$$Rate = k[H_2O_2][I^-]$$

III $k = Rate \div [H_2O_2][I^-]$ = $2.8 \times 10^{-6} \div (0.0010) \times (0.1)$ = $2.8 \times 10^{-6} \div 10^{-4}$

= $0.0280 \ mol^{-1} \ dm^3 \ s^{-1}$

Rate-determining step from rate equations

A reaction mechanism is the steps that must occur during a chemical reaction. Each step has its own rate equation as they occur at different rates. It's the rate of the slowest step that limits the overall rate of reaction, so it is called the **rate determining step**.

If a reaction is first order, there is only one particle in the rate determining step, if it's a second order, then two particles must collide and if it's a third order, then three particles must collide. We can therefore use the rate equation to work out what is in the rate determining step and also use this to write an equation for the rate determining step (including the correct stoichiometry).

So, if: -

   Rate = k[Br⁻][C₄H₆], rate-determining step reactants are: 2Br⁻ + C4H6 → products

Conversely, if: -

   Rate determining step is C₃H₇I + Br⁻ → Products, then Rate = k[C₃H₇I][Br⁻]

> If the proposed mechanism doesn't have a step with the same reactants as in the rate equation, then it will not be the correct mechanism.

Effect of temperature on the rate of a reaction

All we have encountered so far about this topic is the qualitative explanation due to collision theory. This was covered at AS. We will now look at how temperature quantitatively affects a reaction by looking at its effect on the rate constant. This is calculated using the **Arrhenius equation**.

$$k = Ae^{\left(-\frac{E_a}{RT}\right)}$$

k = rate constant
*A = frequency factor
e = mathematical constant (you'll find it on your calculator)
E_a = activation energy (used in **J** mol⁻¹, so you'll have to multiply kJ by 1000!)
R = gas constant, you'll be given this on the data sheet. Units **J** K⁻¹ mol⁻¹

T = temperature in Kelvin (needs converting if temperature is in □C)

*A – Frequency Factor is related to the frequency of collisions. It's treated as a constant over a limited temperature range. Most questions ask you to calculate A at a given temperature (and rate constant) and this is then substituted into a second calculation at another temperature so that you can find the rate constant.
$e^{\left(-\frac{Ea}{RT}\right)}$ shows the fraction of collisions that have enough energy to overcome the activation energy.

In order to perform the calculation, you need information of five of the six factors. R and e are constants, so you will need to know three out of the four factors of k, A, E_a or T so that you can work out the missing one. As mentioned above, many problems will give you data about a rate constant at a certain temperature and ask you to work out A at that temperature. You will then be asked to calculate k at a slightly different temperature using your calculated value of A. This is shown in the example below.

Worked example
The value of the rate constant, k for a reaction at two different temperatures is given below: -

Rate constant/mol^{-1} dm^3 s^{-1}	Temperature/K
0.0742	273
0.2574	285

The activation energy for this reaction is 58.333 kJ mol^{-1}. The Arrhenius equation is: -

$$k = Ae^{\left(-\frac{Ea}{RT}\right)}$$

Calculate the value of the rate constant, k at a temperature of 279K.

If we look at the information we have from the question we see that: -

*   k = 0.0742, T = 273K, A = ?, E_a = 58.333 kJ! (so, 58333 J)), R = 8.314 JK^{-1} mol^{-1}*

We don't know what A is yet, so although the question doesn't ask it, we need to work it out before we can find k for the new temperature.

Rearrange the Arrhenius equation: -

$$A = k/e^{\left(-\frac{Ea}{RT}\right)}$$

A = 0.0742 ÷ e$^{(-58333/8.314 \; x273)}$
*   = 0.0742 ÷ e$^{-25.701}$*
*   = 1.077 x 10^{10} mol^{-1} dm^3 s^{-1}*

Work out k at 279K: -

$$k = Ae^{(-\frac{Ea}{RT})}$$

$k = ?, A = 1.077 \times 10^{10}, E_a = 58333J, R = 8.314\ JK^{-1}\ mol^{-1}, T = 279K$

$k = 1.077 \times 10^{10} \times e^{(-58333/8.314 \times 279)}$
$\quad = 1.077 \times 10^{10} \times e^{-25.15}$
$\quad \underline{= 0.129\ mol^{-1}\ dm^3\ s^{-1}}$

Effect of catalysts on the rate of a reaction

The Arrhenius equation can also explain the effect of catalysts on the rate of a reaction.

We know that catalysts increase the rate of reaction by providing different routes that have lower activation energies. As this does not affect concentration in the rate equation, it is the rate constant that must be changed. If we reduce the activation energy in the Arrhenius equation, then the value of $e^{(-\frac{Ea}{RT})}$ will be increased and therefore so too the rate constant. You will also see the frequency factor changing.

# 3.6 – Enthalpy changes for solids and solutions

Definitions

Hess's Law – the energy change of any chemical reaction is the same regardless of the route taken.
Exothermic reaction – gives out heat. More chemical energy present in the reactants than the products.
Endothermic reaction – takes in heat. More chemical energy in the products than the reactants.
Enthalpy change of reaction, ΔH – the **change** in chemical energy present in the substances as a chemical reaction takes place.

Energy cycles
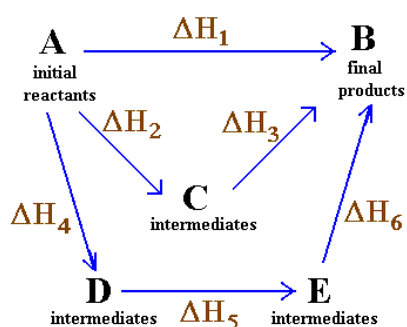
Here's an example of a reaction whose enthalpy cannot be measured directly. It's possible to use Hess's law to calculate the enthalpy from those that are more easily measured.

There are two routes that can be taken to measure ΔH_1 : -

$\Delta H_1 = \Delta H_2 + \Delta H_3$, or

$\Delta H_1 = \Delta H_4 + \Delta H_5 + \Delta H_6$

If you have all the ΔH values except one in either route, you can find the missing one.

If you're asked to calculate the enthalpy of a reaction and are given the enthalpies of **formation only** then there's an easier way of working out the enthalpy change. It's by using the following equation: -

Enthalpy change = $\Delta_f H^\theta$ (products) - $\Delta_f H^\theta$ (reactants)

Remember that if you have numbers before substances in an equation so it balances, you must include these numbers in your calculation or the enthalpies will not balance.

