# A Level Chemistry OCR A 2015

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# Module 1

# Practical skills in chemistry

Practical skills are crucial to chemistry. Chemistry is a practical subject; as such we should understand how to correctly carry out our experiments. Practical skills are a recurring theme throughout the other 4 modules so a good knowledge of these skills is vital to success.

### 1.1 Practical stuff 1.1.1 & 1.1.2

**Planning** is crucial to any and all experiment doing. In this course you should be able to do several things with ease.

Firstly you should understand the range of equipment available and there appropriate usage. You should then have the mental capacity to apply this knowledge to a given situation and, in so doing, design a practical. This understanding comes with time and I will not go into much detail.

Secondly you should understand these distinctions. **Independent** variables are ones which the experimenter changes e.g. the temperature of the heater. **Dependent** variables depend on the independent ones and are measured e.g. the amount of gas released from the reaction. **Control** variables are ones which remain constant and are controlled by the experimenter e.g. the amount of substance added.

Because I like maths think of it like this. Let y be the dependent, x be the independent and c be the control/constant:

Lastly you should be able to evaluate the experimental method to determine whether or not it is appropriate to find the expected outcomes. This part requires critical thinking and an understanding of modules 3-4

**Implementing** is more about usage. I will not go into it fully here but here is an overview.

You need to know your units, techniques and how to use the apparatus. The units will be visited as we explore the rest of this spec.

## 1.2 The reviewing 1.1.3 & 1.1.4

**Reviewing** is necessary, it comprises two parts, that of analysis and of evaluation.

**Analysis** simply the processing and interpretation of qualitative<sup>1</sup> data combined with an understanding of the maths skills involved to explore quantitative<sup>2</sup> data. Basic statistics skills required are as follows:

$$\bar{x} = \frac{\sum_{i=1}^{n} x_i}{n} \tag{1.1}$$

Plotting graphs is important as this exam uses mostly graphical methods to find things such as gradients. Just remember to use a good scale when drawing them.

**Evaluation** is the process in which we look back at the plan and the method and, well, evaluate it. You need to understand the limits of the procedure used, identifying anomalies and refine the experimental design by suggesting improvements to the procedures and apprentice.

 $<sup>^1 \</sup>mbox{Observed}$  data e.g. colour and effer vescence

<sup>&</sup>lt;sup>2</sup>Data that is measured with a numeric output e.g. temperature

# Module 2

# Foundations in Chemistry

This chapter acts as a bridge between A level and GCSEs. It is quite simple with a lot of practice of molar equations, percentages and remembering through rote learning.

## 2.1 Atomic Structures and Isotopes 2.1.1

**Isotopes** are atoms of the same element with different numbers of neutrons and different masses. It is important to note that they also have the same number of protons and electrons.

Chemists compare the masses of subatomic particles using relative masses. This is because the masses are too small.

A proton has basically the same mass of a neutron. An **electron** is  $\frac{1}{1836}$  or 0.0005 the mass of a proton.

Atoms contain the same number of electrons as protons. This means that the overall charge of an atom is zero- as charges cancel. Most atoms contain slightly more neutrons than protons.

Particle	Abbreviation	Relative charge	Relative mass
Proton	p+	1+	1
Neutron	n	0	1
Electron	e-	-1	$\frac{1}{1836}0.0005)$

**Atomic Numbers** show the number of protons and electrons in an element. These are then used to order the elements in the periodic table. For example, Li-2 or O-8.

Chemical reactions solely involve the electrons of an element. Therefore any changes in neutrons or protons do not have an effect on the speed or outcome of reactions. However, there may be slight differences in the **physical properties** of the element e,g, boiling point in Deuterium.

**The Mass number** is the number of protons + number of neutrons. An ion is a charged atom i.e. lost or gained electrons.

The Relative isotopic mass is the mass of an isotope compared to  $\frac{1}{12}th$  of a  $^{12}C$  atom.

The relative atomic mass is the weighted mean mass of an atom relative to  $\frac{1}{12}th$  the mass of a carbon-12 atom. The weighting takes into account percentage abundance and relative isotopic mass.

**To determine** percentage abundance and relative isotopic mass of an element, they are found experimentally using a mass spectrometer. You do not need to know how it works, but if you want, it's mentioned in the OCR A chemistry textbook.

$$m/z = \frac{RelativeMassOfIon}{RelativeCharge}$$

The relative isotopic mass is found on the x-axis and percentage abundance by the peak e.g. if there is 75.78% of CL-35 and 24.22% of Cl-37, you would do this:

$$Relative Atomic Mass = \frac{(75.78*35) + (24.22*37)}{100}$$

Where 75.78x35 is the contribution from Cl-35, 24.22x37 is the contribution from Cl-37 and 100 is the max percentage. Questions like to ask you to guess what the element is by its mass, so make sure you are confident in this skill.

For simple molecules , the term relative molecular mass will be used. For compounds with **giant** structures, the term relative formula mass will be used.

# 2.2 Compounds, formulae and equations 2.1.2

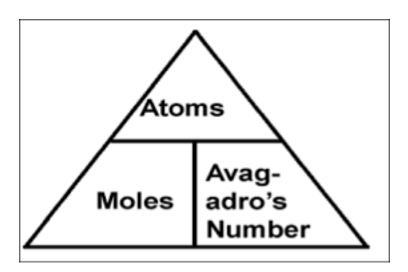
+1	1-	2-	3-
Ammonium	Hydroxide	Carbonate	Phosphate
$NH_4^+$	$OH^-$	$CO_3^2-$	$PO_4^3-$
N/A	Nitrate $NO_3^-$	$SO_4^{2-}$	N/A
N/A	Nitrite $NO_2^-$	Sulphite $SO_3^{2-}$	N/A
N/A	Hydrogencarbonate $HCO_{3}^{-}$	Dichromate(VI) $Cr_2O_7^{2-}$	N/A
N/A	$Manganate(VII)/$ permanganate $MnO_4^-$	N/A	N/A

## 2.3 Amount of substances 2.1.3

### 1. The mole

The amount of substance  $\,$ ,n, is used to count the number of particles in a substance- measured in moles. One mole contains  $6.02*10^{23}$  particles-known as **Avogadro's constant**.

**Molar mass**  $/M_r$  is the mass per mole which is why its units are  $gmol^{-1}$  e.g. carbon has a molar mass of 12, where 1 mole is 12 grams.



A mole of gas fills, in standard conditions (RTP), 24.0 dm3 of space. The number of moles is directly proportional to the space filled. You can find this information on the formula sheet under "Molar gas volume".

When the substance isn't under standard conditions the ideal gas equation is used, pV = nRT. They give us a number called the Gas constant-8.314 J/mol/K. This value is given on the formula sheet, however you have to know non-SI units and working it out takes longer than remembering this figure.

### 2. The determination of formulae

**Empirical Formula** is the simplest whole number ratio of atoms of each element present in a compound.

**Molecular formula** is the number and type of atoms of each element in a molecule e.g.  $H_2SO_4$ .

The determination of formula is a necessary part of this exam. They love questions along the lines of:

- 1. "Raheem has found that his substance has a composition by mass of 23.3
  - (a) Work out the empirical formula

It is assumed that the percentage composition of the element is equal to the mass of the element e.g. 23.3% is 23.3g. We also know the  $M_r$  of each element:

- Magnesium is  $24.3 \ qmol^{-1}$
- Oxygen is  $16 \ qmol^{-1}$
- Sulfur is  $32.1 \ gmol^{-1}$

Next, you find the moles by dividing the mass by the  $M_r$ . Therefore:  $\frac{23.3}{24.3} = 0.959$ ,  $\frac{30.7}{32.1} = 0.956$  and  $\frac{46.0}{16} = 2.875$ . Then you divide by

the smallest number of moles, giving the empirical formula. 0.959/0.956=1, 0.956/0.956=1 and 2.875/0.956=3. This makes the empirical formula:  $MgSO_3$ 

**In other cases** , they may ask you tork out the molecular formula using the empirical formula and the molecular mass given in the question. For example: "Fatima found that a substance had a percentage composition of 40.0

To minimise my working, I shall provide you with the empirical formula CH<sub>2</sub>O. You can try to work out how I did this using the method above.

In order to work out the molecular formula—you need a little algebra. As we know the Mr is 180 and the empirical formula is  $CH_2O$  - Mr 30,as we want to work out the number of each atom you would do:

$$180 = 30x$$

$$\Delta x = 6$$

**Finally,** you multiply the atoms present in the empirical formula by 6 from the above equation. This gives a molecular formula of  $C_6H_{12}O_6$ .

**Hydrated salts** are calculated in much the same way. They are expressed like this  $CuSO4 \cdot nH2O$  and you will be given some numbers to workout n. These are likely the mass of water and mass of anhydrous salt .

Heating a substance removes the H2O making it anhydrous. To Hydrate simply dissolve the salt in water and evaporate the water very slowly.(see pg.24 in book).

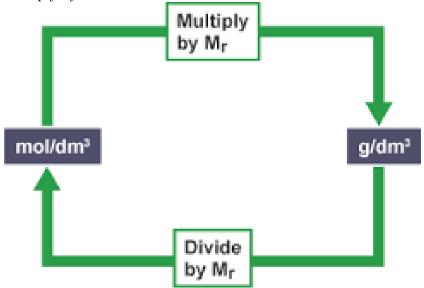
### How accurate is experimental formula?

You need to make an assumption that all water is lost . You can only see the surface of the crystals; the inside is unknown to us, so water could be found there. To reduce error, you should heat to a constant masswhen mass no longer changes when heated. rthis means you can be sure that it is anhydrous.

You also assume there is no further decomposition . Many salts decompose further when heated e.g.  $CuSO_4$  turns into black copper(III) oxide.

# 3. Calculation of reacting masses, gas volumes and mole concentrations

You need to know all the calculations using liquids, gases and solids to find moles. You also need to know how to convert between  $gdm^{-3}$  and  $moldm^{-3}$ . You just need to remember that when you convert from  $moldm^{-3}$  you just multiply by Mr.



You will also need to know how and when to use the ideal gas equation:

$$pV = nRT \tag{2.1}$$
 
$$p = \text{Pressure in Pa}$$
 
$$V = \text{Volume in } m^3$$
 
$$n = \text{moles}$$
 
$$R = \text{ideal gas constant}(8.314 \ Jmol^{-1}K^{-1} \ )$$
 
$$T = \text{temperature}(K)$$

With the ideal gas equation—you assume that: no intermolecular forces; sizes are negligible; random motion and elastic collisions. You will also need to remember how to convert between the units as questions sometimes try to trick you. These are listed here:

- $cm^3$  to  $m^3 = *10^{-6}$
- $dm^3$  to  $m^3 = *10^{-3}$
- °C to K = +273

- kPa to Pa =  $*10^3$
- 1 atm = 101 kPa = 101000 Pa

$$PercentageYield = \frac{ActualYield}{TheoreticalYield}$$
 (2.2)

$$AtomEconomy = \frac{\sum Mr(desired)prod}{\sum MrAllProd}$$
 (2.3)

Percentage yield doesn't really allow 100% in real life because: the reaction may not have fully taken place; side reactions occur and purification leads to loss in product. %age yield is in reference to the percentage of the theoretical yield that was actually yielded i.e. actual yield. Atom economy simply refers to the number of wasted atoms (atoms that form waist products).

