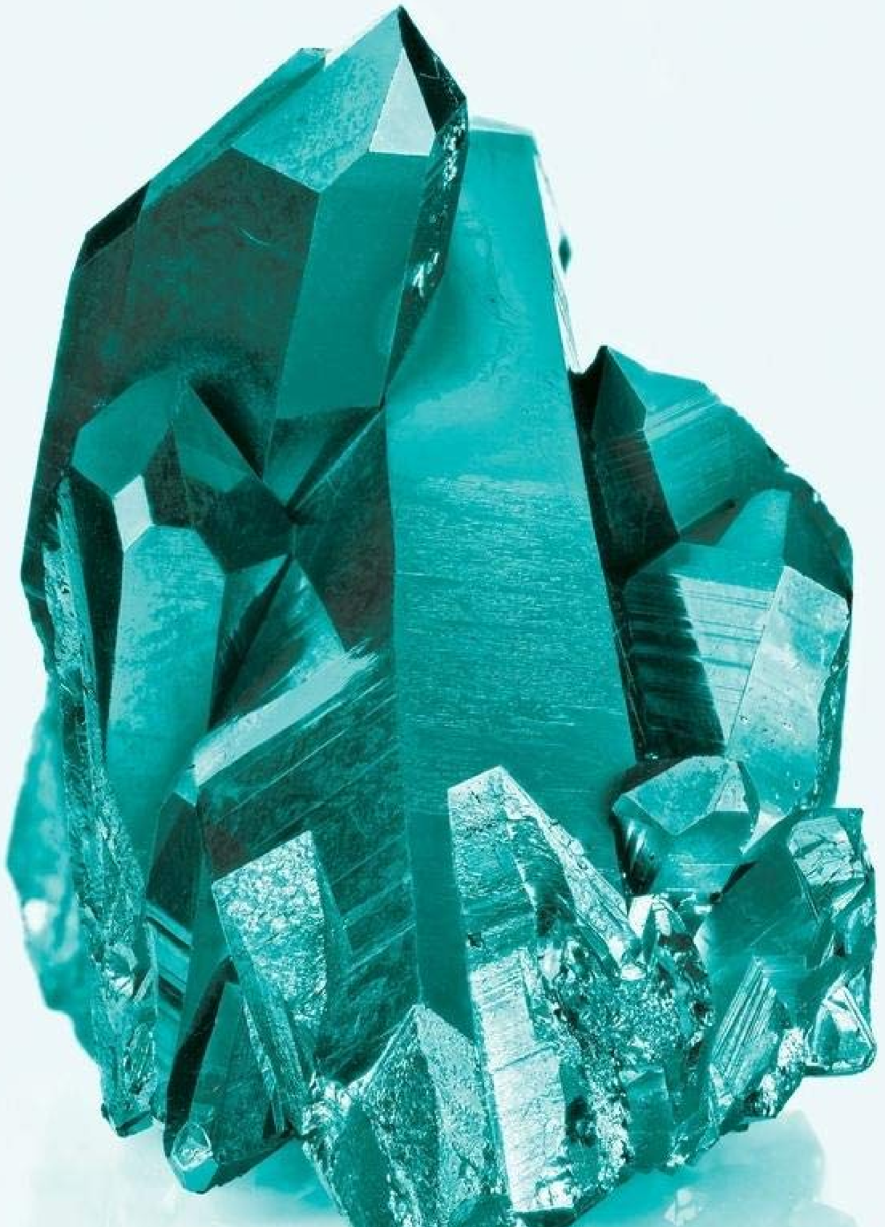
IB Chemistry

Revision Guide

Ray Dexter



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For Áron and Maja, as always.

Thanks to Nadine for her constant support and love throughout the writing of this book. You had a lot more faith than I did!! Thanks to my colleagues at St Edmund's College for their encouragement and comments, especially those in the chemistry and the history departments. Thanks to Emma Baxter for checking my medicinal chemistry and Elizabeth Hartley for her calculations' summary design. Thanks also to Peter Capaldi and Richard Saunders for their usual contribution to my world. Thanks, as ever to Douglas Adams for the quote, "I love deadlines, I love the whooshing sound they make as the go by." It made me hit my deadline!!

To Arch Overbury, my high school chemistry teacher, the greatest of them all. I still hear your voice when I teach. To Brian Orger and James Tearle from Stowe School, the legendary teachers who took me under their wing and taught me all I know when I first started out in this teaching game.

To all the past IB DP students I have ever taught and tried to teach chemistry. This book is the product of our work together. I thank you for being so inspiring; I hope this book can be equally inspiring.

About the Author

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CHAPTER

1 Measurement and data processing

This chapter's contents refer to the material covered in Topics 11.1 and 11.2 of the IB Chemistry Specification.

CORE
SPREAD 1: Uncertainties and errors in measurement and results

Qualitative data includes all non-numerical information obtained from observations not from measurement.

Quantitative data are obtained from measurements, and are always associated with random errors/uncertainties, determined by the apparatus, and by human limitations such as reaction times.

Propagation of random errors in data processing shows the impact of the uncertainties on the final result.

Introduction

All lab work in any science subject isn't perfect. Mistakes will be made. Some will be human error; some will be related to the equipment used. No experimental result has true validity unless these errors are acknowledged and worked into any result. Remember, an error is something that prevents you from getting the true, correct result.

Before we look at the errors let's clarify a few terms related to lab work:

Qualitative data: This is all information obtained from observations not from measurement. For example, a color change or the formation of a precipitate is a qualitative observation. There can be no mathematical content to such observations.

Quantitative data: This is where the numbers come in. This data is obtained from measurements and often requires mathematical processing.

In experiments we typically measure a variable. The independent variable is affected when another variable is changed (the dependent variable). For example, in an experiment to measure how temperature affects the speed of a reaction, the independent variable is the temperature and the dependent variable would be the measured time.

Although errors can be made in recording qualitative data, the majority of errors are associated with quantitative data.

What sort of errors are there?

Essentially three types of error exist:

Systematic error: These are errors that are due to the procedure or equipment you have used. For example, an experiment to measure the quantity of gas produced (see Chapter 7) will have to overcome the gap between mixing the reagents and the gas hitting a gas syringe. Some gas will be lost. As this would be a fault of the procedure the error should be the same each time.

Random errors: These, as the name suggests, are harder to quantify. They are the result of human error, failure to carry out the procedure properly and other factors that can go wrong. They can include the parallax errors of misreading a burette by looking from the wrong angle and simple reaction times of the person carrying out the experiment.

The uncertainty of the apparatus: All pieces of quantitative apparatus have a tolerance. This is the preciseness of the result. For example, the pipette in the picture below is designed to measure 25 ml, but the tolerance is ±0.06 ml. This means that if the pipette is used correctly the actual amount measured from this pipette will be between 24.94 ml and 25.06 ml. You cannot know the actual figure with any greater certainty.

A pipette showing the tolerance at 20°C.

Repeating results

Repetition of results is important for the removal of random errors, but it will have no effect on systematic errors, or the uncertainty of the apparatus.