Standard enthalpy changes

There are several different types of enthalpy change that you need to understand, depending on the type of reaction. Whatever the type of enthalpy change, they must all be quoted under **standard conditions**. These standard conditions are: -

- Temperature of 298K (25°C)
- Concentration of 1 mol dm^{-3} for solutions
- Pressure of 1 atmosphere (atm) or 101 kPa for gases

The **standard state** of a substance is its physical state under standard conditions, e.g. carbon dioxide gas, liquid water or lithium chloride solid.

The next page lists the standard enthalpy changes for different specific reactions. You encountered two of these at AS, enthalpy of formation and enthalpy of combustion. The remaining ones are more likely to be concerned with the calculations involving ionic compounds.

Standard enthalpy change of reaction, ΔH^θ – enthalpy change that happens between molar amounts of reactants in their standard states and under standard conditions.

Standard enthalpy change of formation, $\Delta_f H^\theta$ – enthalpy change when one mole of a substance is formed from its elements in their standard states under standard conditions.

Standard enthalpy change of combustion, $\Delta_c H^\theta$ – enthalpy change when one mole of a substance is completely combusted in oxygen under standard conditions.

Standard enthalpy change of atomisation, $\Delta_{at} H^\theta$ – enthalpy change when one mole of atoms of an element are formed in the gas phase of the element in its standard state.

Standard enthalpy change of lattice formation, $\Delta_{latt} H^\theta$ – enthalpy change when one mole of an ionic compound is formed from ions of its elements in the gas phase.

Standard enthalpy change of hydration, $\Delta_{hyd} H^\theta$ – enthalpy change when one mole of gaseous ions are surrounded by water molecules to make a solution.

Standard enthalpy change of solution, $\Delta_{sol} H^\theta$ – enthalpy change when one mole of an ionic compound dissolves in water to make a solution. It is the sum of enthalpies of lattice breaking (endothermic) and hydration (exothermic). If hydration is greater than lattice breaking, then the salt dissolves.

Ionisation energy, IE – enthalpy change when one mole of gaseous ions are formed from one mole of gaseous atoms when they lose an electron.

Electron affinity, EA – enthalpy change when one mole of gaseous ions are formed from one mole of gaseous atoms when they gain an electron.

Born-Haber cycles

These are energy cycles with several steps that are used to calculate the energy of f_____ of b_____ nds from elements in their standard states. The steps
Born-Haber cycle of
lithium fluoride – note
that the upward arrows
are endothermic
reaction and the
downward arrows are
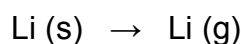exothermic

y transfers mentioned above.
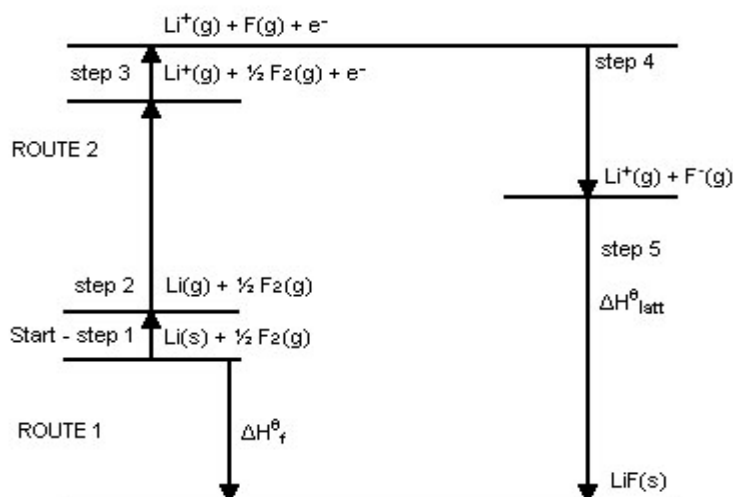
Route 1 shows the energy of formation of LiF from its elements in their standard states.

Route 2 – a series of steps leading to the formation of LiF

Step 1 – **formation one mole of gaseous atoms – enthalpy of atomisation**

Energy required to form one mole gaseous atoms of lithium from standard states: -
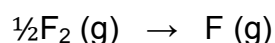
$$Li \ (s) \ \rightarrow \ Li \ (g)$$

Step 2 – formation of lithium cation – ionisation energy

Energy required for one mole of lithium atoms to remove one mole of electrons: -

$$Li \ (g) \ \rightarrow \ Li^+ \ (g) \ + \ e^-$$

Step 3 – conversion of fluorine molecules to atoms – enthalpy of atomisation

$$\tfrac{1}{2}F_2 \ (g) \ \rightarrow \ F \ (g)$$

Step 4 – formation of fluoride anion – electron affinity

Energy usually given out when an atom gains an electron to form an anion. (If the anion requires more than one electron in its formation, energy is usually required).

$$F \ (g) \quad \rightarrow \quad F^- \ (g)$$
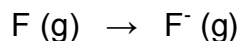
Step 5 – formation of LiF solid from its ions – lattice formation

Energy released when the ions join to form the solid ionic compound. The more exothermic this process is, the more stable the ionic compound.

As for the other cycles we've studied: -

$$Li^+ \ (g) \ + \ F^- \ (g) \quad \rightarrow \quad LiF \ (s)$$

ROUTE 1 = ROUTE 2
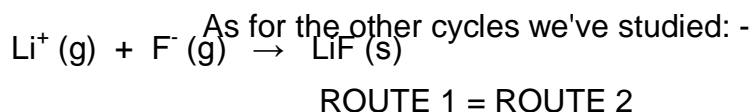
Calculations involving Born-Haber cycles

(i) Where you are given the Born-Haber cycle

The unknown in a calculation is usually **step 5 – lattice formation**, where you need to find the value for the formation of solid LiF from its gaseous ions. As Route 1 = Route 2 for any cycle, we have to go a different way around the cycle to get lattice formation on its own: -

e.g., for LiF: - $\Delta_{latt}H^\theta \ = \ - EA \ (F) - IE \ (Li) - \Delta_{at}H^\theta \ (Li) - \Delta_{at}H^\theta \ (F) + \Delta_f H^\theta \ (LiF)$

Because the path goes against the arrows from lattice formation upwards, then we have to subtract the values, when the path goes with the arrow, it is added.