### 2.4 Acids 2.1.4

The acids to remember are the following:

- HCl is Hydrogen Chloride
- H<sub>2</sub>SO<sub>4</sub> is Hydrogen Sulphate
- NOH<sub>3</sub> is Nitric Acid
- KOH is Potassium Hydroxide
- CH<sub>3</sub>COOH is Ethanoic Acid (although it is commonly called Acetic Acid).

Acids release H<sup>+</sup> ions when in aqueous solution. To examine the strength of an acid we must look at the dissociation of the H<sup>+</sup> ions. Take for example HCl. The dissociation of HCl in aqueous solution looks like this,

$$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$$

As you can see all of the hydrogen atoms have dissociated. This would make HCl a *strong acid*.

Where the H<sup>+</sup> ions only partially dissociate we call it a *weak acid*. Take Ethanoic acid, its dissociation in aqueous solution looks like this,

$$CH_3COOH(aq) \rightleftharpoons H^+(aq)CH_3OO^-(aq)$$

As we can see the H<sup>+</sup> ions haven't entirely dissociated. The  $\Longrightarrow$  implies that the reaction is incomplete and forms an equilibrium, so the acid hasn't completely dissociated.

There is a point to be made that not all ionic compounds with hydrogen atoms are acids. It is only those compounds that form H<sup>+</sup> ions when dissolved in aqueous solution that we call acids.

2.5. REDOX 2.1.5

The common bases are metal oxides, metal hydroxides, metal carbonates and ammonia, NH<sub>4</sub>. Bases neutralise an acid to form a salt.

An Alkali is a special type of base which, when dissolved in water, releases hydroxide ions. They are also known as soluble bases. For example take the base  $Mg(OH)_2$ ,

$$Mg(OH)_2(s) + aq \longrightarrow Mg^{2+}(aq) + 2OH-(aq)$$

We can see that  $Mg(OH)_2$  is an alkali as it releases  $OH^-$  ions when dissolved in aqueous solution.

The alkali and base to remember are the following:

- NaOH is Sodium Hydroxide
- KOH is Potassium Hydroxide
- NH<sub>3</sub> is Ammonia

You need to remember that:

- $H^+ + OH^- \longrightarrow H_2O$ ,
- $CO_3^{2-} + 2H^+ \longrightarrow H_2O + CO_2$
- and finally  $O^{2-} + 2H^+ \longrightarrow H_2O$ .

Using these ionic equations you should be able to form full equations.

**Titrations** are a technique to achieve a neutralisation reaction. We take an acid and a alkali and we slowly add one to the other using a burette.

The preparation of a standard solution simply involves dissolving a exact and known mass of ionic compound and dissolving it in a know volume of water. This is done in a volumetric flask.

### 2.5 Redox 2.1.5

**OIL RIG** is a fantastic acronym. Oxidation Is Loss, Reduction is gain. Remembering this is vital. If we describe a reaction as having *oxidised* X, we mean to say that X has lost electrons. If a reaction is described as having *reduced* X, we mean to say that X has gained electrons. It is important to remember **elements have an oxidation number 0.** 

To write a redox reaction we have equations like this:

$$\begin{array}{c} \text{OX: } -2\text{e}^{-} \\ 2 \text{ Na} + \overset{0}{\text{Cl}_{2}} \longrightarrow 2 \overset{\text{I}}{\text{Na}^{+}} + 2 \overset{-\text{I}}{\text{Cl}^{-}} \\ \text{RED: } +2\text{e}^{-} \end{array}$$

We use Roman numerals to indicate oxidation numbers, memorise the following oxidation numbers:

- Oxygen has the oxidation number -2 unless in peroxide, in which case it is -1
- Hydrogen has the oxidation number +1 unless in a metal hydride in which case it is -1
- Fluorine has the oxidation number -1

So to work out whether a chemical has been oxidised or reduced we do the following.

1. Find the balanced symbol equation,

$$2 \text{ Al} + 3 \text{ H}_2 \text{SO}_4 \longrightarrow \text{Al}_2 (\text{SO}_4)_3 + 6 \text{ H}_2$$

2. Then we fill in the oxidation numbers for the ones we know,

$$2 \text{ Al}^0 + 3 \text{ H}^{\text{II}}_2 \text{SO}^{-\text{II}}_4 \longrightarrow \text{Al}_2 (\text{SO}^{-\text{VI}}_4)_3 + 6 \text{ H}^0_2$$

3. The  $Al_2(SO)_3^{-VI}{}_4$  has no overall charge so the oxidation numbers must add to 0,

$$\mathrm{Al^{VI}_{2}(SO_{4})^{-VI}_{\phantom{-}3}}$$

- 4. Now we have  ${\rm Al^{VI}}_2$  we can see that  ${\rm Al^{III}}$ . So Aluminium went from Al to  ${\rm Al^{III}}$  meaning it has been oxidised in this reaction.
- 5. The hydrogen went from  ${\rm H^{II}}_2$  to  ${\rm H_2}.$  This is a reduction so we say hydrogen has been reduced.

It is important to note that when writing oxidation numbers down in exam questions, it only means for one atom of a molecule. In summary oxidation numbers refer to the number of electrons individual atoms in compounds have lost/gained. They are like charge but apply to atoms and not the overall compound. They are used to explain whether a reaction has oxidised an atom or reduced it.

### 2.6 Electron structure 2.2.1

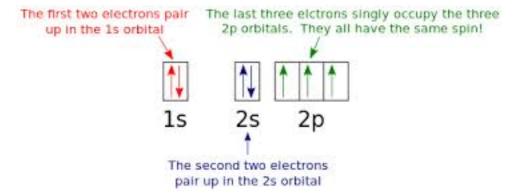
**Shells** are areas where there is a high probability of finding an electron. They are split by looking at major energy levels. The period an atom is in indicates how many shells it has. The number of electrons that can fit into a shell can be worked out by  $2n^2$  where n is the shell number.

**Shells are sub-divided** into sub-shells. The ones you need to know are as follows,

- s orbital which can hold 2 electrons, one in all shells
- p orbital which can hold 6 electrons, one in all but shell 1
- d orbital which can hold 10 electrons, one in all but shells 1 & 2

They fill in order.

**Orbitals** are regions around the nucleus which can hold up to two electrons with opposite spin. This diagram is of a P orbital and the arrows indicate the spin:



Order of fill is as follows,  $1s^22s^22p^63s^23p^64s^23d^{10}4p^6$  in the standard format  $xs^n$  The examination may well ask you to write the electron configuration of an atom. Unless otherwise instructed, a short cut is to use a noble gas as a base. For example if I said write the electron configuration of sodium you can say [Ne]3s<sup>1</sup>. You need to know how to do this for all elements up to and including Kr.

Energy levels are the reason different shells fill differently. As you probably know, lower energy levels need to fill before higher ones. This is why, for example, the s- subshell fills before the p- subshell. As we go up, the shells we also ascend in energy level. The most interesting part is the 4s sub-shell and the 3d sub-shell have very similar

energy levels. The 4s sub-shell is, however, slightly lower so the 4s fills first. When the 3d sub-shell fills the energy level falls meaning, the 4s fills before 3d and the 4s empties before 3d. This is important when looking at the electron configuration of D Block ions.

### 2.7 Bonding 2.2.2

**Ionic bonding** is the **strong electrostatic attraction** between anions and cations. It usually occurs when there is a **metal cation** and a **non-metal anion**.

The giant ionic lattice  $\,$  is the structure of ionic compounds. Each ion is surrounded by oppositely charged ions in a regular structure e.g, in NaCl , each Na $^+$  ion is surrounded by 6 Cl $^-$  ions and vice-versa.

**Ionic compounds have high melting and boiling points** because there needs to be high temperature in order to overcome the strong electrostatic forces between ions. The melting point is higher if the ionic charges are greater and the size of an ion is also a factor.

Ionic compounds usually dissolve in polar solvents such as water. Polar molecules attract and surround each ion in solution and break down the lattice e.g. NaCl dissolves in water. However, in ionic structure with large ionic charges, some polar solvents such as water may not be able to overcome the strong electrostatic attraction.

In a solid state, ionic structures don't conduct electricity because the ions are localised meaning there are no mobile charge carriers. In an aqueous state, however, the ions are free to move as mobile charge carriers allowing electricity to be conducted.

**Dot-and-cross diagrams** are the same as they have always been. Used for drawing the simplest of ionic bonds, that of metal - non-metal. Just remember: the square brackets; only the outer shell is drawn and that the charge is shown as superscript.

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In summary ionic compounds have these properties:

- Have high melting and boiling points
- Tend to dissolve in polar solvents
- Only conduct **electricity** when in **liquid** state or dissolved in aqueous solution.

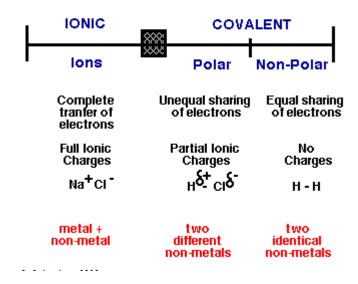
Covalent bonding is the strong electrostatic attraction between a shared pair of electrons and the nuclei of the bonded atoms. It occurs in:

- Non-metallic elements such as H<sub>2</sub> and O<sub>2</sub> form covalent bonds.
- $\bullet$  Non-metallic compounds such as  $H_2O$  and  $CO_2$  form covalent bonds.
- $\bullet$  Even polyatomic ions are covalently bonded such as NH<sub>4</sub><sup>+</sup>

It can also be thought of as an overlap of orbitals each containing one electron to give a shared pair of electrons. This is why when drawing a dot and cross diagram for this, you draw overlapping circles with electrons shared. These electrons are attracted to the nuclei of both the bonded atoms. The bonded atoms often have the same elec. config. as the nearest noble gas. There are the following three types of covalent bonding that you are expected to know about,

- 1. Single covalent bonding, this is where there is one shared pair of electrons per nuclei.
- 2. Multiple covalent bonding, this is where there are multiple pairs of shared electrons per nuclei e.g. double bond in  ${\rm CO}_2$
- 3. Dative covalent bonding, this is where the shared pair is supplied by only one of the atoms.