CORE
SPREAD 2: Applying uncertainty readings to a calculated number

Experimental design and procedure usually lead to systematic errors in measurement, which cause a deviation in a particular direction.

Repeat trials and measurements will reduce random errors but not systematic errors.
The uncertainty involved with all numerical readings on apparatus needs to be factored in to any calculation made. It is known as the percentage uncertainty. It is easy to calculate:

$$\frac{\text{Uncertainty of apparatus}}{\text{Measured value}} \times 100\%$$

For example, using the pipette above which measures 15 ml with an uncertainty of ±0.03 ml is

$0.03/15 \times 100 = 0.2\%$

The calculation can get more complicated when the required reading needs two measurements, for example on a burette reading, or recording a temperature change, starting and end temperature. Here BOTH readings have the uncertainty quoted, and so the uncertainty is doubled.

For example, with these burette readings:

	Volume (ml) ±0.05
End reading	24.75
Start reading	0.10
Titer	24.65

So the percentage uncertainty here is 0.05 × 2/24.65 × 100 = ±0.41%.

In an experiment where many readings are made the uncertainty of all measurements needs to be calculated and then added together to give a total percentage uncertainty for the experiment.

Example from thermochemistry

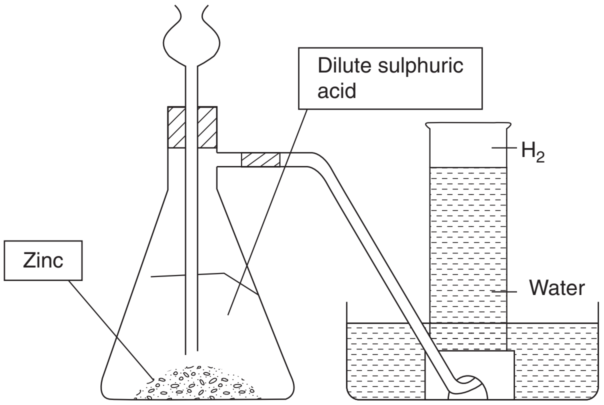
The heat capacity of a copper can is 25 $JK^{-1} \pm 1$. Using it to carry out a calorimetric experiment a temperature rise of 8°C is recorded on a thermometer with an uncertainty of ±1°C. What is the total uncertainty?

Calorimeter uncertainty = 1/25 × 100 = 4%
Thermometer uncertainty (0.1 + 0.1)/8 × 100 = 2.5%
Total uncertainty = 6.5%

What can be done to reduce systematic error?

There are two ways to approach reducing systematic errors and uncertainty errors. This mainly involves reviewing either the procedure itself, or to use apparatus that will reduce the potential for error.

Let's take the example of gas collection with upturned measuring cylinder and gas syringe. Discuss the variables and the problems.



There are many problems with this setup. The potential for gas to escape, or to dissolve in the water: the inaccuracy of the measuring scale on the gas jar.

When it comes to reducing percentage uncertainty often the quantities used can cause the problem. See the example below:

A student weighs out 0.5 g on a balance with an uncertainty of 0.1 g and again on a balance with an uncertainty of 0.01 g (20% and 2%).

The student then weighs out 5 g on the 0.1 balance and the 0.01 balance (2%) and 0.2, so the percentage uncertainty of the apparatus also depends on the measured quantity. As a rule of thumb a good way of reducing percentage uncertainty is to increase the quantity measured.

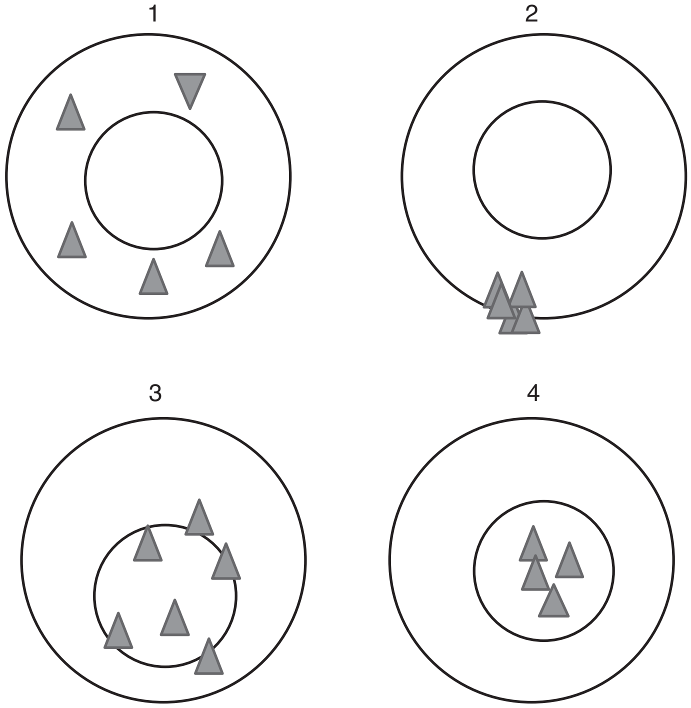
CORE
SPREAD 3: What is the difference between accuracy and precision?

This is a concept that can cause confusion, as the two words are used in the real world interchangeably, but in science they have very specific meanings:

Accuracy means how close the answer is to the true answer.

Precision means how reproducible is the result, or the resolution of the result (the number of decimal places).

In IB chemistry often target diagrams are used to illustrate the point.



In diagram 1 there is low accuracy and low precision because none of the points are in the inner ring (low accuracy) and the points are far apart (low precision).

Diagram 2 is also low accuracy because no points hit the inner ring, but the results are precise because they are all close together.

Diagram 3 shows a high accuracy because all the points are in the inner ring, but the precision is poor.

Diagram 4 has high accuracy and high precision.

Repetition can increase the precision of results but is unlikely to affect the accuracy; often a redesign of the experiment is required there.

Calculation of percentage error

The technique for working out how ACCURATE you've been is the percentage error. Here you will have to look up the true value from a reliable source (and reference it).

Then you simply divide your answer by the correct answer and multiply by 100 and quote this value. If your answers are enthalpy changes and have negative numbers it is OK to work this out by ignoring the sign. All we care about is how far apart the numbers are from each other.

Any experimental work that is to be assessed needs to have percentage error and percentage uncertainty calculated. If your answer's percentage uncertainty brings it close to the true answer, that is, they overlap, you can argue in an evaluation that the limitations of your apparatus might be a factor. If they are way out you may have to look for other reasons.