(ii) Where you have to construct a Born-Haber cycle from provided equations

You will be provided with an overall equation of formation and some other equations. You use the data in the other equations to produce a Born-Haber cycle, e.g.
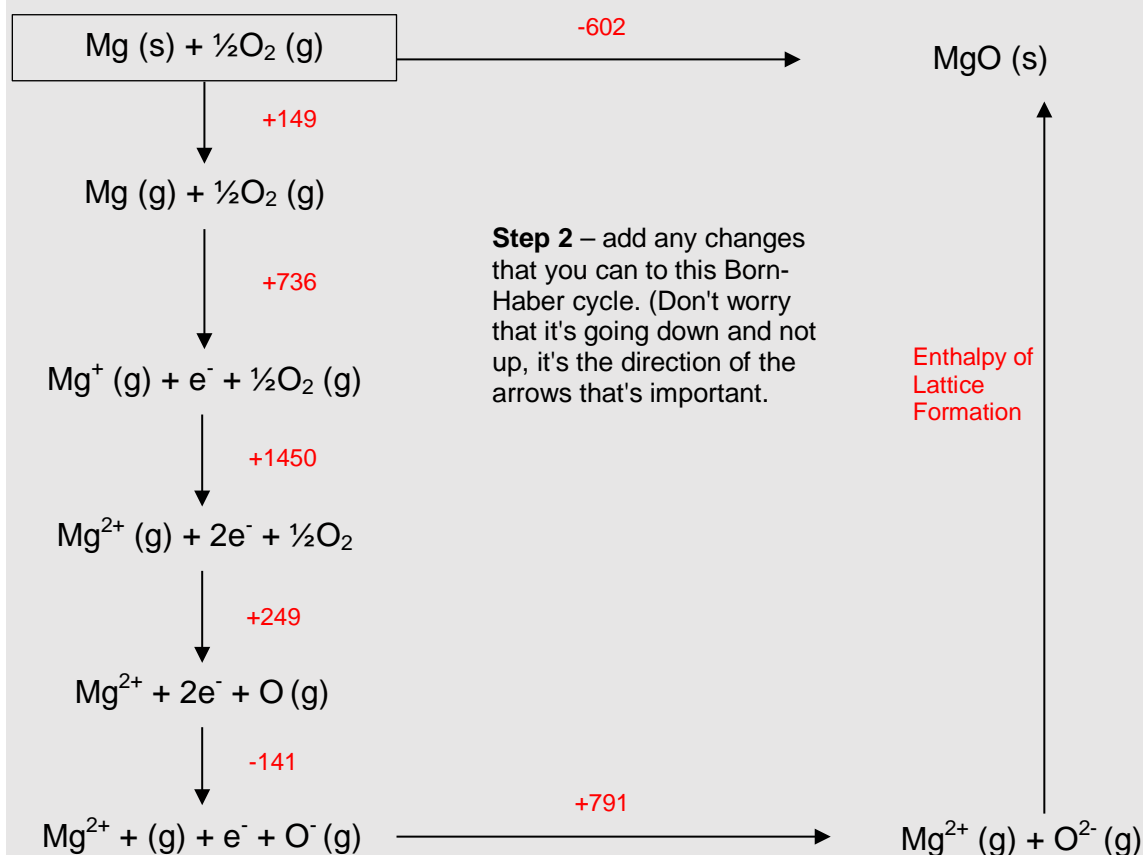
Worked example

Calculate the enthalpy of the lattice formation for magnesium oxide, MgO, using the data provided: -

$$Mg\ (s)\ +\ ½O_2\ (g)\ \rightarrow\ MgO\ (s)\quad \Delta_fH^\theta = -602\ kJ\ mol^{-1}$$

	Enthalpy change/kJ mol^{-1}
$Mg\ (s)\ \rightarrow\ (Mg)\ (g)$	+149
$Mg\ (g)\ \rightarrow\ Mg^+\ (g)\ +\ e^-$	+736
$Mg^+\ (g)\ \rightarrow\ Mg^{2+}\ (g)\ +\ e^-$	+1450
$O_2\ (g)\ \rightarrow\ 2O\ (g)$	+498
$O\ (g)\ +\ e^-\ \rightarrow\ O^-\ (g)$	-141
$O^-\ (g)\ +\ e^-\ \rightarrow\ O^{2-}\ (g)$	+841

+145

Step 1 – start with the equation given and then add in the unknown value: -

Mg (s) + ½O$_2$ (g) →(-602) MgO (s)

↓ +149

Mg (g) + ½O$_2$ (g)

Step 2 – add any changes that you can to this Born-Haber cycle. (Don't worry that it's going down and not up, it's the direction of the arrows that's important.

↓ +736

Mg$^+$ (g) + e$^-$ + ½O$_2$ (g)

Enthalpy of Lattice Formation

↓ +1450

Mg^{2+} (g) + 2e$^-$ + ½O$_2$

↓ +249

Mg^{2+} + 2e$^-$ + O (g)

↓ -141

Mg^{2+} + (g) + e$^-$ + O$^-$ (g) →(+791) Mg^{2+} (g) + O^{2-} (g)

Step 3 – Complete the calculation

+149 +736 +1450 +249 + (-141) + 791 + Enthalpy = -602
3234 + Enthalpy = -602
Enthalpy = -602 – 3234 = <u>-3836 kJ mol^{-1}</u>

Stability of compounds

When we talk about the stability of compounds, we are referring to their stability relative to the elements that make them. If the enthalpy change of formation is negative, then the compound is stable. This is because energy is released when the compound is formed from its elements. The more negative the enthalpy, the more stable the compound.

If the enthalpy change of formation is positive, then the converse is true, the compound is unstable compared to its elements. The compound can exist, but it takes energy to create it. They tend not to decompose once formed as the process is too slow.

3.7 – Entropy and feasibility of reactions

Definitions

Entropy - can be described as a quantitative value of how much order is in a system, eg in a solid, the particles are ordered and unable to move, so they are said to have a low entropy, whilst a gas has particles moving all over the place, so is said to have a high entropy. You could also describe it as the freedom of molecules or atoms within molecules to move. This is a very simplistic view, but helps to understand the meaning of the term.

Feasible - 'whether it's possible or practical to do something easily' is the dictionary definition.

Entropy

Low entropy is experienced by a system with atoms in fixed positions that have little or no freedom to move, eg solid.
Greater entropy is experienced by a system which has atoms that are free to move in any direction, but must stay close together, eg liquid.
Highest entropy is experienced by a system whose atoms are free to move in any direction and move to any position, eg gas.