## Comparison of lonic, Polar, and Non-Polar Bonding

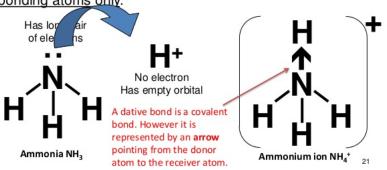


 $\mathrm{NH_4}^+$  is a good example of a dative covalent bond. A H<sup>+</sup> ion meets ammonia and ammonia provides the electron pair for the covalent bond. The dative covalent bond is shown by a  $\rightarrow$  to the hydrogen i.e.

# Forming covalent bonds

### **Dative bonds**

A special kind of covalent bond where **both electrons** used to form the covalent bond are donated by <u>one of the</u> bonding atoms <u>only</u>.



You will need to learn all of the types of covalent bonds. Using your GCSE or A-level textbook for any practice you require is very useful to master this skill.

**Average Bond Enthalpy** is simply a measure of the covalent bond strength, take a Br-Br **covalent** bond for example. <sup>1</sup> The larger the value of the average bond enthalpy, the stronger the covalent bond.

## 2.8 The shapes of simple molecules and ions 2.2.2

You need to know the shapes of, and bonding angles in, molecules and ions with up to six electron pairs (including lone pairs) surrounding the central atom as predicted by electron pair repulsion.

Electron pair repulsion is used for explaining and predicting shapes of covalently bonded molecules as well as the relative repulsive strengths of paired and unpaired electrons. It works on the principle that electron pairs repel to arrange themselves around an atom as far apart as possible. They do this in 3D, which may sound obvious, but so far in chemistry we have worked only with 2D models. To draw 3D diagrams we need to understand the following standards,

- A B is used for a bond in the same plane as the paper
- A ·······B is for bonds going into the plane of the paper

**Lone pair** repulsion is greater than that of bond pair. This is because the lone pair of electrons occupy more space than the bonded pair, overall resulting in a slightly higher repulsion from the lone pair. The bonding angle is, therefore, reduced by around 2.5° for every lone pair.

Common, and basic examples are molecules such as,  $CH_4$  which has a bonding angle of 109.5° and no lone pairs and forms a tetrahedral structure;  $NH_3$  which has a bonding angle of 107° with one lone pair and this is pyramidal; finally  $H_2O$  which is non-linear and with its two lone pairs has a bonding angle of 104.5°.

The last shapes to be familiar with are trigonal planar which have a bonding angle of 120°, linear which are 180° and octahedral which are 90°.

<sup>&</sup>lt;sup>1</sup>Note that you only need to understand the concept of avg. bond enthalpies; definitions for this are not required.

## 2.9 Electronegativity and bond polarity 2.2.2

**Electronegativity** is the ability of an atom to attract bonding electrons in a covalent bond.

The Pauling scale is a scale used to measure the *electronegativity* of an atom. As we go right, across the periodic table, the electronegativity increases alongside a decrease in atomic radius. As we move up the table we see an decrease in the number of shells, hence a decrease in atomic radius, so we see then another increase in electronegativity. So the nearer F in the table, the higher the electronegativity.

Covalent, Polar covalent and ionic bonds are defined as the difference in electronegativity of the bonding atoms. Where the difference is zero we call the bond covalent/non-polar covalent. Where the electronegativity difference is less than 1.8 (but greater than 0) we call it polar covalent and where it is greater than 1.8 we call it ionic.

**Polar bonds** are covalent bonds between two elements with **unequal** electronegativities.  $H^{\delta+} - Cl^{\delta-}$  is an example of a polar bond, and by extension a polar molecule. Hydrogen has a lower electronegativity than chlorine causing the chlorine in the covalent bond to become slightly negative. This type of bonding is called a permanent dipole.

Larger molecules are interesting because we need to look at structure to see if the overall molecule is polar or non-polar(due to dipoles cancelling each other out due to their direction). Take  $H_2O$ , this has a non-linear structure. Both the  $H^{\delta+} = O^{\delta-}$  bonds are polar and given its non-linear structure, these polar bonds don't cancel out. This makes  $H_2O$  a polar molecule because it has an overall **dipole- the separation of opposite charges**. It has a permanent dipole as the dipole doesn't change.

However, take  $CO_2$ , a similar covalent molecule with two  $C^{\delta+} = O^{\delta-}$  polar bonds. But this is where it changes. The structure is linear. This means that the two polar bonds cancel out

### 2.10 Intermolecular Forces 2.2.2

An important distinction from ionic or covalent bonding is that these are forces between different molecules rather than what holds a molecule together. Permanent dipole–dipole and induced dipole–dipole interactions can both be referred to as van der Waals' forces. This is important to know if your teacher isn't aware of this change to the syllabus.

Permanent dipole - dipole interactions are caused by polar molecules attracting each other and forming a permanent electrostatic interactions. This is quite similar to giant ionic lattices but occurs with polar covalent molecules such as water rather than ions. The distinction is that it is between separate molecules e.g. water molecules. See the example below:

$$H^{\delta+}$$
 $O_{1111111}H$ 
 $O_{\delta-}$ 
 $S+$ 
 $S+$ 
 $S+$ 

Generally permanent dipole interactions are conducive to a higher boiling point, given the **extra energy required to break the interaction.** 

**Hydrogen bonding** is a special type of permanent dipole-dipole interaction. More specifically, it is "intermolecular bonding between molecules containing N, O or F and the H atom of –NH, –OH or HF".

Hydrogen bonding has a significant influence on the properties of many molecules. Water, for example, is affected by hydrogen bonding. Hydrogen bonding allows for the formation of a more open lattice structure by holding the molecules further apart. The water molecules in ice are further apart than water. Therefore ice is less dense than liquid water and floats. The bond angle in hydrogen bonding is close to 180°, creating an open tetrahedral lattice full of holes. It also contributes to the high melting and boiling points of water.

London Forces are induced dipole-dipole interactions. Electrons move randomly, which may produce polarity in a molecule. This temporary polarity may allow the formation of an instantaneous dipole, which induces dipole on neighbouring molecules. This interaction occurs in every molecule causing attraction between them. This, on a micro scale, isn't a long lasting, however when we look on a macro scale with a massive number of molecules this has a large affect.

London forces strength is dependent on the number of electrons. Elements with large number of electrons have stronger London forces due to the greater probability of an interaction. So as we move down the periodic table we would expect a higher boiling point (where London forces are the primary interaction).

Simple molecular lattices are formed when a simple molecular substance  $^2$  are in their solid form. They are simply put "covalently bonded molecules attracted by weak intermolecular forces, e.g.  $I_2$ , in a simple molecular lattice structure". The molecules in simple molecular lattice are held together by repetitively weak intermolecular forces. The atoms within the molecules are held together by very strong covalent bonds.

**Solubility** of these different types of compounds follow this basic rule, in general: Polar compounds will be soluble in polar solvents and non-polar compounds will be soluble in non-polar solvents. It is important to note that most simple molecular lattices are non-polar, so are insoluble in polar solvents.

The reason for some polar molecular compounds being soluble in polar solvents is that the polar solvent attracts the polar compound. This attraction, in a similar way to ionic compounds, acts to pull apart the permanent dipole-dipole bonds and causing the compound to dissolve.

The reason for the non-polar compounds dissolving in non-polar solvents is much the same. The intermolecular interactions are the same so the solvent is able to break down the simple covalent lattice.

**Electrical conductivity** is nil for simple molecular structures. There are no mobile charged particles meaning that there will be no way for the substance to be conductive.

They have low melting and boiling points because they are held together by weak intermolecular forces. They are solidified by reducing the temperature low enough. When melting, the covalent bonds do not break.

 $<sup>^2\</sup>mathrm{A}$  simple molecular substance is one with a defined number of atoms and with defined molecular formula e.g.  $\mathrm{H}_2$ 

# Module 3

# Periodic table and energy

The focus of this module is inorganic and physical chemistry, the applications of energy use to everyday life and industrial processes, and current environmental concerns associated with sustainability.

## 3.1 The Periodic table 3.1.1

**Simply put** the periodic table lists the known elements in order of atomic number<sup>1</sup>

**Periodicity is** when periods show repeating trends in **physical and chemical** properties. This section focuses on periodicity of the following properties: elec.config., ionisation energy, structure and melting points.

In period 2 the highest orbital sub-shell filled are the 2s and 2p ones. In period 3, the highest are the 3s and 3p sub-shells. In period 4, the 3d subshell is filled as well as the 4s and 4p subshells only.<sup>2</sup>

**Groups, or vertical columns** , generally contain chemicals of similar properties. This is because they all have the same amount of electrons missing in the outer shell<sup>3</sup>. Periods or horizontal rows gives the number of the highest energy electron shell in an element's atoms

### Ionisation energies

First ionisation energy is the amount of energy required to remove one electron from each atom in one mole of gaseous substance. There

<sup>&</sup>lt;sup>1</sup>A number derived from the number of protons

<sup>&</sup>lt;sup>2</sup>Important to remember as it cuts down time in exam.

<sup>&</sup>lt;sup>3</sup>Sort of true for first three periods

are several things which affect first ionisation energy which I will now go into. e.g.  $Na_{(g)} \longrightarrow Na_{(g)}^+ + e^-$ 

The first ionisation energy generally increases as we go across the period and decreases as we go down the group in general. This is because as we move across the period the nuclear charge gets greater. This then affects the atomic radius, making it smaller. This means that the electrons on the outer shells are more attracted to the nucleus and so the first ionisation energy increases. (revert back to definition if you don't understand)..

### Factors affecting ionisation energies

- 1. Atomic radius- the greater the distance, the less attraction to the outer electron, decreasing ionisation energy.
- 2. Nuclear charge- if there are more protons and therefore electrons, the attraction between the nucleus and electrons is higher. This makes the atomic radius smaller, thus increasing first ionisation energy.
- **3. Electron shielding-** as electrons are -ve charged, the **inner electrons** repel outer electrons. This is called the **shielding effect**. It reduces the attraction between the nucleus and outer electrons, reducing first ionisation energy.

#### Successive ionisation energies

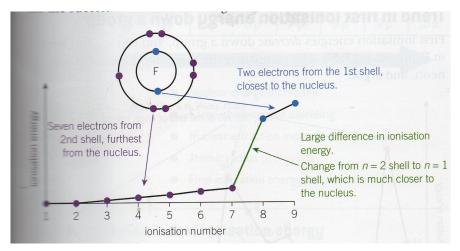
An element has as many ionisation energies as its number of electrons. This means that as you go down a group, there are more ionisation energies. For example helium has 2 electron, so:  $\operatorname{He}_{(g)} \longrightarrow \operatorname{He}^+_{(g)} + e^-$  and  $\operatorname{He}^+_{(g)} \longrightarrow \operatorname{He}^{2+}_{(g)} + e^-$ .