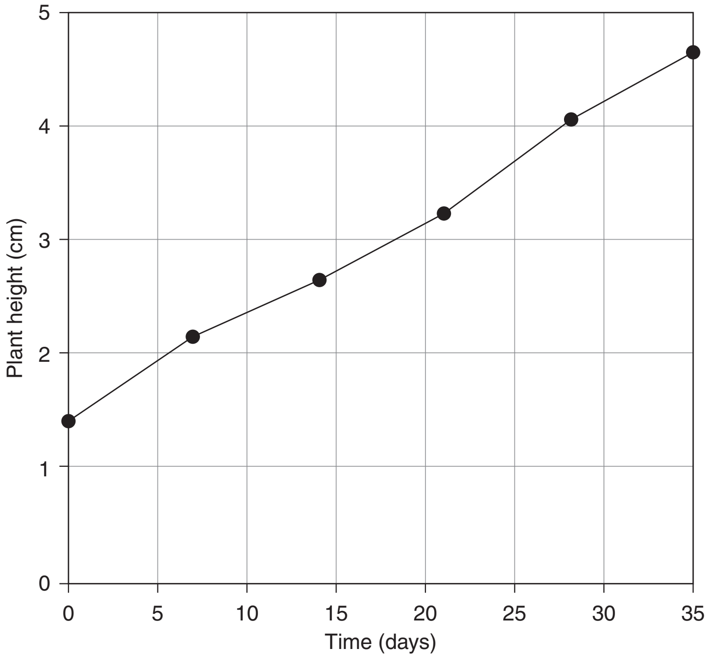
CORE
SPREAD 4: Graphical techniques

Graphical techniques are an effective means of communicating the effect of an independent variable on a dependent variable, and can lead to determination of physical quantities.

Sketched graphs have labelled but unscaled axes, and are used to show qualitative trends, such as variables that are proportional or inversely proportional.

Drawn graphs have labelled and scaled axes, and are used in quantitative measurements.

Many of the quantitative relationships you meet on a chemistry course can be more easily interpreted with a graph. There are many types of graphs, but the most common type encountered in chemistry is some kind of plot with a line or curve of best fit. Graphs are only of use if the correct choice of axes is chosen and the scale is sensible. As a general rule the bigger you can make the plot the more useful the graph is. Typically the dependent variable is plotted on the *y* axis, and the independent variable is measured on the *x* axis. So the *x* should represent the change you make, and the *y* is the result of that change.



Sometimes it is acceptable to sketch a graph and not worry about the preciseness of the plotting, and the detail of the axes. This is when you are merely showing a positive correlation or proportionality in the results.

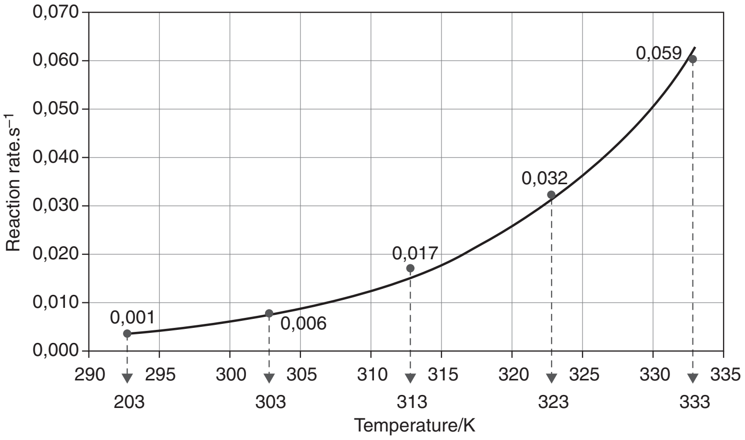
Using graphs to predict unknown values

Plotting graphs is a skill you will also have to master in other aspects of your IB diploma. I do not intend to go into detail here. However, there are a few skills you should be aware of:

Plotting best fit lines and curves is essential for all graphs that you attempt to plot a best fit line or curve. A common mistake for the physicists out there is to assume all plots should have a best fit line. In chemistry a best fit curve is also common, so watch out for them.

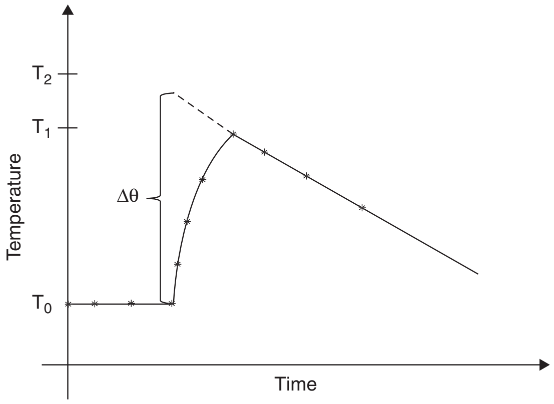
Graphs can also be used to predict results where no experiment has been performed.

Interpolation is when a value is worked out from within the parameters of known results.



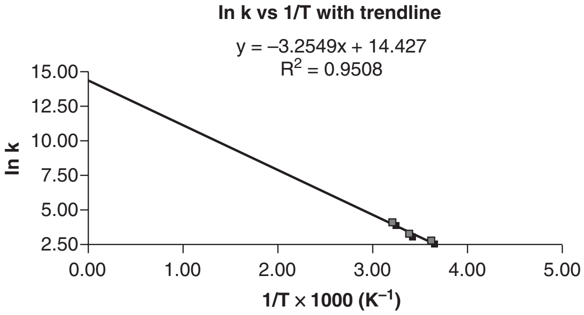
In this graph we would be able to predict the rate for any temperature recorded between the minimum and maximum.

Extrapolation is when the best fit line is extended beyond the experimental line to give results outside the range of the performed experiment. In calorimetry experiments because of the time lag on the thermometer the true temperature rise is often calculated using extrapolation from the straight line plot.

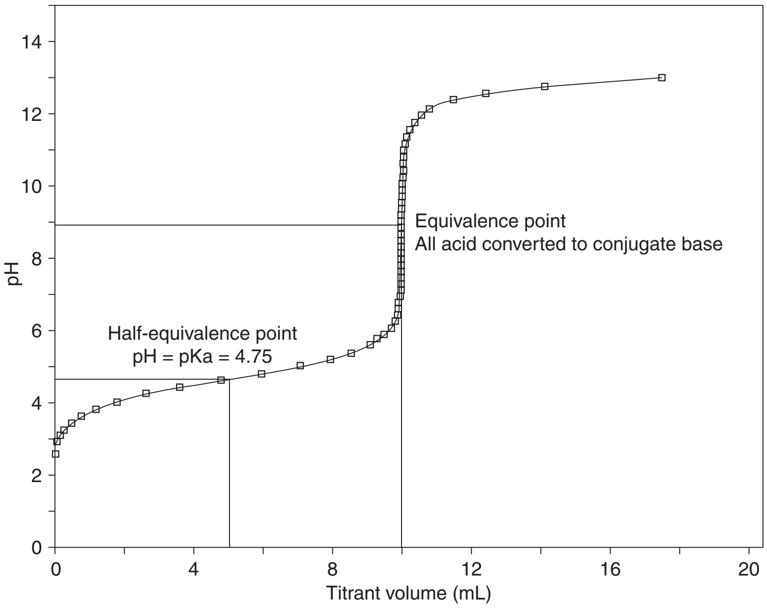


Gradients and intercepts

Measuring gradients is an important aspect of graph plotting, especially in the kinetics section. The gradient is d*y*/d*x*, not forgetting to use the correct units and scale to use on the axis. Here activation energy can be calculated by use of the gradient. See Chapter 7.



Intercepts are also useful. This is where the trend line is extrapolated until it crosses the axis. This is useful for calculating the steric factor in kinetics and working out pK_a of a weak acid from a pH curve using the Henderson–Hasselbach technique.