The symbol for entropy is **S** and units are **joules per kelvin ($J \, K^{-1}$)** and standard entropies (at 298K and 1atm) are given as **$J \, K^{-1} \, mol^{-1}$.**

Here are a few examples of entropy, firstly showing water in its three physical states and therefore increasing entropy and then the two oxides of carbon, showing entropy increasing as the molecule gets more complicated.

Substance	Entropy/$JK^{-1} \, mol^{-1}$
Solid water – ice	48 (approx.)
Liquid water	69.9
Gaseous water – steam	189
Carbon monoxide	197.6
Carbon dioxide	213.6

Entropy changes during reactions

Entropy is calculated from the standard entropy of the substances involved, with values being obtained from data books (or data sheets in the exam!). You need to use the following calculation: -
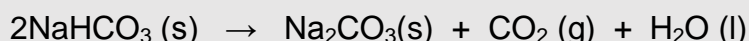
$$\Delta S = \Sigma S^\theta \text{ (products)} - \Sigma S^\theta \text{ (Reactants)}$$

With Σ meaning 'the sum of'. This can be simplified to: -

Change in entropy = what you end up with – what you started with

Worked example
Work out the enthalpy change during the following reaction: -

$$2NaHCO_3 \text{ (s)} \rightarrow Na_2CO_3\text{(s)} + CO_2 \text{ (g)} + H_2O \text{ (l)}$$

Compound	Entropy/JK^{-1} mol^{-1}
$NaHCO_3$ (s)	101.7
Na_2CO_3(s)	135.0
CO_2 (g)	213.6
H_2O (l)	69.9

Entropy of things you end up with = 135.0 + 213.6 + 69.9 = 418.5 JK^{-1} mol^{-1}
Entropy of things you started with = 2 x 101.7 = 203.4 JK^{-1} mol^{-1}
ΔS = 418.5 – 203.4 = +215.1 JK^{-1} mol^{-1}

The entropy of the system has increased, which is not surprising as a solid has produced a gas and a liquid as well as a solid. This means that the products are more disordered than the original sodium hydrogencarbonate. Any reaction where there is an increase in gas molecules is bound to increase in entropy.

Gibbs free energy, ΔG

This is a value that links enthalpy, entropy and temperature. It's important because you may think from work you've done on thermochemistry that chemical reactions only occur when they are exothermic, but several endothermic reactions occur as well. This can be explained if we consider the relationship between entropy and enthalpy. The relationship is: -

$$\Delta G = \Delta H - T\Delta S$$

The units for the three changes must be expressed in the same units, usually kJ, so entropy is usually divided by 1000.

If ΔG is **negative**, then a reaction will occur spontaneously, but if ΔG is **positive**, then the reaction will not occur spontaneously. If the reaction has its temperature changed to change ΔG, then it may occur spontaneously.

For ΔG to be negative, temperature/entropy change must be large. Increase in entropy can be attained by heating or dissolving in water for example. This gives greater freedom to particles in liquid or gas phase and increases entropy significantly. When some salts are thermally decomposed, gases are produced, and this increases entropy.

Discovering minimum temperature for a reaction to occur

ΔG can be used to discover the minimum temperature required for a reaction to take place. We know that ΔG changes as temperature changes, so if we have a value for ΔG that is just negative (ie, 0) then we can use that value to find out the temperature required for a reaction to become feasible.

This question is taken from a WJEC exam paper: -

Worked example
Another group 4 element is tin. At low temperatures tin exists in its grey form. At higher temperatures the white form is stable. The change can be represented by the equation: -

$$Sn_{(grey)} \rightarrow Sn_{(white)} \quad \Delta H^{\theta} = 1.92 \text{ kJ mol}^{-1}$$

The standard entropy values are 44.8 $JK^{-1}mol^{-1}$ for grey tin and 51.5 $JK^{-1}mol^{-1}$ for white tin.
Calculate the minimum temperature required to cause grey tin to turn to white tin.

Assu Remember to convert the entropy value from joules to kilojoules by dividing by 1000. Change in entropy = products – reactants.

$T = 1.92 \div 0.0067 = \underline{286.6K}$

3.8 – Equilibrium constants

When a reaction is at equilibrium the concentrations of reactants and products are constant because the rates of forward and reverse reaction are equal. Le Chatelier's principle enables you to work out the effect changes in temperature have on concentration, but not the actual concentration values. To do this, you need to use equilibrium constants.
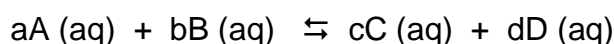
Equilibrium constants

There are two types: -

K_c – equilibrium constant in terms of concentration. Usually used for reactions in solution, but can be used for all types of reaction involving concentrations.

K_p – equilibrium constant in terms of partial gas pressures. Only used for reactions involving gases.

Writing equilibrium constants
i) K_c

Let's say you have the following equilibrium reaction: -

$$aA \text{ (aq)} + bB \text{ (aq)} \leftrightharpoons cC \text{ (aq)} + dD \text{ (aq)}$$

The equilibrium constant for this reaction is: -
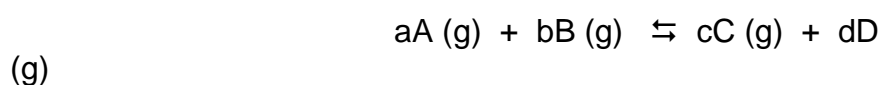
$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

the square brackets denote concentrations of the reactants.

Top line = concentrations of products raised to the powers of the balancing numbers, multiplied together.
Bottom line = concentrations of reactants raised to the powers of the balancing numbers, multiplied together.

Partial pressure = the pressure exerted by an individual gas in the mixture. Sum of all the partial pressures is equal to the total pressure exerted by all the gases. It's proportional to the concentration of the gas.

ii) K_p

For the equilibrium reaction: -

$$aA \text{ (g)} + bB \text{ (g)} \leftrightharpoons cC \text{ (g)} + dD \text{ (g)}$$

The equilibrium constant for this reaction is: -

$$K_p = \frac{P_C{}^c P_D{}^d}{P_A{}^a P_B{}^b}$$ 　　where P_C represents the partial pressure of gas C etc

Top line = partial pressures of the products raised to the powers of their balancing numbers, multiplied together.

Bottom line = partial pressures of the reactants raised to the powers of their balancing numbers, multiplied together.

> ### Remember that the formula for equilibrium constants have
> ## PRODUCTS OVER REACTANTS

Calculating K_c or K_p

These are straightforward to calculate if you have the concentrations of reactants and products at equilibrium (for K_c) or the partial pressures of any gases (for K_p).