The second ionisation energy of helium—is much greater than than the first because there are two protons attracting two electrons. When an electron is removed, the single electron is more strongly attracted to the nucleus. This increases the ionisation energy.

The second ionisation energy is the amount of energy required to remove 1 electron from each atom in a +1 ion of a gaseous element to form 2+ ions.

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### Successive ionisation energies and shells

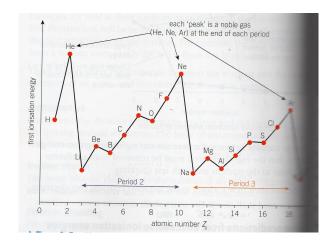


The large increase between the 7th and 8th ionisation energies can be explained by the 1s shell being reached, which has the strongest attraction to the nucleus. This means that more energy is needed to remove electrons in this subshell.

You can make predictions from the successive ionisation energies. These are the group of the element, the number of electrons in the outer shell and the identity of the element.

### Trends in ionisation energies

There is a general increase in ionisation energies across a period. However, there is a sharp decrease in first ionisation energy between the end of a period and the start of a new one(noble gases are peaks).



First ionisation energy decreases down all groups because the atomic radius increases and electron shielding increases. Although nuclear charge increases, these effects outweigh it.

**First ionisation energy increases across periods.** This is due to similar levels of electron shielding as they are in the same shell.Next, there is a greater nuclear charge, increasing nuclear attraction as the atomic radius is smaller. This means that it is harder to remove electrons form elements.

Electrons in the same p sub-orbital repel each other. This makes it easier to remove an electron, decreasing first ionisation energy e.g. with N and O.

### 3.2 Periodic trend in structure 3.1.1

Metallic bonding is the a "strong electrostatic attraction between fixed cations (positive ions) and a sea of delocalised electrons". This bonding is between metal atoms and forms giant metallic lattices.

Metals are able to conduct electricity because of the sea of delocalised electrons created each metal donating its electrons to a shared pool of electrons. Metals are almost always solid at room temperature, except for mercury. This is because **metallic bonding is very strong**, but dependent on how many electrons the elements lose i.e. how positive cations are, as well as well as other factors.

The melting point of metallic structures is dependant upon the strength of the electrostatic attraction between cations and electrons. Metals do not dissolve. This is even true with polar solvents as metals react rather than dissolving.

Giant covalent lattices are, unlike simple molecular lattices, atoms not molecules bonded by covalent bonds. This can make for some **incredibly strong compounds**. Carbon, boron and silicon are examples of atoms that can form giant covalent lattices. Carbon can form Diamond, graphite and graphene.

Other than graphite and graphene, giant covalent lattices will not conduct electricity. This is because the electrons are immobile. However graphite has a free electron per carbon atom. These electrons join a sea of delocalised electrons and can move between the layers in the carbon. These mobile charge carriers are what allow graphite and graphene to be conductive.

**Solubility** Both metals and giant covalent lattices are, on the whole insoluble. In the case of metals, they may well react when in polar solvents not dissolve. In the case of giant covalent lattices, the bonding is far too strong to be broken by solvents.

**Graphene** is the latest wonder allotrope of carbon. It consists of a single layer of graphite, composed of hexagonally linked carbon atoms. It has the same electrical conductivity of copper and is the thinnest, strongest element ever made. The reason for its electrical conductivity is that it has, like graphite, delocalised electrons- as it doesn't use all electrons for bonding. These act as mobile charge carriers.

There is potential for this to be used in micro-computing to replace silicone, this could serve to further decrease the size and cost of computer processors.

**Melting points** for giant metallic/covalent structures are very high. This means the following (for periods 2 and 3):

- As we move from groups 1 to 14 we see a rise in melting temperatures as these elements form *giant structures*.
- A sharp drop is seen at group 14 to 15. This is because group 15-18 elements don't form giant structures.
- Group 15 to 18 are comparatively low. This is because are *simple molecular structures*.

# 3.3 Group 2 -3.1.2

**S sub-shell** Is filled in all the group two elements. This means that they contain two more electrons than the Nobel gas before it. Note that redox reaction are the most common ones involving Group 2 elements. In redox reactions these substances loose two electrons and from 2+ ions. The next part is just revisiting redox and so I will just summarise. You should know how group two elements from Mg $\rightarrow$ Ba react with water, oxygen and weak acids. Just know that group 2 elements are oxidised by +2.

**Reactivity** increases as we go down the group because the group two elements in a reaction lose electrons. So as we learned before, as we move down the group the first (and in this case second) ionisation energies decrease due to greater shielding<sup>4</sup> and a greater atomic radius, reducing nuclear attraction. e.g.  $\text{CaO}_{(\text{s})} + \text{H2O}_{-}(l) \longrightarrow Ca^{2+}_{-}(aq) + 2OH_{(\text{aq})}^{-}$ 

<sup>&</sup>lt;sup>4</sup>Shielding is where electrons from other shells repel electrons in the outer shells.

Note that alkalinity increases if you shake Group 2 metals in water, going down the group. This is because the solubility of OH<sup>-</sup> ions increases as you go down the group. Also, Ca(OH)2 is used in agriculture to neutralise acid soils and Mg(OH)2 and CaCO3 are used as 'antacids' in treating indigestion.

## 3.4 The halogens 3.1.3

Boiling trends in halogens are caused because of there existence as diatomic molecules. The boiling point increases down the group because of the stronger London forces (caused by more electrons to allow extra random motion causing induced dipoles).

**Redox again** is found here. Much the same as all the others but this time they are oxidising agents. This is because they need only gain one electron to have the electron configuration of a noble gas. They form anions.

**Displacement reactions** occur when a significantly **more reactive chemical** is reacted with a compound containing a similar, but less reactive, compound. Using displacement reactions we can see that reactivity decreases down the group.

Halogen-halide displacement The reactions are as follows,

- a chloride solution will not be displaced by bromine or iodine. This is because chlorine is the most reactive.
- a bromide solution will react when chlorine is added. It will turn orange as the Br<sup>-</sup> ions are displaced and so from Br<sub>2</sub>,

 $Cl_2(aq) + 2 Br^-(aq) \longrightarrow 2 Cl^-(aq) + Br_2(aq)$  However given that iodine is less reactive still there will be no reaction between  $I_2$  and bromide.

• As the least reactive iodide solution will be displaced by both chlorine and bromine to form a brown solution,

$$\operatorname{Cl}_2(\operatorname{aq}) + 2\operatorname{I}^-(\operatorname{aq}) \longrightarrow 2\operatorname{Cl}^-(\operatorname{aq}) + \operatorname{I}_2(\operatorname{aq})$$
  
 $\operatorname{Br}_2(\operatorname{aq}) + 2\operatorname{I}^-(\operatorname{aq}) \longrightarrow 2\operatorname{Br}^-(\operatorname{aq}) + \operatorname{I}_2(\operatorname{aq})$ 

To tell apart the similar brown and orange we can add a non-polar solvent like cyclohexane to dissolve the halogen. When  $I_2$  is dissolved we can see the cyclohexane layer go a deep violet.

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The reason for decreasing reactivity is that it is the opposite to group two. To gain an electron we need more attraction. As such more shielding and a grater atomic radius just cause less attraction to the electron and make it less reactive.

**Disproportionation** is what we call a reaction when the same element undergoes reduction and oxidation. This is illustrated by the following,

- The treatment of water with chlorine
   Cl<sup>0</sup><sub>2</sub>(aq) + H<sub>2</sub>O(l) → HCl<sup>I</sup>O(aq) + HCl<sup>-I</sup>(aq)
   As we can see, Chlorine has been both oxidised and reduced.
- The reaction of chlorine with cold, dilute aqueous sodium hydroxide,  $Cl^{0}_{2}(aq) + 2 NaOH(aq) \longrightarrow NaCl^{I}O(aq) + NaCl^{-I}(aq) + H_{2}O(l)$

Water treatment using chlorine is extremely useful. This is because chlorine kills bacteria. However, there are some hazards in using chlorine. Toxic chlorine gas and the risk of forming carcinogenic chlorinated hydrocarbons (when reacting with plant matter) and chloride ions can damage human tissue i.e. cancer.

The Halide tests are reactions used to test for halide ions in aqueous solution. This is done by adding aqueous silver ions (by using  $AgNO_3$ ). The ionic equation is as follows (where X is any halide ion),

$$Ag^{+}(aq) + X^{-}(aq) \longrightarrow AgX(s)$$

As we can see, this reaction creates a precipitate. Now we can derive the precise halide ion by looking at the colour of the precipitate. Chlorine will form a white precipitate, Bromine a cream and iodine yellow.

Adding dilute aqueous ammonia will dissolve the precipitate AgCl, and by adding concentrated aqueous ammonia we dissolve both AgCl and AgBr.

### 3.5 More tests 3.1.4

Three tests you need to know for this section. They need to be done in the following order,

- 1. Carbonate  $(CO_3^{2-}(aq))$  test
- 2. Sulfate  $(SO_4^{2-}(aq))$  test
- 3. halide (Cl<sup>-</sup>(aq),Br<sup>-</sup>(aq) and I<sup>-</sup>(aq)) test

Carbonate ions are tested by adding a dilute acid. It is by the following ionic equations,

$$CO_3^{2-}(aq) + 2H^+(aq) \longrightarrow H_2O(l) + CO_2(g)$$

As you can see  $CO_2$  is formed, which is gaseous. So if a  $CO_3^-(aq)$  ion is present we will see effervescence when we add it. We will see why we need to do this first. (remember to use an acid which will not interfere in the other two tests like NHO<sub>3</sub>.

Sulphate ions are tested for by adding  $Ba^{2+}(aq)$ . This is now by the following equations,

$$Ba^{2+}(aq) + SO_4^{2-} \longrightarrow BaSO_4(s)$$

We see a white precipitate form (BaSO<sub>4</sub>(s)). However this needs to be done after the carbonate test because  $\mathrm{Ba^{2+}}$  ions will form  $\mathrm{BaCO_3(s)}$ , which is also a white precipitate.

The halide tests are mentioned above.

Testing for ammonium ions is simple. Just react with warm aqueous NaOH,

$$OH^{-}(aq) + NH_4^{+}(aq) \longrightarrow NH_3(g) + H_2O(l)$$

So by adding NaOH we will see the solution effervesce if the  $NH_4^+$  ions.

### Why is there a correct order?

- 1. Carbonate test- because when you add dilute acid, you are looking for effervescence. None of the other ions bubble when dilute acids are added to them, so it's OK to do it first.
- 2. Sulphate test- when you add a solution containing  $Ba^{2+}$ , you are hoping for a white precipitate of  $BaSO_4$ .