CHAPTER

2 Stoichiometric relationships

This chapter's contents refer to the material covered in Topic 1 of the IB Chemistry Specification.

SPREAD 1: Writing formulae

- *Atoms of different elements combine in fixed ratios to form compounds, which have different properties from their component elements.*
- *Mixtures contain more than one element and/or compound that are not chemically bonded together and so retain their individual properties.*
- *Mixtures are either homogeneous or heterogeneous.*
- *Calculating relative molecular mass (RMM). Molar mass (M_r) has the units g mol^{-1}.*

You can't begin a chemistry course until you have these basic ideas sorted out. Simplistically there are three types of substance: element, compound and mixture.

Elements are substances made of only one type of atom. Elements cannot be broken down into anything simpler that will have a form of chemical existence. They behave differently from their constituent elements. For example, table salt (sodium chloride) is a relatively benign white solid that isn't toxic, whereas the elements sodium and chlorine are both very dangerous, as we will see.

Compounds are substances made of two or more elements chemically bonded together (see Chapter 4). Compounds can be written in the form of chemical formulae. This shows the fixed ratio of elements in the compound. For example, in magnesium carbonate, the formula is $MgCO_3$—one magnesium, one carbon and three oxygens.

What is the difference between copper sulfide and copper sulfate?

In simple terms "ide" can be taken to mean combined in a compound, so copper sulfide is just copper and sulfur CuS. "Ate" can be taken to mean "with oxygen as well," so copper sulfate is $CuSO_4$. The exact nature of "ate" will be discussed further in the chapter on bonding.

Mixtures are elements or compounds (or both) chemically uncombined. Mixtures that contain chemicals in the same chemical state are called HOMOGENEOUS (from the Greek *homo*—the same, *genous*—combining from). A good example is air. HETEROGENOUS mixtures contain chemicals in different states (*hetero*—different). An example would be sea water. As the components in a mixture are not chemically combined they retain their individual characteristics.

Substances can occur in three states: solid (s), liquid (l) and gas (g). If you have a solution (a mixture of a substance dissolved in water) then it is called aqueous (aq) (from the Latin via French for water). These bracketed signs should appear next to any chemical formulae in equations.

A chemical reaction is one where chemistry occurs. Chemical reactions can be represented by chemical equations. Chemical equations are stoichiometrically correct (which means the proportions of each chemical are shown correctly). One of the skills needed on the IB DP course is to be able to balance chemical equations so that the stoichiometry is correct.

Balancing equations

NOTE: BEFORE WE START: WE NEVER WRITE 1 IN CHEMICAL EQUATIONS. It's implied because it's there, so it's H_2O not H_2O_1

Easy example

$H_2 + O_2 \Rightarrow H_2O$

Atoms can't simply disappear. The same number must be on the left as on the right. Here there are two hydrogens on both sides, two oxygens on the left, but only one on the right. The equation is not balanced.

You cannot change the formulae, so all you can do is change the quantities, by putting a large number in front of the equation's components.

So a good place to start is to double the thing that is lacking, the right hand side (RHS):

$H_2 + O_2 \Rightarrow 2H_2O$

This helps the oxygen; there are two on either side. But of course there are now four hydrogens on the RHS, so we need to fiddle with the left hand side.

$2H_2 + O_2 \Rightarrow 2H_2O$

Harder example

$C_3H_8 + O_2 \Rightarrow CO_2 + H_2O$

With questions involving hydrocarbons the rhythm is easier to find. How many carbons on the left? Three. So there MUST be three CO_2 molecules.

$C_3H_8 + O_2 \Rightarrow 3CO_2 + H_2O$

Eight hydrogens mean eight hydrogens on the RHS

$C_3H_8 + O_2 \Rightarrow 3CO_2 + 4H_2O$

Now we just balance for oxygen. There are ten oxygens on the RHS, so make $O_2 = 10$

$C_3H_8 + 5O_2 \Rightarrow 3CO_2 + 4H_2O$

Plenty of practice on this will go a long way in helping you become more confident. Balancing problems will usually occur in the first three or four questions of a multiple choice paper. Practice a few below.

Working out the RMM

The periodic table contains all the information you need for the masses of atoms. It is given as the relative atomic mass. The mass of a compound is simply the sum of all the elements in the compound.

So copper sulfate $CuSO_4 = 63.5 + 32 + (16 \times 4) = 159.5\ \text{g mol}^{-1}$

SPREAD 2: Avogadro's number and the mole concept

The mole is a fixed number of particles and refers to the amount, n, of a substance.

Masses of atoms are compared on a scale relative to ^{12}C *and are expressed as relative atomic mass (*A_r*) and relative formula/molecular mass (*M_r*).*

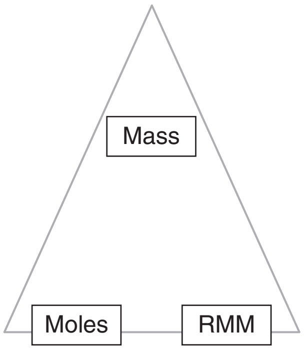
Chemistry calculations: The basics

All chemistry calculations revolve around the concept of the mole. The problem with any calculation is that there is a difference between quantities that we understand as humans (mass, volume) and the quantities at an atomic level, where simply the number of atoms is important. The two are not compatible. Therefore the mole is the bridge between the two worlds.

Essentially the mole is 6.02×10^{23} of anything, but it always refers to atomic particles of some sort. This is also known as Avogadro's number. It is the scaling up factor between the atomic world and our world. If 1 atom of sulfur weighs 32 mass units (an arbitrary term based on a relative mass compared to hydrogen (see Chapter 2) then 1 mole of sulfur (6×10^{23} atoms) weighs 32 grams. As the mole is effectively a constant we can use it as our scalar to do calculations.

Converting to moles is pretty much the first thing you ever have to do in any calculation. Every calculation you see in this book requires it at some stage.

With solids it's very simple: moles = mass/RMM. RMM is calculated as in the earlier spread.



1) How many moles are there in each of the following?
   a) 72 g of Mg
   b) 4 kg of CuO
   c) 1 ton of NaCl
2) What is the mass of each of the following?
   a) 5 moles of Cl_2
   b) 0.2 moles of Al_2O_3
   c) 0.01 moles of Ag

Avogadro's number in calculations

Avogadro's number can be used to find out the number of particles in a given mass of a substance. We know that one mole of any substance contain 6×10^{23} particles. So, for example, if we had 6 g of carbon we would have half a mole of carbon.

6/12 = 0.5 moles.

We would therefore have $0.5 \times 6 \times 10^{23}$ atoms of carbon, which is 3×10^{23}.

These are quite common multiple choice questions and are often the first questions you meet. A lot of skill is required to do this. It is best to look at a few examples:

1) What is the total number of hydrogen atoms in one mole of ethanol (C_2H_5OH)?

   One mole of ethanol contains 6 hydrogens (count them). Therefore there would 6 lots of 6×10^{23} atoms of hydrogen per mole, or 36×10^{23}, more correctly written as 3.6×10^{24}.
2) How many molecules are there in a drop of water weighing 1.8×10^{-3} grams?