K_c

$$H_2\,(g)\ +\ I_2\,(g)\ \leftrightarrows\ 2HI\,(g)$$
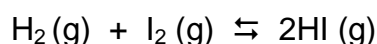
At equilibrium (at 764K), the mixture was found to contain: -
- H_2 - 2.484×10^{-3} mol dm^{-3}
- I_2 – 2.514×10^{-3} mol dm^{-3}
- HI – 1.695×10^{-2} mol dm^{-3}

Calculate a value for K_c

$$K_c = \frac{[HI]^2}{[H][I]}$$

$$K_c = \frac{(1.695 \times 10^{-2})^2}{(2.484 \times 10^{-3})(2.514 \times 10^{-3})}$$

$$=\ \underline{46.0}\ \ \text{(no Units)}$$

Note that amounts of gas are expressed in moldm^{-3}, so we must find out K_c. If it were expressed in partial pressures, then we would find out K_p.

There are no units as there are two concentrations on the top line and two on the bottom line. These cancel out. If there are unequal concentrations, then some cancel out and some are left. This is similar to what happens with the units in kinetics.

Units are KPa as there are two on the top and one on the bottom. One of the top units is cancelled out, leaving the other one.

K_p

$$N_2O_4\,(g)\ \leftrightarrows\ 2NO_2\,(g)$$
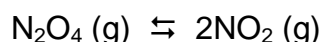
At equilibrium at 350K, the partial pressures of the gases were as follows: -
- N_2O_4 – 24.6 kPa
- NO_2 – 98.4 kPa

$$K_p = \frac{P^2{}_{NO_2}}{P_{N_2O_4}}$$

$$= \frac{98.4^2}{24.6}$$

$$= \underline{394 \text{ kPa}}$$

What can we learn from equilibrium constants?

- If $K_c = 1$, then the equilibrium has equal amounts of starting materials and products.
- If K_c is much less than 1, then the equilibrium is favouring the side of the reactants, with very few products being formed. We can relate this to ΔG. As this reaction is not spontaneous, ΔG is positive
- If K_c is much greater than 1, then we have an equilibrium favouring the side of the products, with most of the reactants being converted. This reaction is occurring spontaneously, so ΔG will be negative.

This is different to what we can learn from rates of reaction. We can learn a reaction mechanism from rates, i.e. what is happening during the reaction. With equilibrium constants, we can learn about the relative stability of reactants and products and the free energy changes that happen between them.

Using data to work out equilibrium mixtures

Sometimes, questions don't include the concentrations of all reactants or products, so you must work them out. You will usually be given the concentrations of the reactants at the beginning and one product at equilibrium.

Worked example

A and B are reacted and allowed to reach equilibrium. Their concentrations are 0.5 mol dm^{-3} each. The equilibrium mixture contains 0.2 mol dm^{-3} of C. Calculate the value of K_c.

$$A + B \leftrightharpoons C + 2D$$
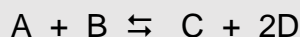
We start by writing what we know in a table: -

	[A]	[B]	[C]	[D]
At Start	0.5	0.5	0	0
At equilibrium	0.3	0.3	0.2	0.4

At the start, we have no C and D, so these have 0 written in the table. At equilibrium, we have C = 0.2. The equation states that for every C, we have 2D, so there must be 0.4D.

0.2 moles of D must be made by 0.2 moles of A and 0.2 moles of B, so we must take 0.2 away from the starting amount of 0.5. This leaves us with 0.3 moles of both A and B.

We now write an expression for K_c and work out its value having put these values in it: -

$$K_c = \frac{[C][D]^2}{[A][B]} \qquad = \qquad \frac{0.2 \times 0.4^2}{0.3 \times 0.3} \qquad = \qquad \underline{0.356 \text{ mol dm}^{-3}}$$

Effect of temperature on rate constants

This is the only factor that will affect the value of K_c or K_p. We can't do the calculation as it's too complicated for A level, but we can use Le Chatalier's Principle to work out its effect on the position of equilibrium.

If the temperature of a reaction is **increased:** -
- **Exothermic** reactions shift the equilibrium to the left (endothermic direction). This makes the bottom line of the equilibrium constant larger and the top line smaller, thereby **decreasing the equilibrium constant**.

- **Endothermic** reactions shift the equilibrium to the right (exothermic direction). This makes the bottom line smaller and the top line larger, thereby **increasing the equilibrium constant.**

Example
The reaction to form ammonia is an exothermic reaction: -

$$N_2 \text{ (g)} + 3H_2 \text{ (g)} \leftrightharpoons 2NH_3 \text{ (g)} \quad \Delta H = -92 \text{ kJmol}^{-1}$$
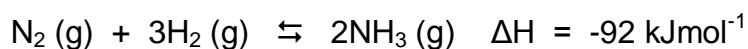
$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

Increasing temperature shifts equilibrium to the reactants, thereby increasing the value at the bottom of the equation and decreasing the value at the top of the equation. Kc will therefore **decrease.**

Using equilibrium and rate equations in industry

Chemical manufacturers want to produce the maximum amount of product as quickly as possible and using the least energy they can. They will think of all the kinetic, energy and equilibrium data they have so they can plan the reaction most efficiently. There may have to be a compromise, but they will get as close as they can to the optimum value.

Rates will be made as fast as possible by increasing temperature or pressure or by adding a catalyst.

Energy calculations can discover how much energy needs to be put into a system for the reaction to occur. This avoids the use of unwanted energy. Also, if there is an exothermic reaction, the energy will be harnessed in order to reuse it.
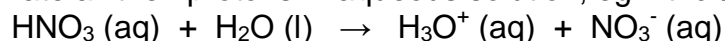
Equilibrium yield of a product can be increased by changing temperature, concentration or pressure. The equilibrium constant can be used to tell manufacturers which values of pressure or concentration will give high yield.
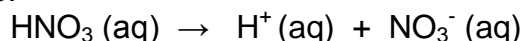
3.9 Acid-base equilibria

Brőnsted-Lowry definition of acids and bases

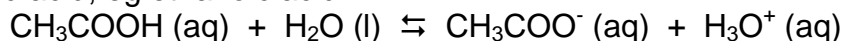- Acids are proton (H^+) donors
- Bases are proton acceptors