 $\mathbf{BaCO}_3$  is white and insoluble in water, therefore, if you perform a sulphate test on a carbonate, yyou will still get a white precipitate, giving false results.

**3.** Halide test- when you add Ag<sup>+</sup> in AgNO<sub>3</sub>, you are looking for a precipitate(yellow,cream or white).

Silver carbonate, Ag<sub>2</sub>CO<sub>3</sub>, and Silver sulphate, Ag<sub>2</sub>SO<sub>4</sub> are both insoluble in water, forming precipitates. This means you will get inaccurate results.

#### What about a mixture of ions

- Carbonate test- add dilute HNO3 until effervescence stops if there is any, This makes sure there are no  $CO_3^{2-}$  ions to react in the next test. (H2SO4 has sulphate ions and HCl has chloride ions)
- Sulphate test- add excess Ba(NO3)2 forming precipitate. Filter out the precipitate. Chloride ions would show up if BaX (halide) used.
- Add AgNO3, therefore precipitate should form if previous steps done correctly. Add NH<sub>3</sub> to confirm what precipitate.

### Test for cations

## Test for ammonium NH<sub>4</sub><sup>+</sup>

Aqueous ammonium ions and OH- ions(aq) react to form  $NH_3gas$  when heated together. The equation is:

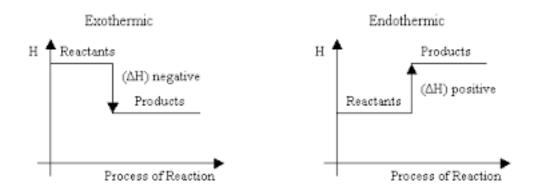
$$Nh_{4 (aq)}^{+} + OH_{(aq)}^{-} \longrightarrow NH_{3(g)} + H_{2}O_{(l)}$$
 (3.1)

- 1.  $NaOH_{(aq)}$  added to solution containing ammonium ion
- 2. Ammonia gas produced- no bubbles as ammonia very soluble in water.
- 3. Mixture warmed and ammonia gas released.
- 4. You can smell the ammonia, but use moist **pH indicator paper** turns blue.

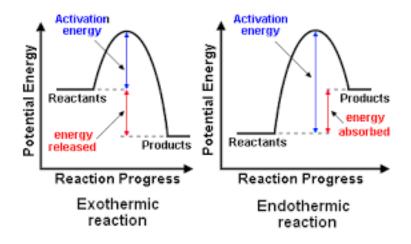
## 3.6 Enthalpy 3.2.1

Exothermic reactions are when energy/heat is transferred to the surroundings from the system. Enthalpy change( $\Delta H$ ) is negative because :  $\Delta H = H(\mathbf{products}) - H(\mathbf{reactants})$ .

**Endothermic reaction are when** energy is transferred from the surroundings into the system. The temperature of the surroundings decreases.



The minimum energy to break bonds in order to begin a reaction is the Activation Energy( $E_a$ ).



These are the standard conditions needed for physical measurements such as enthalpy changes:

• Std. pressure: 100 kPa

• Std. temp: 298K/25°C

• Std. states: state that the chemical is in under these conditions.

formation, neutralisation, combustion

The enthalpy change of formation is the enthalpy change that takes place when 1 mole of a compound is formed from its elements in their standard states, under standard conditions.

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The enthalpy change of combustion is when 1 mole of a fuel fully reacts with oxygen to form CO2 and H2O under standard conditions with all reactants and products in std. states.

The enthalpy change of neutralisation is when 1 mole of water is formed from the reaction of an acid and an alkali under standard conditions with all reactants and products in their standard states.

• :Mg<sub>(s)</sub> + 
$$\frac{1}{2}$$
 O2<sup>·</sup>(g)  $\longrightarrow$  MgO<sub>(s)</sub> :formation

• 
$$C_4H_{10(g)} + \frac{13}{2}O_{2(g)} \longrightarrow 4CO_{2(g)} + {}_5H_2O(l)$$
: combustion

• 
$$H_{(aq)}^+ + OH_{(aq)}^- \longrightarrow H_2O_{(l)}$$
: ionic for neut.

• 
$$HCl_{(aq)} + NaOH_{(aq)} \longrightarrow H_2O_{(l)} + NaCl(aq)$$

### Bond enthalpies

### Average bond enthalpies

Average bond enthalpy is the amount of energy required to break one mole of a specified type of bond in a gaseous molecule. They are always endothermic- therefore values are +ve, but enthalpy of reaction can be -ve.

Bond breaking is endothermic, bond forming is exothermic. The difference between the two determines if a reaction is exo/endothermic i.e. in an exothermic reaction, there would be more bond forming than bond breaking.

$$\Delta_r H = \Sigma(bond - enthalpies - reactants) - \Sigma(bond - enthalpies - products)$$
(3.2)

### Worked example: Combustion of propane

Using average bond enthalpies, calculate  $\Delta_r H$  for the reaction of propane with oxygen.

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$$

**Table 2**  $\Delta_{\mathbf{r}}$ H calculation for the reaction of propane with oxygen

Equation	$C_3H_8(g)$ +	$5O_2(g) \rightarrow 3C$	$O_2(g)$ + $4H_2O(g)$
Bonds	H H H H H H H H H H H H H H H H H H H	0=0 0=0 0=0 → 0=	=C=O + HO H =C=O + HO H H O H
Bonds broken	8(C—H) 2(C—C)	5(O=O) 6(0	C=O) 8(O-H)
	8 × 413 2 × 347	5 × 498 6 :	× 805 8 × 464
Energy / kJ mol <sup>-1</sup>	(3304 + 694 +	2490) - (4	4830 + 3712)
KJ IIIOI	6488		8542
$\Delta_{r}H$		-2054 kJ mol <sup>-1</sup>	

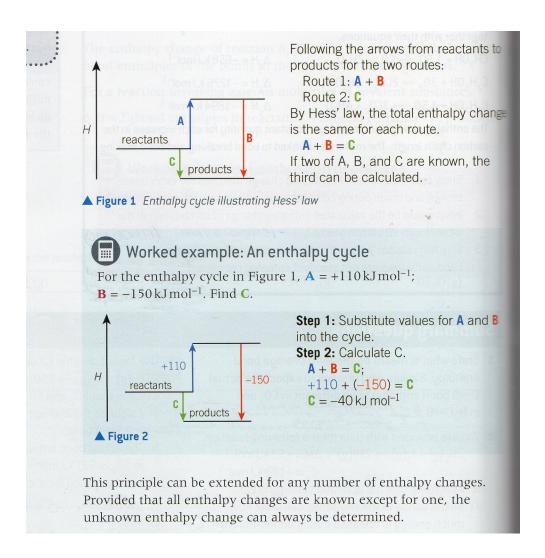
### Limitations

As you are using average bond enthalpies, the actual energy involved in breaking and making individual bonds would be slightly different (the bonds may be in different environments).

### Hess' law and enthalpy cycles

Hess' law allows enthalpy changes to be found indirectly. It states that if a reaction can take place by 2 routes, and start and end conditions are the same, the enthalpy. It comes from the idea of conservation of energy.

You need to remember for enthalpy change of formation A+B=C and for enthalpy change of combustion, C+A=B., where A is from reactant to product, B is elements to reactants and C is elements to product.



#### 3.7 Rates of Reaction 3.2.2

Collision theory hasn't changed at all from GCSE. Sill we look at the microscopic consequences of pressure, concentration and temperature (kinetic energy) on individual molecules. Successful collisions are needed which is when the reactive atoms in a molecule collide.

Catalysts are substances that, when added to a chemical reaction, serve to increase the rate of reaction without reacting itself.

This effect is achieved by the catalyst decreasing the required activation energy, thus providing a faster pathway for the reaction to take place.

**Homogeneous catalysts** refers to a catalyst that is in the same state as the reactants. This works by forming intermediate products.

**Heterogeneous catalysts** are catalysts which differ in state from the reactants. These act by a series of absorption and desorption.

Catalysts have massive importance in industry. They are used to reduce the amount of energy (in heat and pressure) in industrial reactions. This then reduces the amount of fossil fuels needing to be burnt, thus reducing CO<sub>2</sub>.

**Measuring** rates of reaction can be done in many ways. This can involve measuring gas or mass over time.

**The Boltzmann distribution** is a frequency distribution used to predict the energy of molecules. The area under the curve represents the number of molecules with a given energy. The curve changes when the temperature rises (skews negativity).  $E_a$  moves to the left when a catalyst is added.

# 3.8 Chemical equilibrium 3.2.3

A dynamic equilibrium exists in a closed system when the rate of the forward reaction is equal to the rate of the reverse reaction and the concentrations of reactants and products do not change.

le Chatelier's principle states that "When any system at equilibrium is subjected to change in concentration, temperature, volume, or pressure, then the system readjusts itself to (partially) counteract the effect of the applied change and a new equilibrium is established."

Remember that catalysts do not affect the position of equilibrium as they only affect the activation energy, and the reaction goes both ways so this cancels out.

Investigating equilibrium with concentration is done by the following,

$$2 \operatorname{CrO}_4^{2-}(aq) + 2 \operatorname{H}^+(aq) \Longrightarrow \operatorname{Cr}_2 \operatorname{O}_7^{2-}(aq) + \operatorname{H}_2 \operatorname{O}(l)$$

This reaction is sensitive to the acid concentration. Adding acid concentration will shift the point of equilibrium to the 'right'. We can see this because  ${\rm CrO_4^{\,2^-}(aq)}$  solution is yellow and  ${\rm Cr_2O_7^{\,2^-}(aq)}$  solution is yellow. So by raising the concentration of the acid we see the solution got from yellow to orange. Procedure is as follows:

1. Add a solution of yellow potassium chromate to a beaker

- 2. Add dilute sulfuric acid drop by drop until there is no further change in colour (orange).
- 3. Add aqueous sodium hydroxide until there is no further change in colour (yellow).

You have now witnessed equilibrium in action.

Investigating equilibrium with temperature is done by the following,

$$[\mathrm{Co}(\mathrm{H_2O})_6]^{2+}(\mathrm{aq}) + 4\,\mathrm{Cl^-(aq)} \, \Longrightarrow \, \mathrm{CoCl_4^{\,2-}(aq)} + 6\,\mathrm{H_2O(l)}$$

As temperature increases the reaction shifts right (in the endothermic direction) and vice-versa. This reaction can be done by the following steps,

- 1. Dissolve cobalt chloride in a boiling tube. Add a small quantity of hydrochloric acid. Then put the solution in ice to cool it until it turns pink (because  $[Co(H_2O)_6]^{2+}$ (aq) solution is pink).
- 2. Set up a boiling water bath and transfer the boiling tube. Wait until it turns blue (because  $\text{CoCL}_4^{2-}$  is blue).
- 3. Transfer back to ice water and observe the change back to pink.