   $1.8 \times 10^{-3} = 0.0018$ g which is 0.0001 moles. 1 mole contains = 6×10^{23}, so it would be 6×10^{19} molecules.

The best advice is to work out a ball park figure. For example, in the first you know it would be higher than one mole, so eliminate answers that are smaller than 6×10^{23}. The opposite is true for the second. This is clearly going to be smaller than 6×10^{23}, so eliminate answers larger than it.

SPREAD 3: Empirical and molecular formula

The empirical formula and molecular formula of a compound give the simplest ratio and the actual number of atoms present in a molecule respectively.

The first and most traditional calculation using moles is the empirical formula. Here a chemical is analyzed, and the relative proportions of each element are deduced. This can either be as a percentage, or in simple mass terms. Either way we need to convert them into moles and see if we can see a ratio.

Easy example

A sodium compound was analyzed and found to contain the following:

Na 29.1%; *S* 40.5%; *O* 30.4%

Work out the empirical formula:

Draw a table and work through.

	Na	S	O
Mass/or %	29.1	40.5	30.4
Relative atomic mass (RAM)	23	32	16
Moles	1.2655217	1.2656	1.9
Divide through by smallest	1.26/1.26	1.256/1.256	1.9/1.256
Ratio	1	1	1.5

The ratio is now clear to see: 1:1:1.5 or 2:2:3

Formula $Na_2S_2O_3$

You must never round up or down numbers, otherwise you can get the wrong number.

Molecular formula is the true formula, where the empirical formula is the simplest ratio. If you know the RMM you can calculate the molecular formula.

A hydrocarbon with a relative molecular mass (M_r) of 28 g mol^{-1} has the following composition: Carbon 85.7%; Hydrogen 14.3%. Calculate its molecular formula.

	C	H
Mass/or %	85.7	14.3
RAM	12	1
Moles	7.1416	14.3
Divide through by smallest	7.1416/7.1416	14.3/7.1416
Ratio	1	2

Empirical formula is CH_2. But its RMM is 14. The real RMM is 28. Therefore the molecular formula must be

C_2H_4

Brutal example

Crocetin consists of the elements carbon, hydrogen and oxygen. Determine the empirical formula of crocetin, if 1.00 g of crocetin forms 2.68 g of carbon dioxide and 0.657 g of water when it undergoes complete combustion.

This is a classic question as it relates to actually how they get the amounts of each element in the compound (for real).

You'll notice there are no masses, so how do you start?

1) Work out the moles of CO_2

2.68/44 = 0.061 moles. As the formula is CO_2 there must be 0.061 moles of carbon. This carbon came from the crocetin, therefore the mass of carbon in the crocetin must be:

$0.061 \times 12 = 0.731$ g

2) Work out the hydrogen

Same idea

0.657/18 =0.0365 moles of water.

This time the formula is H_2O, so the moles of hydrogen in the molecule is double:

0.0365 × 2 = 0.073 moles

The mass of hydrogen is therefore 0.073 × 1 = 0.073 g

3) Working out the oxygen

The mass of crocetin was 1 g, 0.073 g was hydrogen and 0.731 g was carbon.

So oxygen is 1 – 0.731 – 0.073 = 0.196 g

Now you can use the empirical formula!!

	C	H	O
Mass or %	0.731	0.073	0.196
RAM	12	1	16
Moles	0.061	0.073	0.0122
Divide through by smallest	0.061/0.0122	0.073/0.0122	0.01222/0.0122
Ratio	4.98	5.98	1

So the formula is C_5H_6O.

SPREAD 4: Calculations (a summary)

Interconversion of the percentage composition by mass and the empirical formula.

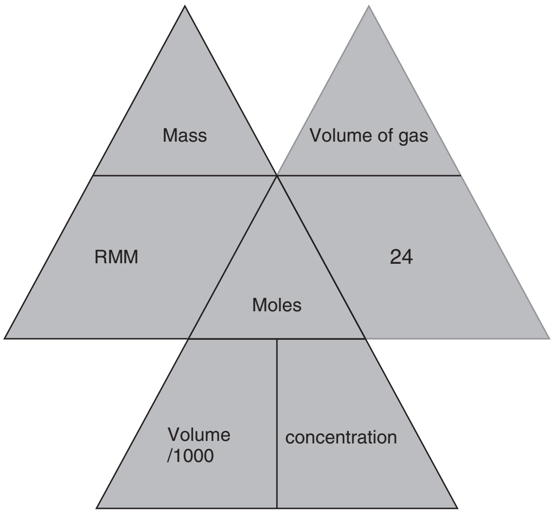
Determination of the molecular formula of a compound from its empirical formula and molar mass.

Obtaining and using experimental data for deriving empirical formulas from reactions involving mass changes.

The molar concentration of a solution is determined by the amount of solute and the volume of solution.

A standard solution is one of known concentration.

We are going to assume you know how to do the basic calculations. Instead below you will find a two-page spread summarizing the different types of mole calculations and a triangle that will help you learn.



An ability to manipulate your way around these calculations using moles as your first step is crucial to success.

SPREAD 5: Limiting reagent, percentage yield

Reactants can be either limiting or excess.

The experimental yield can be different from the theoretical yield.

Life in the real world is a little bit more complicated. For example, a manufacturer of bicycles has 120 wheels in his yard and 27 frames. How many bicycles can he make? We can all see that the answer is 27. It doesn't matter how many wheels he has. The limiting reagent is the frames. The wheels are in excess. Applying this to chemical reactions is important too, and the chemical equation tells us the ratios:

2 (Wheels) + frame ⇒ Bicycle

Easy example

5.00 g of iron and 5.00 g of sulfur are heated together to form iron (II) sulfide. Which reactant is in excess, and what is the maximum mass of iron (II) sulfide that can be formed?

$Fe + S \Rightarrow FeS$

First work out the moles of both

Iron 5/56 = 0.089 moles
Sulfur 5/32 = 0.157 moles

The limiting reagent is iron. Sulfur is in excess. The limiting reagent dictates the moles of products, so 0.089 moles of FeS is formed and so

$0.089 \times 88 = 2.75$ g

These calculations can get harder if the stoichiometry is harder.

Harder example
In the manufacture of sulfur trioxide, what mass of sulfur trioxide can theoretically be formed when 1 kg of sulfur dioxide reacts with 0.5 kg of oxygen?

$2SO_2 + O_2 \Rightarrow 2SO_3$

Here the calculation requires ratios:

Moles of SO_2 = 1/64 = 0.0156 moles
Moles of oxygen 0.5/32 = 0.0156 moles
The ratio is 2:1:2

So which will drive it here? Well, the equation says you need twice as much SO_2 as O_2. Do we have that? No, so SO_2 must be the limiting reagent.

So 0.0156 moles of SO_3 will be produced.

$0.0156 \times 128 = 2$ kg

Percentage yield calculations

In any experiment the equation tells you how much you will make of a product. A mole calculation will tell you how much you should get. In reality you never get 100% yield, all the reactants turning into products. Side reactions happen, and reagents are wasted. Many things can "go wrong."

The trick is to work out how in moles you should make and work out (in moles) how much you actually made.