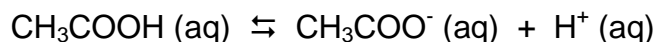**Strong acids** donate all their protons in aqueous solution, eg nitric acid: -

$$HNO_3 \ (aq) \ + \ H_2O \ (l) \ \rightarrow \ H_3O^+ \ (aq) \ + \ NO_3^- \ (aq)$$

This can be simplified to: -

$$HNO_3 \ (aq) \ \rightarrow \ H^+ \ (aq) \ + \ NO_3^- \ (aq)$$

Weak acids donate only some of their protons, ie they only partly dissociate into H^+ ions and negative ions. The free ions form a dynamic equilibrium with the undissociated acid, eg ethanoic acid: -

$$CH_3COOH \ (aq) \ + \ H_2O \ (l) \ \rightleftharpoons \ CH_3COO^- \ (aq) \ + \ H_3O^+ \ (aq)$$

Simplified to: -

$$CH_3COOH \ (aq) \ \rightleftharpoons \ CH_3COO^- \ (aq) \ + \ H^+ \ (aq)$$
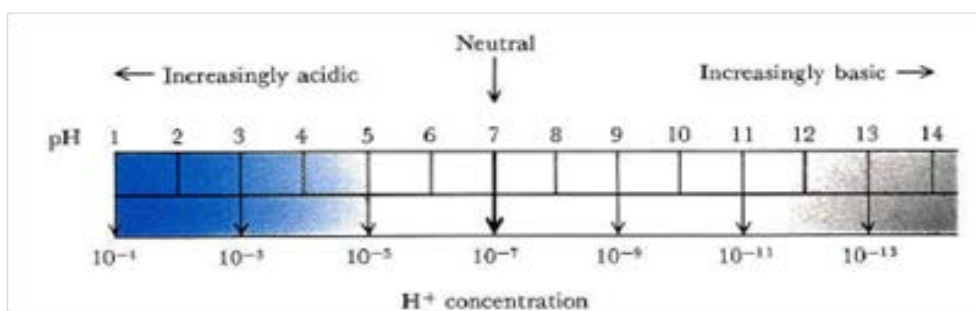
Water is accepting a proton, so is classed as a base. There is a second base in the equilibrium, which is CH_3COO^- (in the reverse direction). This brings about the idea of **conjugate acids and bases**: -

CH_3COO^- is the conjugate base of CH_3COOH and
H_3O^+ is the conjugate acid of H_2O

pH

The pH scale quotes the strength of acids, usually from 0 (strongest) to 14 (strong alkali).

The numbers on the pH scale are calculated from the concentration of H^+ (aq) ions in the solution: -

$$pH = -\log_{10} [H^+ \ (aq)]$$

eg, H^+ (aq) concentration of 0.0250 mol dm^{-3}, pH = $-\log_{10} (0.0250)$ = 1.6.

If you want to work out the H^+ (aq) concentration in a solution, then you use this formula: -

$$[H^+ \text{ (aq)}] = 10^{-pH}$$

You will often see questions that ask you to use the concentrations of solutions that have different pHs, eg in order of reaction calculations. As pH is a log scale, **one unit on the scale is equivalent to a 10x change in concentration. So if you have 2x unit change, it is a 100x change in concentration and so on.**

Acid equilibrium constants

Because the dissociation of acids is an equilibrium process, it has an equilibrium constant, generally expressed as: -

$$HA \text{ (aq)} \leftrightharpoons H^+ \text{ (aq)} + A^- \text{ (aq)}$$
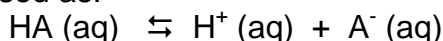
$$K_a = \frac{[H^+][A^-]}{[HA]}$$

Note that it is called K_a, a = *acid*.
- The stronger the acid, the more dissociated it is, giving more ions, so K_a will be a larger value.
- A weak acid has less dissociation, so K_a will be smaller.

Because the range of K_a values can be large, from 24 mol dm^{-3} for HNO_3 to 1.7×10^{-5} mol dm^{-3} for CH_3COOH, chemists use pK_a values, which are calculated in the same way as for pH: -

$$pK_a = \log_{10}(K_a)$$

This would give a pK_a value of -1.38 for HNO_3 and 4.77 for CH_3COOH.

Calculating pH for strong and weak acids

We need to know $[H^+]$ for an acid before we can calculate its pH. This is easy for a strong acid: -

Strong acids

Because all the molecules of acid in a strong monobasic acid (one H atom) release H^+ ions, then $[H^+]$ will equal the concentration of the acid. eg 0.01 mol dm^{-3} HCl

$$pH = -\log_{10}[H^+] = -\log_{10}(0.01) = 2$$

Weak acids

Not all the molecules of acid dissociate, so the $[H^+]$ will be less than the acid concentration. This varies from acid to acid. If we know K_a for the acid, we can use it to calculate $[H^+]$. This is done by doing an equilibrium calculation: -

eg, for ethanoic acid, K_a = 1.7 x 10^{-5} mol dm^{-3}, so if we want to find $[H^+]$ in a 0.01 mol dm^{-3} solution we can use the following calculation. (Note that we need to make some assumptions here.): -

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

Each molecule of acid that dissociates gives us one H^+ and one CH_3COO^-, so $[H^+]=[CH_3COO^-]$

and $\quad K_a = \dfrac{[H^+]^2}{[CH_3COOH]}$

We can also assume that, as very little dissociation happens, the concentration of CH_3COOH is the same as what was put in it. The above equation can therefore be rearranged to give: -

$[H^+] = \sqrt[2]{Ka\ x\ [acid]}$, in this example, K_a = 1.7 x 10^{-5} and [acid] = 0.01

$\quad = \sqrt[2]{.000017\ x\ 0.01} = 0.00041$ mol dm^{-3}

pH $\quad = -\log_{10}(0.00041) = \underline{3.4}$

K_w – the ionic product of water and neutralisation

Pure water can conduct small amounts of electricity because it has ions dissolved in it. These ions are there because water dissociates into H^+ and OH^- ions, producing the following equilibrium: -

$$H_2O\ (l)\ \leftrightarrows\ H^+\ (aq)\ +\ OH^-\ (aq)$$
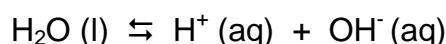
With the equilibrium constant being: -

$$K_c\ =\ \frac{[H^+][OH^-]}{[H_2O]}$$

The amount of water that dissociates is tiny, so the equilibrium lies almost completely to the left. This means that the concentration of water can be thought of as constant and we can combine it into the equilibrium constant and rename it K_w, **the ionic product of water**, written as: -

$$K_w\ =\ [H^+][OH^-]$$

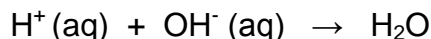This is constant at a particular temperature, eg at 25°C, it's 1.0 x 10^{-14} $mol^2\ dm^{-6}$.