And you have now witnessed a shift in equilibrium.

# 3.9 The equilibrium constant, $K_c$ 3.2.3

**Equilibrium constant** is calculated by,

In the reaction 
$$aA + bB \implies cC + dD$$

$$K_c = \frac{[\mathbf{C}]^c[\mathbf{D}]^d}{[\mathbf{A}]^a[\mathbf{B}]^b} \tag{3.3}$$

This requires a little explaining, The A, B, C and D values are the *equilibrium* concentrations of the reactants (in mol dm<sup>-3</sup>).

Where  $K_c = 1$  it indicates that the reaction is halfway between reactants and products.

Where  $K_c > 1$  it indicates that the position of equilibrium is shifted to the right (the products).

Where  $K_c < 1$  it indicates that the position of equilibrium is shifted to the left (the reactants).

# Module 4

# Core organic chemistry

This module introduces organic chemistry and its important applications to everyday life, including current environmental concerns associated with sustainability.

## 4.1 The basics 4.1.1

**IUPAC rules** on the nomenclature of organic compounds is as follows,

Firstly let me explain the parts of the name. Stem, prefix and suffix. The stem refers to the number of carbon atoms in the longest chain (just remember Monkeys Eat Peanut Butter + Greek); the prefix is in reference to a side chain (or a functional group); the suffix is added to indicate functional groups.

We have three types of hydrocarbons, aliphatic, acyclic and aromatic. We will mostly focus on aliphatic hydrocarbons of which there are three homologous<sup>1</sup> series alkanes, alkenes and alkynes.

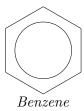
Aliphatic hydrocarbons are one which are joined in chains e.g,

 $<sup>^{1}</sup>$ A group of chemicals with the same functional group, differing by an addition of CH<sub>2</sub>

Alicyclic hydrocarbons join in cyclic shapes and look like this,



**Aromatic** hydrocarbons have benzene rings which contain all or some of the carbon atoms,



Functional groups (prefixes) are as follows,

Functional group	Prefix	Suffix	Displayed
carboxylic acids	none	-oic acid	OH OH
aldehydes	none	-al	—С
ketones	none	-one	C—————————————————————————————————————
alchols	hydroxy-	-ol	—-ОН
amines	amino-	-amine	
ethers	alkoxy-	-ether	
fluorine	fluoro-	none	
chlorine	chloro-	none	
bromine	bromo-	none	
iodine	iodo-	none	

I included a few more, I should imagine you only need the first 3 and the haloalkane ones (given that they are the ones in the textbook).

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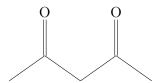
**Displaying formula** There are three ways to display chemical formula (for the exam). These being the following,

General formula is the simplest algebraic formula of a member of a homologous series. For example, for an alkane  $C_nH_{2n+2}$ .

Structural formula is the minimal detail that shows the arrangement of atoms in a molecule. We write out each alkile group<sup>2</sup> and there surrounding atoms. E.g. for 2,4-pentandione we have CH<sub>3</sub>COCH<sub>2</sub>COCH<sub>3</sub>.

Displayed formula is where the full molecule is drawn so in the case of 2,4-pentandione,

Skeletal formula is the simplified organic formula, shown by removing hydrogen atoms from alkyl chains, leaving just a carbon skeleton and associated functional groups. So in the case of 2,4-pentandione,



**Definition** time (and summary, straight from the horse's mouth),

- homologous series (a series of organic compounds having the same functional group but with each successive member differing by CH<sub>2</sub>)
- functional group (a group of atoms responsible for the characteristic reactions of a compound)
- alkyl group (of formula  $C_nH_{2n+1}$ )
- aliphatic (a compound containing carbon and hydrogen joined together in straight chains, branched chains or non-aromatic rings)
- alicyclic (an aliphatic compound arranged in non-aromatic rings with or without side chains)
- aromatic (a compound containing a benzene ring)
- saturated (single carbon–carbon bonds only) and unsaturated (the presence of multiple carbon–carbon bonds, including C=C, C/C and aromatic rings)

 $<sup>^{2}\</sup>mathrm{C}$  atoms in the main chain

**Structural isomers** are compounds with the same molecular formula but different structural formulae. Take, for  $C_4H_{10}$ . Sound simple,



But now imagine a possible combination that could share the same molecular formula,



This is called a structural isomer. Both 2-methylpropane and butane are  $C_4H_{10}$ . This is where structural formula and skeletal diagrams come in handy.

#### 4.2 Reaction Mechanisms 4.1.1

**Homolytic fission** is where a covalent bond breaks and the electrons are shared evenly with each bonding atom receiving one electron from the bonded pair, forming two radicals.

**Heterolytic fission** is where a covalent bond breaks and the electrons are not shared evenly with one bonding atom receiving both electrons from the bonded pair.

**Radicals** are a species with an unpaired electron. We use a dot to show this, e.g.  $H_3C-CH_3 \longrightarrow H_3C \bullet + CH_3 \bullet$ . This being homolytic fission as each bonded atom receives one electron.

**Curly arrows** are used to describe the movement of an electron pair. They show either heterolytic fission or the formation of a covalent bond.

**Reaction mechanism diagrams** are used to show reaction mechanisms. They need to be sufficiently detailed, to show clearly the movements of an electron pair, with curly arrows and relevant dipoles.

#### 4.3 Alkanes 4.1.2

**Alkanes** are saturated hydrocarbons containing single C–C and C–H bonds as  $\sigma$ -bonds (overlap of orbitals directly between the bonding atoms); free rotation of the  $\sigma$ -bond.

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**A**  $\sigma$ -bond is the result of two overlapping orbital in. It is a single covalent bond.

The bond angle formed when a carbon atom has 4  $\sigma$ -bonds is 109.5°.

**Trends in boiling points** are also obvious. The larger the molecule the more London forces there are at play. This means that the larger the molecule the more energy is needed to break the intermolecular forces and hence boiling the alkane. We also see the boiling point lower if the molecules branch. This is due to less surface area.

**Reactivity** of alkanes is low. This is because of the relative stability<sup>3</sup> and very low polarity of the  $\sigma$ -bonds.

The combustion of alkanes is seen everywhere. This is because fossil fuels like methane are alkanes. The longer the chain the more energy released per mole. The combustion reaction is as standard producing  $CO_2$  and  $H_2O$ .

Alkanes and halogens can react in the presence of UV radiation,

$$CH_4(g) + Br_2(l) \xrightarrow{UV} CH_3Br(g) + HBr(g)$$

However you need to know the mechanism of this reaction. It is as follows:

- 1. First the bond in the bromine molecule is broken up by homolytic fission Br-Br  $\xrightarrow{UV}$  Br• + •Br
- 2. Next we have the propagation steps. This forms a chain reaction,

a) 
$$CH_4 + Br \bullet \longrightarrow \bullet + HBr$$

b) 
$$\bullet CH_3 + Br_2 \longrightarrow CH_3Br + Br \bullet$$

3. Finally there is the termination, in which the two radicals collide forming a molicule with all the electron pairs. There are a number of ways this could happen.

• 
$$\operatorname{Br} \bullet + \bullet \operatorname{Br} \longrightarrow \operatorname{Br}_2$$

• 
$$\bullet CH_3 + \bullet CH_3 \longrightarrow C_2H_6$$

• •
$$CH_3 + •Br \longrightarrow CH_3Br$$

<sup>&</sup>lt;sup>3</sup>High bond enthalpy

#### 4.4 Basics in Alkenes 4.1.3

**Alkenes** are unsaturated hydrocarbons containing a C=C bond comprising a  $\pi$ -bond (sideways overlap of adjacent p-orbitals above and below the bonding C atoms) and a  $\sigma$ -bond (overlap of orbitals directly between the bonding atoms). The  $\pi$  bonds prevent the C=C bond from rotating freely. I will explain later.

The structure is trigonal planar with the bonding angle around each C=C alkenes is 120°.

**Stereoisomers** are compounds with the same structural formula but with a different arrangement in space. We look at E/Z isomerism. This is when we see stereoisomers are formed due to a restriction of rotation around the C=C group.

**cis—trans isomerism** special case of E/Z isomerism in which two of the substituent groups attached to each carbon atom of the C=C group are the same.

Cahn–Ingold–Prelog (CIP) priority rules are used to strictly define EZ isomers. It is based on 'priority' of the atoms bonded to the C=Cs. The 'priority' is down to the relative height of atomic number.

$$CH_3$$
  $H$   $CH_3$ 

Will be an E isomer because C has a higher atomic number than H.

$$C \longrightarrow C$$
 $CH_3$ 
 $CH_3$ 

And be a Z isomer.

## 4.5 Reactions of Alkenes 4.1.3

The  $\pi$ -bond has a low bond enthalpy. This makes alkenes far more reactive than alkanes because it is so easy to break the  $\pi$ -bond.

Addition reactions are reactions in which add atoms to an alkene by breaking the double bond. Here are the reactions (remember them),

- $\bullet$   $\mathrm{CH_{2n}+H_{2}} \xrightarrow{\mathrm{Ni}}$   $\mathrm{CH_{2n+2}}$  is called hydrogenation reactions.
- $CH_{2n} + X_2 \longrightarrow CH_{2n}X_2$  where X is a halogen. This is a common test for unsaturated hydrocarbons. We add a halogen like bromine and if the solution goes clear it is saturated and a dihaloalkanes has been formed
- $CH_{2n} + HX \longrightarrow CH_{2n+1}X$  where X is a halogen. This reaction forms haloalkanes.
- $CH_{2n} + H_2O(g)CH_{2n}OH$  is called a hydration reactions. We need an acid catalyst and it forms alcohols.

Markownikoff's rule is used to predict the formation of a major organic predict in addition reactions of H-X to unsymmetrical alkenes, e.g H-Br to propene.

To do this we look at the number of hydrogen atoms attached to the carbon atom. The more positive ( $H^{\delta+}$  will be attracted to the carbon on the side of the double bond with the most hydrogen. For example,

$$\begin{array}{c|c} H & H & H \\ \hline & & & \\ \hline & & & \\ \hline & & & \\ H & & & \\ \hline & & & \\ H & & & \\ H & & & \\ \hline & & & \\ H & & & \\ H & & \\ \hline & & \\ H & & \\ & & \\ H & & \\ & & \\ C & & \\ C & & \\ & & \\ H & & \\ H & & \\ \end{array}$$

Η

Η

 $\oplus$ 

When drawing in exams use curly arrows

**Polymerisation** remains the same. This time you need to know how to determine n from the number of monomers. Just rearrange the question into the following and it is easy,

$$\mathbf{C} = \mathbf{C}$$

**Environmental impact** of waste polymers is a serious issue. To deal with waste polymers we can do the following,

- 1. We can use burn waste polymers for energy production.
- 2. We can use 'Feedstock recycling' to reclaim monomers, gases or oil from waste polymers.
- 3. We can simply sort and recycle polymers to be used again.