So percentage yield = mass you made/you should have made × 100%

Example
Iron is extracted from iron oxide in the blast furnace as shown.

$Fe_2O_3 + 3CO \Rightarrow 2Fe + 3CO_2$

One ton of iron oxide produced 650 kg of iron. Calculate the percentage yield.

Moles of Fe_2O_3 = mass (g) = 1,000,000 = 6266 moles

RMM Iron oxide 159.6
Check the ratio 1:2

Moles of Fe = 2 × 6266 = 12,530 moles
Mass of Fe = Moles × RMM = 12,530 × 55.8 = **699 kg**

Calculate the percentage yield.

650/699 × 100% = 93%

Atom economy

Atom economy is a green chemistry premise. It looks more at the other products of a reaction made when you are trying to make something else.

It is: $\frac{\text{RMM of desire product}}{\text{RMM of all products}} \times 100\%$

Example, from above

$Fe_2O_3 + 3CO \Rightarrow 2Fe + 3CO_2$

The atom economy is 112/244 × 100 = 45%

This is a low value. If a way could be found to use the CO for some other process this would increase the atom economy. Alternatively if another method could be found that gave a higher atom economy then this would satisfy green chemistry principles a lot more. More on atom economy in the options are at the back of the book.

SPREAD 6: Gas calculations

Avogadro's law enables the mole ratio of reacting gases to be determined from volumes of the gases.

The molar volume of an ideal gas is a constant at specified temperature and pressure.

Gas calculations

As we saw in the more general spread on calculations one mole of any gas occupies the same volume as any other gas provided the temperature and pressure remain the same. This means that at 273 K (0°C) and 1×10^5 Pa (1 atmosphere) pressure one mole of any gas occupied 22.7 dm^3 (22,700 cm^3). This makes calculations easy because to work out the moles you just divided the volume of gas by 22.7.

What happens if it's not?

You need to use the ideal gas equation

$PV = nRT$

where P = pressure in Pascals
T = temperature in Kelvin
V = volume in m^3 (be careful here)
n = number of moles
R = the gas constant = 8.314 $JK^{-1}\ mol^{-1}$.

Usually the equation would be used to work out the number of moles, so the equation is changed to:

$n = PV/RT$

WATCH OUT FOR VOLUME!

Meters cubed is 10^6 centimeters cubed.

So to convert 25 cm^3 to m^3 it is 25×10^{-6} m^3.

Example
How much oxygen in grams is present in 375 cm^3 at 295 K and 1.12×10^5 Pascal pressure?

$n = PV/RT$
$1.12 \times 10^5 \times 375 \times 10^{-6}/8.314 \times 295 = 0.017$ moles
Mass $= 0.017 \times 32 = 0.5$ g

The other gas equation

This allows to see how the three quantities are affected if one is changed. It is worth having a feel for how the three factors will affect a gas.

A high pressure will squeeze a gas to a smaller volume if the temperature is kept constant.

A high temperature will expand a gas if the pressure is kept the same.

It is worth having a feel for these because a popular multiple choice question is to ask about such things. As you can see, temperature and pressure could cancel each other out.

The mathematics to this is with the equation below.

It is another favorite of the multiple choice paper as it doesn't need difficult math. Again remember that temperature and pressure must be in their standard units.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Example

If 2 dm^3 of a gas at 273 K and 1 atmosphere pressure is heated to 373 K what happens to the volume?

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Let $x = V_2$
So $1.2/273 = 1.x\,/373$

$2/273 = 0.007$
$0.007 = 1.x/373 \Rightarrow 0.007 = x/373 \Rightarrow 373 \times 0.007 = 2.611$ atmospheres.

Real gases

Wouldn't it be good if all gases worked the way the gas laws say! Unfortunately they don't. The ones that do are call ideal gases. The one that don't are called real gases. It is to do with the forces of attraction between the molecules, which can mess up the calculations. The higher the temperature and pressure the more likely that a real gas will behave like an ideal gas. This is because the forces of attraction are more likely to have been broken.

CHAPTER

3 Atomic structure

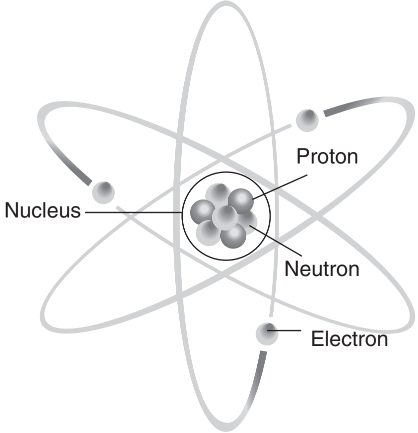
This chapter covers material from Topics 2 and 12 of the IB DP syllabus.

CORE

SPREAD 1: The nuclear atom[1]

Atoms contain a positively charged dense nucleus composed of protons and neutrons (nucleons).

Negatively charged electrons occupy the space outside the nucleus.



For the purposes of this course an atom consists of a central nucleus containing protons and neutrons (see diagram). The number of protons defines the type of atom you have. For example, any atom with six protons in is a carbon atom. The neutrons, in simplistic terms, stabilize the atom. Smaller sub-atomic particles called electrons orbit the nucleus. The table below summarizes the nature and mass of the particles.

Sub-atomic particle	**Charge**	**Mass/mass units***	**Where found?**
Proton	+1	1	Nucleus
Neutron	No charge	0	Nucleus
Electron	−1	0.0005 (negligible)	Orbiting the nucleus

* Mass units are clearly a very arbitrary measurement of the mass of these tiny particles. Really they just give you an idea of relative mass to each other. A proton's mass is actually 1.672×10^{-27} kg. A neutron weighs 1.674×10^{-27} kg, and an electron weighs 9.109×10^{-31} kg.

On the table the atomic number (Z) and the mass number/relative atomic mass (A) are listed. Your data book has the information you need. The atomic number tells you the number of protons (in a neutral atom, the number of electrons). The relative atomic mass is given with the other number (A). This is the weighted mean mass of the atom relative to 1/12th of the mass of an

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[1] January 21, 2005, 01:35 Fast fission 356×356× (14,962 bytes) *Diagram of an [[atom]] by [[User:Fastfission]].*

atom of Carbon-12. Although this a formal definition based on a calibration to a standard in more simple terms it is the mass of an atom (essentially the number of protons and neutrons). The problem is that various different versions of each element exist with different amount of neutrons. These are called isotopes.

As stated, isotopes of each element must be considered when calculating the relative atomic mass. For example, there are three isotopes of Carbon: Carbon-12 with six protons and six neutrons, Carbon-13 with seven neutrons and Carbon-14 with eight neutrons.[2] Their chemical reactions would be identical, so they occupy the same place on the periodic table, but their relative atomic mass must consider that any reaction involving carbon can/and will involve all three isotopes. The masses and abundance of each isotope can be deduced from a MASS SPECTROMETER. In old IB DP specifications you needed to know how these machines work. That is not the case anymore, but you may be asked to interpret data from a machine.

CORE
SPREAD 2: Working out RAM

The mass spectrometer is used to determine the relative atomic mass of an element from its isotopic composition.