If you want to calculate $[H^+]$ for water, then you must realise that $[H^+] = [OH^-]$, so $K_w = [H^+]^2 = 10^{-14}$, $[H^+]^2 = 10^{-14}$
$[H^+] = \sqrt[2]{0.00000000000001}$

$[H^+] = 0.0000001$,
$pH = -\log_{10} (0.0000001) = 7$

When an acid reacts with a base, the reaction is the reverse of the above and the equation for the neutralisation reaction is: -

$$H^+ (aq) + OH^- (aq) \rightarrow H_2O$$

pH for strong bases

When a strong base is dissolved in water, the OH^- ions have the same concentration as the original base. If we want to find out the pH, the $[H^+]$ ion concentration needs to be known, even in a solution of a base. These will come from the water, so if we use the expression for K_w we can find out $[H^+]$ concentration: -
$$K_w = [H^+][OH^-], \text{ so } [H^+] = \frac{K_w}{[OH^-]}$$

So, $[OH^-] = [NaOH]$, if the base in question is sodium hydroxide.

Worked example
What's the pH of a solution of NaOH with concentration 0.8 mol dm^{-3}, with $K_w = 1.0 \times 10^{-14}$ mol^2 dm^{-6}

$$[H^+] = \frac{K_w}{[OH^-]}$$
$$= \frac{1.0 \times 10^{-14}}{0.8}$$
$$= 1.25 \times 10^{-14}$$
$$pH = -\log_{10} (1.25 \times 10^{-14})$$
$$= \underline{13.9}$$

Buffers

A buffer is a solution whose pH stays almost constant if a small amount of acid or alkali is added to it. It removes any added H^+ or OH^- ions. It is usually made from a mixture of a weak acid and a salt of the same acid, eg CH_3COOH and CH_3COONa. Buffers are very important in the maintenance of biological systems which rely on a narrow range of pH values.
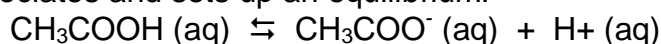
How do they work?

There are two dissociations that occur in an **acidic buffer**: -
- The salt dissociates fully: -
$$CH_3COONa (aq) \rightarrow CH_3COO^- (aq) + Na^+ (aq)$$
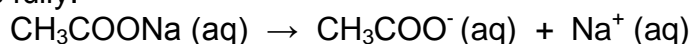
- The acid partly dissociates and sets up an equilibrium: -
$$CH_3COOH (aq) \leftrightharpoons CH_3COO^- (aq) + H+ (aq)$$

This equilibrium will be pushed far to the left as there is a high concentration of ethanoate ions from the salt, so the acid won't dissociate very much.

The concentration of H^+ ions are increased as you add acid to the buffer, so according to Le Chatelier, equilibrium will shift to the left. This removes the H^+ ions as they react with the ethanoate ions.

A base added to the buffer will react with the H^+ ions. This shifts the equilibrium to the right and releases more H^+ ions from the ethanoic acid.
A **basic buffer** can be made using a mixture of ammonium chloride and ammonia solution. The important equilibrium is: -

$$NH_4^+ \leftrightarrows NH_3 + H^+$$

- Adding a base removes H^+ ions, causing the equilibrium to move to the right, producing more H^+.
- Adding an acid shifts the equilibrium to the left, removing the H^+ ions from the acid.

Calculating the pH for buffers

We need to make two assumptions: -
- as all salt dissociates, $[CH_3COO^-] = [CH_3COONa]$
- as none of the acid dissociates, $[CH_3COOH]$ = same as original concentration.

$K_a = \dfrac{[H^+][CH_3COO^-]}{[CH_3COOH]}$ rearrange to give $[H^+] = \dfrac{K_a \times [CH_3COOH]}{[CH_3COO^-]}$

Worked example
Calculate the pH of a buffer solution that contains 0.20 mol dm^{-3} CH_3COOH and 0.40 mol dm^{-3} CH_3COONa (K_a for CH_3COOH = 1.7 x 10^{-5} mol dm^{-3}).

$[H^+] = \dfrac{K_a \times [CH_3COOH]}{[CH_3COO^-]}$

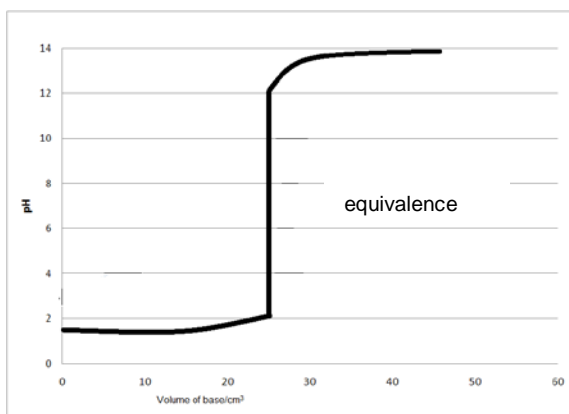$= \dfrac{1.75 \times 10^{-5} \times (0.20)}{(0.40)}$ $= 8.75 \times 10^{-6}$

$pH = -\log_{10}[H^+] = -\log_{10}(8.75 \times 10^{-6}) = \underline{5.1}$

Acid-base titration curves

A neutralisation reaction occurs when an alkali is added to an acid, leading to an increase in the pH. If you were to plot a graph of volume of alkali against pH, it would not be a straight line. The graph shape depends on whether the acid and base are strong or weak.