The concern when burning polymers are the toxic gasses that are produced. An example of this id the combustion of halogenated plastics forming HCl. HCl is toxic so needs to be removed.

Biodegradable polymers are ones which can be broken down by microorganisms into water and  $CO_2$ . These polymers are usually made from starch or cellulose and the advantages to using them are obvious. When burred in a hole (a landfill) they will be less dangerous and degrade quickly. This will help save the environment.

**Photodegradable polymers** are much the same. Except this time it is light that we use to break down the polymer. These are oil-based polymers which contain bonds that weaken when they absorb light. This kick-starts the degradation. Alternatively light absorbing additives can be used.

#### 4.6 Alcohols 4.2.1

**Alcohols** have the functional group -OH (or hydroxyl group). They are, overall, polar due to the difference in electro-negativity of the O-H bond, however, the rest of the molecule isn't polar.

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The Intermolecular forces acting on alcohols are as follows,

The hydrogen bond between the O-H groups in the alcohol. There will be week London forces on acting upon the rest of the structure.

This means that alcohols have a lower boiling point than alkanes with the same number of carbon atoms, because the energy needed to break the hydrogen bond in the alcohol is greater that the London forces in alkanes.

**Solubility in water** is high in alcohols. This is because it used hydrogen bonds, like in water.

**Classification** into primary, secondary and tertiary is simple. Just follow these rules,

Primary alcohols are attached to a carbon atom which is then attached to two hydrogen atoms and one alkyle group (with methanol being the only exception as it is still a primary alcohol

ethanol is a primary alcohol

Secondary alcohols are ones witch are attached to a carbon atom attached to only one hydrogen atom and two alkyle groups.

butan-2-ol is a secondary alcohol

Tertiary alcohols are ones which are attached to a carbon atom attached to no hydrogen atoms and three alkyle groups.

$$H - CH_3 H$$
 $H - C - C - C - H$ 
 $H - OH H$ 

2-methylpropan-2-ol is a tertiary alcohol

**Combustion of alcohols** is about as simple as it gets. Here is an example equation  $C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$ . The products are water and  $CO_2$ .

The Oxidation of primary alcohols is as follows,

- We take Potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) acidified with sulphuric acid and use it as an oxidising agent for our primary alcohol.
- To produce a aldehyde we do the following (O is the oxidising agent),  $C_nH_{2n+1}OH + [O] C_nH_{2n}O + H_2O$
- To produce a carboxylic acid we do the same just under reflux,  $C_nH_{2n+1}OH + 2[O] C_nH_{2n-1}OOH + H_2O$

The oxidation of secondary alcohols to form ketones uses the same oxidation agent. The equation is,

$$C_nH_{2n+1}OH + [O] C_nH_{2n}O + H_2O$$

**Tertiary alcohols** do not undergo oxidation. The acidified dichromate remains orange when added.

**Dehydration of alcohols** can be done in the presence of an acid catalyst is heated under reflux. It looks like this,

$$C_nH_{2n+1}OH C_nH_{2n} + H_2O$$

Substitution with halide ions is done in the presence of an acid and sodium halide (e.g. NaBr/H<sub>2</sub>SO<sub>4</sub>) (heated under reflux). It is done by the following,

$$NaBr(s) + H_2SO_4(aq) \longrightarrow NaHSO_4(aq) + HBr(aq)$$
  
 $Then$   
 $C_nH_{2n+1}OH + HBr \longrightarrow C_nH_{2n+1}Br + H_2SO_4$ 

## 4.7 Haloalkanes 4.2.2

**Hydrolysis** is a chemical reaction in which the OH<sup>-</sup> ion causes a bond in a molicule to break. In the context of this section, haloalkanes, the OH<sup>-</sup> ion will have broken down the C-X bond (where x is the relevent halogen). An example of this would be as follows,

$$\begin{array}{c|c} CH_3 & CH_3 \\ \hline \\ H & -C & Cl + OH^- \longrightarrow H & -C & -OH + Cl^- \\ \hline \\ H & H & H \end{array}$$

$$C_2H_5Cl + OH^- \longrightarrow C_2H_5OH + Cl^-$$

# Module 5

# Rates of reactions

# 5.1 Order, rate equation and rate reactions

#### Rate of reaction

Rate of reaction is measured by observing changes in quantity over time e.g.  $cm^3s^{-1}$ . In this chapter, you will mainly be dealing with concentration, so knowing the standard unit for it is important(mol  $dm^{-3}$ ).

Chemists use shorthand to describe the concentration of compounds. This notation is [A], where A is the compound, and the square brackets mean 'concentration of'.

 $Rate \propto [A]^n$  – rate is directly proportional to the concentration of A (5.1)

#### Orders of reaction

The rate of reaction will often increase as the concentration is increased. It is directly proportional to the concentration raised to a power i.e.

$$rate \propto [A]^n \tag{5.2}$$

The power is the order of reaction with respect to the concentration of the compound.

#### Zero order

This is when  $rate=[A]^0$ , meaning that a change in concentration has no effect on the rate of reaction. This is due to anything to the power of 0=1.

#### First order

This is when  $rate=[A]^1$ . Essentially, what happens to the concentration happens to the rate i.e. concentration  $x^2$  means rate  $x^2$ .

#### Second order

This is when rate= $[A]^2$ . So when concentration doubles, rate  $x2^2 = 4$ . Basically the rate is the square of the change in concentration.

#### Rate equation and rate constant

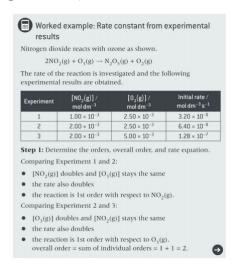
The rate equation is  $rate = k[A]^n[B]^m$ . The overall order can be found by adding the powers together. When a question says both concentrations are changed, you use the overall order to find the rate.

The units of the rate constant are usually moldm<sup>-3</sup>s<sup>-1</sup>. However, this can be derived by rearranging the rate equation to make k the subject as this is the rate constant. It is useful to remember that the concentrations are measured in moldm<sup>-3</sup>.

#### Determining orders from experimental results

The best way to learn this is by doing past paper question. Some great resources can be found on: pastpapers.com; physicsandmathstutor.co.uk or http://www.a-levelchemistry.co.uk/.

**The questions** will usually contain a table with the headings: Experiment, Concentration of respective elements and the initial rate. The way to go about these questions is by first seeing how the concentration change between experiments e.g. x2. Then look at initial rate. See how this changes to determine the rate e.g. if it's x4, this would be second order.



## 5.2 Concentration-time graph

You can measure rates by looking for a **change** in mass or by gas collection in a certain **time**. You can also use a colorimeter if some of the compounds are coloured.

#### Concentration-time graph

The gradient of the concentration-time graph is the rate of reaction. The order of reaction can be deduced from the shape of the graph.

#### Zero order

This graph slopes down i.e. it has a negative gradient. The line is straight meaning that the rate is constant as concentration falls over time(as reactants used up). The gradient of the line is the rate constant-k.

#### First order

This graph is a downward-sloping curve . The gradient decreases over time, slowing the reaction down. The half-life( time taken for concentration to halve) is constant. (INSERT GRAPHS WHEN BOTHERED)

#### Second order

This graph is steeper at the beginning than the first order. However, it tails off more slowly

#### Half-life

**Half-life,** which can be represented by  $t_{1/2}$  is the time taken for half of the reactant to be used up. First order reactions halve the concentration every half life. The curve is exponential, showing **exponential decay** 

#### Determination of rate constant from rate

You can draw a tangent to the curve on a concentration-time graph. This will give you the rate of reaction. Then, you insert this into your re-arranged rate equation, where k is the subject. This should give you the rate constant, all you need to do is figure out the units.

You can also use an awesome formula:

$$k = \frac{\ln 2}{t_{1/2}} \tag{5.3}$$

This method is more accurate than drawing a tangent.

## 5.3 Rate-concentration graphs and initial rates

Always be careful to check the axes of your graph. Here, the rate is on the left and concentration along the bottom. Normally, as concentration increases, so does rate due to kinetics i.e. more particles etc. Therefore the curves usuallyslope up rather than down.

#### Orders from shapes

#### Zero order

The gradient is 0, meaning there is no slope. Rate is not affected by a change in concentration (a visual representation of its definition). The y-intercept gives you the rate constant-k.

#### First order

This is a upward-sloping straight-line graph beginning at the origin. This is because when concentration is 0, rate is zero. The rate constant her is the gradient of the line.

#### Second order

This is an upward sloping curve. Therefore the gradient constantly increases. It also means that the rate constant cannot be worked out directly by the curve. Instead, you need to **plot a second graph** of the rate against  $[A]^2$  (concentration squared). This will give you a straight line graph through the origin, where the gradient is k.

#### Initial rates method

The initial rate is the instantaneous rate when t=0.It can be measured by drawing a tangent where t=0 on a concentration-time graph.It can be obtained by separate experiments using different concentrations of one of the reactants.Clock reactions are an approximation of this method.

A clock reaction is a convenient method of obtaining the initial rate. It is done by measuring time from the beginning of an experiment to a visual change. This change will often be a precipitate or colour.

**As long** as there isn't a significant change in rate, it's assumed that the average rate of reaction is equal to the initial rate. The initial rate is then proportion

tional to  $1\frac{1}{t\dot{T}he experiment is then repeated with different concentrations and values of \frac{1}{t}}$  are calculated each time.

**Iodine clock reactions** are simple and you've probably done this as a PAG. You mix together sodium thiosulphate, starch and iodine. The endpoint of the reaction is when a blue-black colour appears- as iodine racts with starch as soon as the Sodium thiosulphate is used up.

#### The rate determining step

**Given the stoichiometry** of chemical reactions, some are very unlikely to be completed in one step. In fact, there is probably more than one, the *slowest* being called the **rate determining step**<sup>1</sup>.

**An example** would be the reaction:  $H_2O_2 + HI \longrightarrow H_2O \equiv I_2$  As the ionic equation is  $H_2O_2 + {}_2\Gamma \equiv {}_2H^+ \longrightarrow I_2 + {}_2H_2O$ , all the ions would have to collide at the same time for the reaction to take place in one step. The following is the most likely to happen:  $H_2O_2 + HI \longrightarrow H_2O + HOI$  SLOW(RDS) and then  $HOI + HI \longrightarrow H_2O + I_2$  FAST.