Relative atomic mass calculations: Example 1

To calculate the relative atomic mass,

Essentially it's:

$$\frac{\left(\text{Mass of isotope A} \times \text{\% abundance of isotope A}\right) + \left(\text{mass of isotope B} \times \text{\% abundance of isotope B}\right)}{\text{Total of abundances}\left(\text{usually } 100\right)}$$

Worked example 1

Neon exists as three isotopes:

^{20}Ne abundance	90.9%
^{21}Ne	0.26%
^{22}Ne	8.8%

Work out RAM from given mass and abundances:

$(20 \times 90.9) = 1818$
$(21 \times 0.26) = 5.46$
$(22 \times 8.8) = 193.6$

Now add together and divide by the total:

$$\frac{1818 + 5.46 + 193.6}{99.96} = 20.18\,\text{gmol}^{-1}$$

Note, the total percentage does not equal 100. It is ALWAYS worth checking to ensure it does rather than making that assumption.

Worked example 2

Working out abundances from a relative atomic mass.

This is the curveball question and requires more algebraic math skill.

If chlorine has an RAM of 35.5, work out the abundances of its two isotopes ^{35}Cl and ^{37}Cl.

---

[2] Carbon actually has 15 known isotopes, but only the above 3 exist in nature.

Let the 35 isotope abundance = x

So Cl 37 abundance must be $1 - x$

Using the same equation above but with x you get $(35x) + 37(1 - x) = 35.5$

Multiplying out (like you do in math)

$$35x + 37 - 37x = 35.5$$

Then $-2x = 35.5 - 37 \Rightarrow -2x = -1.5x = 1.5/2 = 0.75 \times 100 = 75$

So ^{35}Cl abundance is 75, and so ^{37}Cl must be 25.

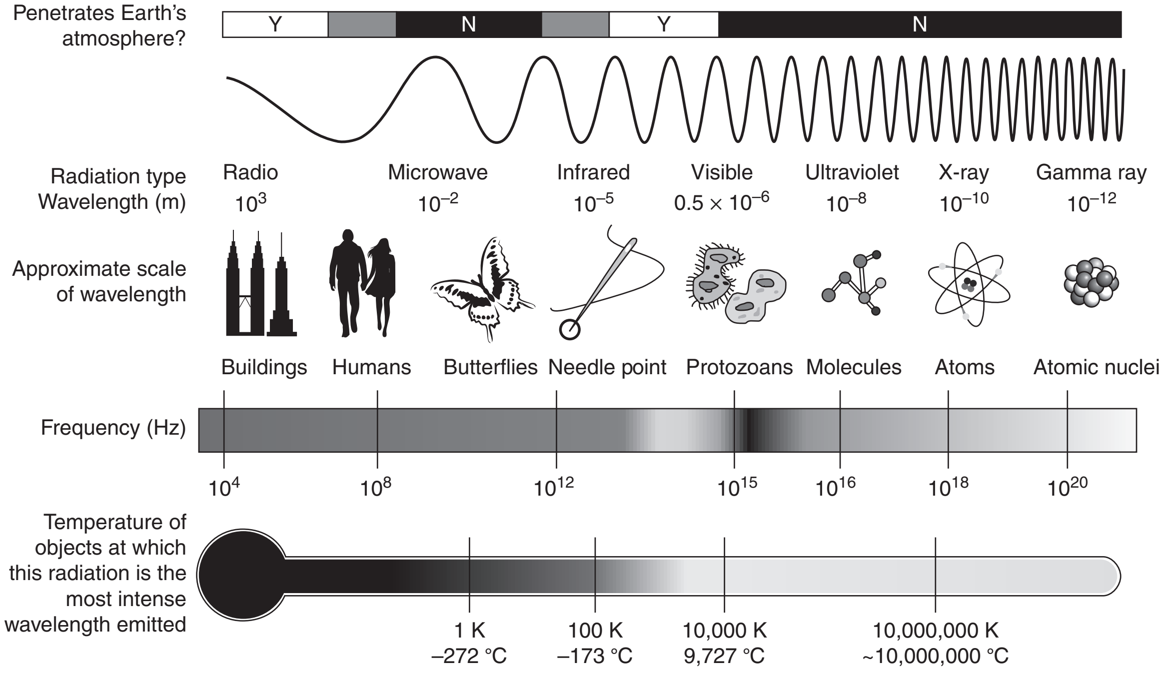
CORE
SPREAD 3: Electronic configuration

Emission spectra are produced when photons are emitted from atoms as excited electrons return to a lower energy level.

The line emission spectrum of hydrogen provides evidence for the existence of electrons in discrete energy levels, which converge at higher energies.

This is a course about chemistry, and chemistry is really all about electrons and the way they move. The IB DP course starts from first principles and wants you to understand how we know about where the electrons are in an atom. This was shown in early twentieth-century experiments involving light. To understand them you need a basic understanding of the electromagnetic spectrum.

The electromagnetic spectrum is mentioned below:[3]



It is also given in the data booklet, in Topic 3.

As you can see the electromagnetic spectrum is a chart of various electromagnetic radiation and the wavelength that they have. Visible light is in the middle with a wavelength around 10^{-6} meters. You will be familiar with a light spectrum (rainbow) with the colors merging together to form one continuous spectrum. Combined together these light waves give us white light.

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[3] By Inductive Load, NASA (GFDL [http://www.gnu.org/copyleft/fdl.html] or CC-BY-SA-3.0 [http://creativecommons.org/licenses/by-sa/3.0/]), via Wikimedia Commons.

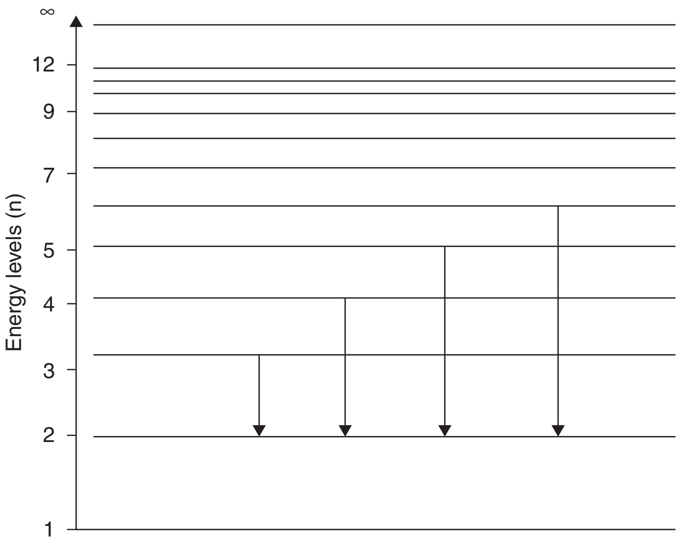
Understanding the electromagnetic spectrum is important.

A summary of the trend is below: learn!