Strong acid/strong base

NaOH is added slowly to HCl and you see the pH increasing very slowly until the volume of base added equals the volume of acid, then you see a very sharp increase in pH. This region of the curve is vertical, which rises until it levels off at the end. The middle of the vertical line is called the *equivalence point*, where amount of alkali added = amount of acid.
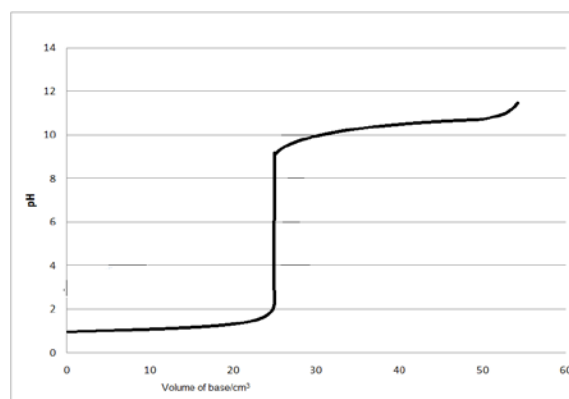
Weak acid/strong base
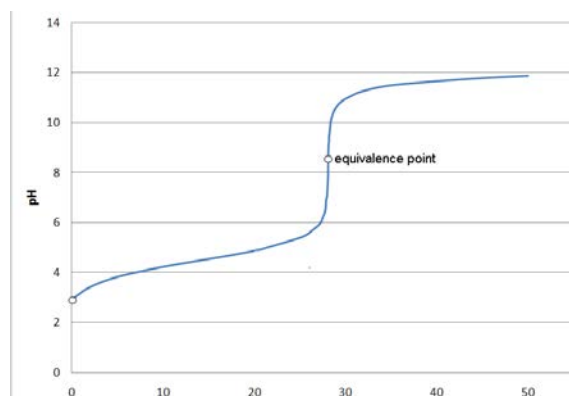
NaOH is added to CH_3COOH and the pH rises slowly to around 4. When the volume of NaOH reaches half the volume of the acid, the pH levels off. A mixture is formed with unreacted acid and the salt of the acid and this acts as a buffer. pH will not change much then for a while.

pH then increases vertically after pH 6.5 to around pH 12.

Strong acid/weak base

You'll see that the pH up to 7 is the same as the first curve. The line then becomes vertical but levels off due to the buffer effect. The pH then increases up to a pH of around 12.

If you're asked to sketch a titration curve, you must start by including any points you know: -
• The pH of the initial acid
• The pH at half neutralisation
• The pH at the equivalence point
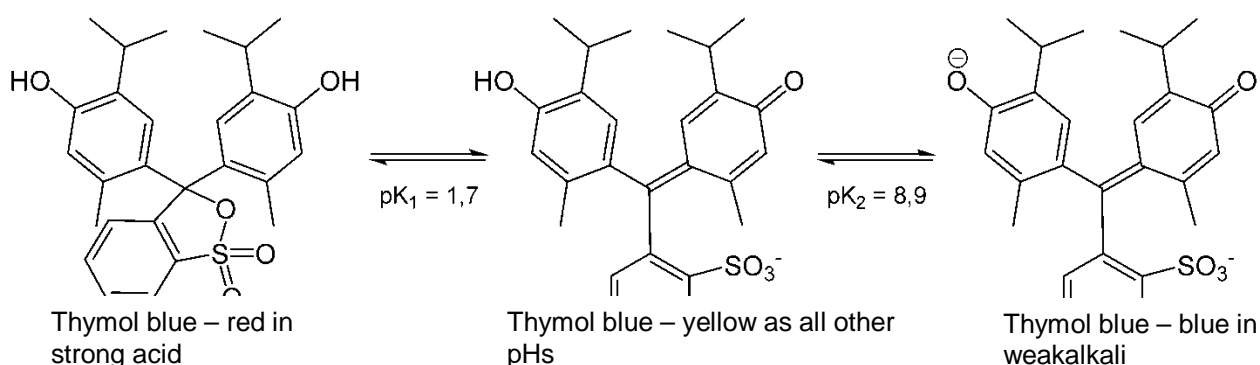
64

Weak acid/weak base
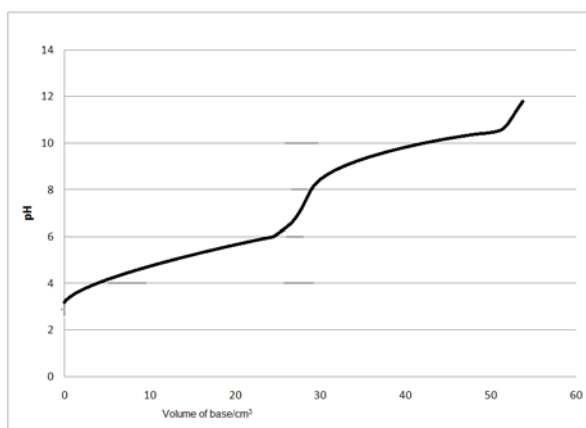
There is no clear vertical line in this graph, so it makes it harder to find an equivalence point. If you don't have this, then it's hard to choose an indicator for the reaction (see below). It's better to use a pH probe to find the equivalence point.

Make sure yo
point is whe
alkali and **en**
indicator cha

Equivalence
vertical line c
can be used
the pH can b
concentration

Indicators

Change colour as the pH changes. They are weak acids and the original molecule and dissociated ions have different colours.

Thymol blue – red in strong acid

Thymol blue – yellow as all other pHs

Thymol blue – blue in weakalkali

Indicators change over a range of pH values, with a different range for each indicator. If the range lies within the vertical part of the pH curve, then the colour change will happen when just a single drop of the alkali is added. Here are some values for some indicators: -

Indicator	Colour change range
Phenolphthalein	8.3 – 10.0
Bromothymol Blue	6.0 – 7.5
Litmus	4.0 – 6.5
Methyl orange	3.2 – 4.4

pH of salts

When a neutralisation reaction reaches completion, a salt is formed. At the equivalence point for each of the above reactions, a solution of salt is formed, with the pH of this solution being at the mid-point of the vertical section of the curve. This is 7 for a strong acid-strong base, so the salt formed is neutral. With other combinations, the salt formed is not neutral, with a weak acid and strong base forming a basic salt. Anions released by the salt formed react with the H^+ ions, removing them: -

$$H^+ \text{ (aq)} + CH_3COO^- \text{ (aq)} \leftrightarrows CH_3COOH \text{ (aq)}$$
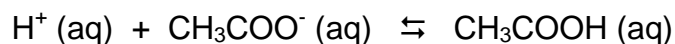
Conversely, if you have a strong acid and a weak base, you have an acidic salt (pH 4 – 6). The cation can dissociate to release H^+ ions in a reversible reaction: -

$$NH_4^+ \text{ (aq)} \leftrightarrows NH_3 \text{ (aq)} + H^+\text{(aq)}$$
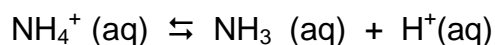
Acknowledgment

Section	Image	Acknowledgment
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