 $<sup>^{1}\</sup>mathrm{I}$  shall now refer to this as RDS

# Module 6

# Organic chemistry and analysis

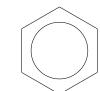
'This module introduces several new functional groups and emphasises the importance of organic synthesis. This module also adds NMR spectroscopy to the instrumentation techniques used in organic and forensic analysis.'

# 6.1 Aromatic Compounds 6.1.1

**Benzene** has had two models, the evidence for each we will later examine, they are as follows:



Kekulé model of benzene



Benzene delocalised model

The Kekulé model of benzene hypothesises that there are 3  $\pi$  bonds and 6  $\sigma$  bonds. This was a convenient way to describe the bonding in benzene but has, in recent years, been replaced by the more accurate delocalised model of benzene.

The Delocalised model of benzene is the one that is now generally accepted. It describes benzene's bonding in terms of a sideways overlap of the P orbitals (in the carbon atoms) above and bellow the plain, in a delocalised 'system' of  $\pi$  bonds.

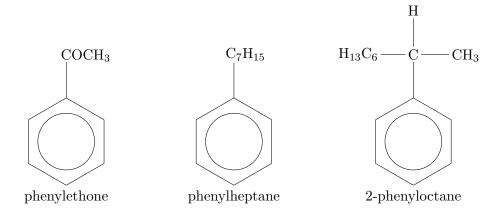
#### The evidence against the Kekulé model,

- 1. The resistance to reaction of benzene suggests that there are no double bonds present. WS This is down to the low electron density of a delocalised  $\pi$  bond system, as oppose to the localised  $\pi$  bonds in alkenes. The C=C bond present should decolourise bromine water, however benzene doesn't decolourise bromine water.
- 2. The differing bond lengths in benzene appear to refute the Kekulé model. This is because all bond lengths are the same in benzene however, in  $\pi$  bonds, we would expect shorter bond lenths than  $\sigma$  bonds.
- 3. The enthalpy change of hydrogenation in benzene. We would expect the enthalpy of hydrogenation in benzene to be triple that in cyclohexene (following the Kekulé model). However it isn't, less energy is produced than expected, leading us to the conclusion that it is more stable than Kekulé's model would suggest.

# **IUPAC** rules of nomenclature for systematically naming substituted aromatic compounds:

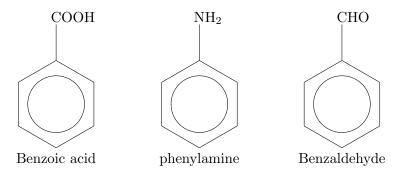
Benzene is, generally, considered the parent chain where one substituent group is monosubstituted. This means that we can name substences like Chlorobenzene, nitrobenzene and, if a small alkyl group is monosubstituted, ethylbenzene.

Where an alkyl group has 7 or more carbon atoms it becomes the main chain and the benzene the substituent group. In these cases phenol is used as the prefix. This is also the case if the alkyle chain has a functional group. e.g:



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There are some noteable exceptions however, (just remember them):



**Electrophilic substitution** reactions occer in benzene when an electrophile replaces a hydrogen atom in benzene. The following reactions are covered in this section:

• Concentrated nitric acid in the presence of concentrated sulphuric acid. The nitration of benzene:

$$+ \text{ HNO}_3 \xrightarrow{\text{H}_2\text{SO}_4} + \text{H}_2\text{O}$$

This reaction is done in a water bath to maintain a steady temperature.

• The next reaction is in the presence of a halogen carrier, to generate the halogen electrophile. Halogen carriers include iron, iron halides and aluminium halides. The halogenation of benzene:

$$+ Br_2 \xrightarrow{AlBr_3} + HBr$$

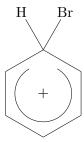
• Last, but not least, is the Friedel–Crafts reaction. This is a haloalkane (or an acyl chloride) in the presence of a halogen carrier and its reaction with benzene. This reaction is important as it forms a C-C bond to an aromatic ring. In the case of a haloalkane:

$$+ C_2H5Cl \xrightarrow{AlCl_3} + HCl$$

and in the case of a acyl chloride

$$+ CH_3COCl \xrightarrow{AlCl_3} + HCl$$

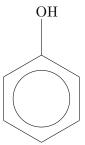
You are, of course, expected to know some related reaction mechanisms.



## TO BE CONTINUED]

You should, from this, be able to predict the mechanisms of similar but unfamiliar electrophilic substitution mechanisms of aromatic compounds.

**Phenol** is a specific aromatic compound with a hydroxyl group (OH group). It has the following structure:



Phenol is weekly acidic, as shown by it's neutralisation reaction with NaOH, however it cannot react with carbonates.

## List of phenol electrophilic substitutions :

• The bromination of phenol:

$$\begin{array}{c} OH \\ OH \\ Br \\ \end{array} \\ + 3Br_2 \\ \end{array} \\ \begin{array}{c} OH \\ Br \\ \end{array}$$

• The nitration of phenol:

$$\begin{array}{c|c} OH & OH \\ \hline & NO_2 \\ \hline & + H_2O \end{array}$$

Note that nitration with phenol does not require concentrated  $\mathrm{HNO}_3$  or the presence of a concentrated  $\mathrm{H}_2\mathrm{SO}_4$  catalyst (like benzene).

As you can see, phenol undergoes electrophilic substitution with relative ease, as compared to phenol. This is because the OH group 'activates' the ring. Meaning the oxygen donates an electron pair (from the P orbital) to the

delocalised  $\pi$  bond system, this subsiquently increases the electron density and allows the ring 'attack' molecules and produce electrophiles.

The two electron donating groups (that are covered) are OH and  $\rm NH_2$ . There are also electron withdrawing groups, which make the ring less susceptible to electropilic substitution (which become important when considering directing). The one covered here is  $\rm NH_2$ .

**Directing** of groups is determined by whether the aromatic molecule has an electron donating group, or an electron withdrawing group. Electron donating groups (like OH and NH<sub>2</sub>) cause a 2-, 4- directing effect; Electron withdrawing groups (like NH<sub>2</sub>) cause a 3- directing effect.

[THERE IS PROBABLY MORE TO SAY]

# 6.2 Carbonyl compounds 6.1.2

**Further oxidations** Ketones can undergo further oxidation to form carboxylic acids. This is exactly the same as the reaction seen in section 4.6.

**Nucleophilic addition** reactions of carbonyl compounds:

• Reducing an aldehyde

• reducing a ketone

• Reaction with HCN (works with ketones too) adds across the C=O bond.

[TBC: the mechanism for nucleophilic addition reactions of aldehydes and ketones with NaBH4 and HCN need also to be learnt]

**Testing for carbonyl compounds** is done by a multi-stage process. We use a compound called 2,4-dinitrophenylhydrazine (2,4-DNP) to test for the precence of a carbonyl group then use Tollens' regent (ammonical silver nitrate) to further distinguish between aldehydes and ketones.

- 1. Mix 2,4-DNP, dissolved in methanol, with sulphuric acid to form a pale orange solution
- 2. Add about 5cm of this solution to a test tube
- 3. Add a few drops of the unknown solution
- 4. Add a few drops of sulphuric acid
- 5. If an orange/yellow precipitate forms this indicated the presence of an aldehyde or ketone (If no precipitate end here, a carbonyl group isn't present)<sup>1</sup>
- 6. Now add, to another test tube, 3cm of aqueous silver nitrate
- 7. Add sodium hydroxide until a brown precipitate is formed (Silver Oxide)
- 8. Add dilute ammonia to dissolve the the brown solution, leaving you with a colourless solution, this is known as Tollens' regent

<sup>&</sup>lt;sup>1</sup>To identify the specific carbonyl compound a melting point test can be done. This will require filtration of the solution and a data table to compare results.

- 9. Into another test pour 2cm of the unknown solution
- 10. Add, to this, an equal amount of the fresh Tollens' regent (made earlier)
- 11. Leave this test tube in a water bath at around 50°C for about 10-15 minutes
- 12. If a 'silver mirror' forms then the solution is an aldehyde, else it is a ketone

**Tollens' reagent** or ammoniacal silver nitrate distinguishes between aldehydes and ketones. It does this through the oxidation of aldehydes to carboxylic acids and the reduction of silver ions to silver.

$$R \longrightarrow C \qquad + \quad [O] \qquad \xrightarrow{Oxidation} \qquad R \longrightarrow C \qquad OH$$

$$Ag^{+}(aq) + e^{-} \qquad \xrightarrow{Reduction} \qquad Ag(s)$$

# 6.3 Carboxylic acids and esters 6.1.3

**Properties of carboxylic acids** Carboxylic are water soluble, this is as a result of hydrogen bonding between the carboxylic acid and water. The O-H<sup> $\delta$ +</sup> and C=O<sup> $\delta$ -</sup> groups can hydrogen bonded to the O<sup> $\delta$ -</sup> and H<sup> $\delta$ +</sup> respectively in water. The smaller the non-polar carbon chain, the more soluble in water the carboxylic acid is (as a higher proportion of the molecules can hydrogen bond).

**Reactions with metals** Carboxylic acids react with metals in a redox reaction to form a carboxlite salt and hydrogen gas.

Reactions with carbonates Carboxylic acids react with carbonates to form water and  $CO_2$ .

**Reactions with metal oxides** Carboxylic acids react with metal oxides to form salt and water.

**Reactions with alkalis** Carboxylic acids react with alkalies to form a salt and water.

Esterification The esterification of carboxylic acids can be done with alcohol and a  $H_2SO_4$  catalyst. The products are the carboxylic acid and water.

Acid anhydrides can also form esters in a simalar fashion. In the presence of an alcohol they break at the O atom and form a carboxylic acid and an ester as a product.<sup>2</sup>

**Hydrolisis of esters** an ester can be 'turned back' into a carboxylic acid and alcohol. This is done by the addition of hot aqueous acid.

By adding hot aqueous alkili we can form carboxylate salts and alcohols.

**Acyl chlorides** are formed from carboxylic acids with SOCl<sub>2</sub>. They are very reactive and so useful in organic synthisis. Acyl chlorides can be used to form esters, carboxylic acids and secondary amides.

- Acyl chlorides can be used to make esters with alcohols with the ester and HCl being the products. Carboxylic acid are not reactice enough to from esters with phenol, however Acyl Chloride can.
- Acyl chlorides can be used to make carboxylic acid by adding water. This will result in a rather violent reaction releasing HCl.
- To be added, figures are required.

 $<sup>^2\</sup>mathrm{An}$  acid anhydride is a compound that has two acyl groups bonded to the same oxygen atom.

<sup>&</sup>lt;sup>3</sup>Try not to breath hydrogen chloride in.