	Frequency	**Energy**	**Wavelength**
Ultraviolet	High	High	Short
Infrared	Low	Low	Long

The secrets of the electron clouds are revealed by a different form of visible light: photons. Photons are not light waves but little packets of light energy. When elements are heated they emit energy in the form of photons—some of it visible, some in the infrared and some ultraviolet. The emission spectrum is unique to that element. It is also not a spectrum. Instead it is a series of lines. It is not continuous. Below is the visible spectrum for hydrogen.[4] Note how the lines converge toward shorter wavelengths.

The lines represent various ENERGY LEVELS in an atom. You may know these as orbitals or shells. This is where the electrons can exist in an atom. For reasons beyond the scope of this book (mathematically) electrons can only exist at certain energy levels. When an atom gets excited the electrons take the energy and use it to leap from one energy level to another. When they return back to their original level (their ground state) they have to emit the energy again. This is in the form of these photons of light with their unique frequency. Every atom has a lot of lines because every atom has lots of potential energy levels. Below is a more familiar diagram of the emission spectrum of a hydrogen atom.



It's important to understand a diagram like this (indeed you may have to reproduce it in paper 2), so look at the notes below:

- The lines converge at higher energy levels.
- The lines on this one are for the VISIBLE region, and these correspond with electrons dropping to the second energy level. ULTRAVIOLET is for $N = 1$. INFRARED for $n = 3$.
- The arrows go down to show the emission of the energy.
- Note the arrow from the ground state ($N = 1$) to infinity. This represents when an electron gets enough energy to completely escape the atom. This is known as the IONIZATION ENERGY (more later).

So: PIECE OF EVIDENCE FOR OUR MODEL OF THE ATOM 1: the emission spectrum of gaseous atoms provides evidence of electron shells.

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[4] By Merikanto, Adrignola (File:Emission spectrum-H.png) [CCO], via Wikimedia Commons.

HL
SPREAD 4: Electrons in atoms

Trends in first ionization energy across periods account for the existence of main energy levels and sub-levels in atoms.

Successive ionization energy data for an element give information that shows relations to electron configurations.

A more detailed look at where the electrons are held is required and the tool for working this out is IONIZATION ENERGY. This is defined as: *The energy required to remove an electron from one mole of gaseous atoms.* Worth learning. You will be expected to know what this means and how to write an equation for it:

$M(g) \Rightarrow M^+(g) + e^-$

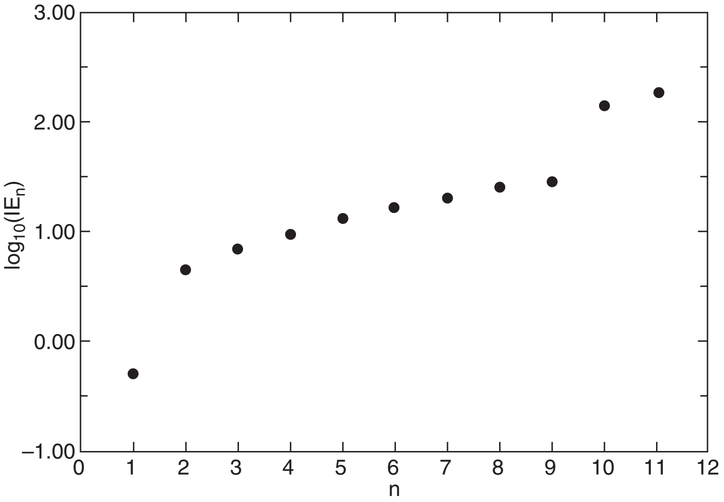
It's worth thinking of ionization energies as a hammer by which we bash open an atom to see what it's made of. The second ionization energy removes the second electron.

$M^+(g) \Rightarrow M^{2+}(g) + e^-$

Etc.

Plotting a graph of the logarithm of ionization energies (to make the numbers manageably small) (on the *y* axis against) the successive electrons (*n*) on the *x* axis and produces a very interesting graph:

Look at this graph of sodium:



- The general trend is upwards: more energy required to remove successive electrons.
- The first electron is easy to remove, there is a big jump, followed by eight electrons of a similar energy, then two more.

This can be plotted for any element's electrons, and the pattern is the same. The conclusion is that certain numbers of electrons fit into the energy levels described in the preceding section: 2, 8, 8, 18 and so on. More than that there are orbitals within each shell where pairs of electrons can live.

An orbital is defined as a region of space where there is a high probability of finding an electron.

CORE
SPREAD 5: Orbital shapes

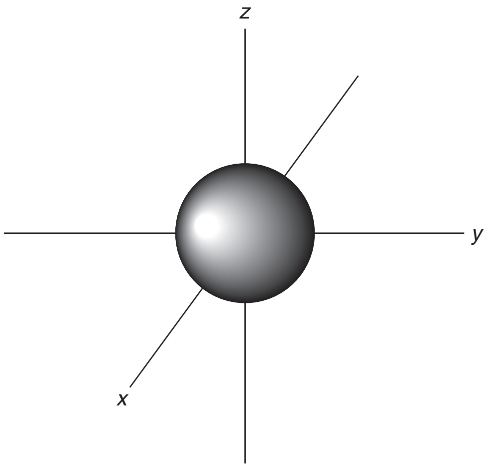
A more detailed model of the atom describes the division of the main energy level into s, p, d and f sub-levels of successively higher energies.

Sub-levels contain a fixed number of orbitals, regions of space where there is a high probability of finding an electron.

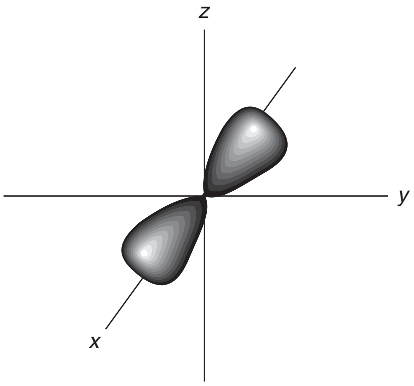
Each orbital has a defined energy state for a given electronic configuration and chemical environment and can hold two electrons of opposite spin.

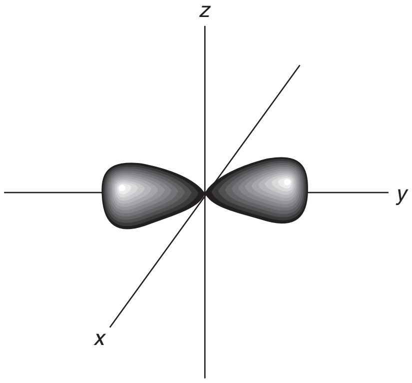
There are three types of orbital:[5]

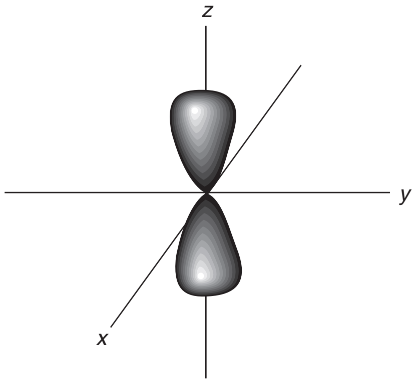
s-Orbitals. These are spherical orbitals.



p-Orbitals. Figure of eight-shaped orbitals. They come in threes, one on each axis (*x*, *y*, *z*). You would be expected to draw a sketch of p-orbitals.







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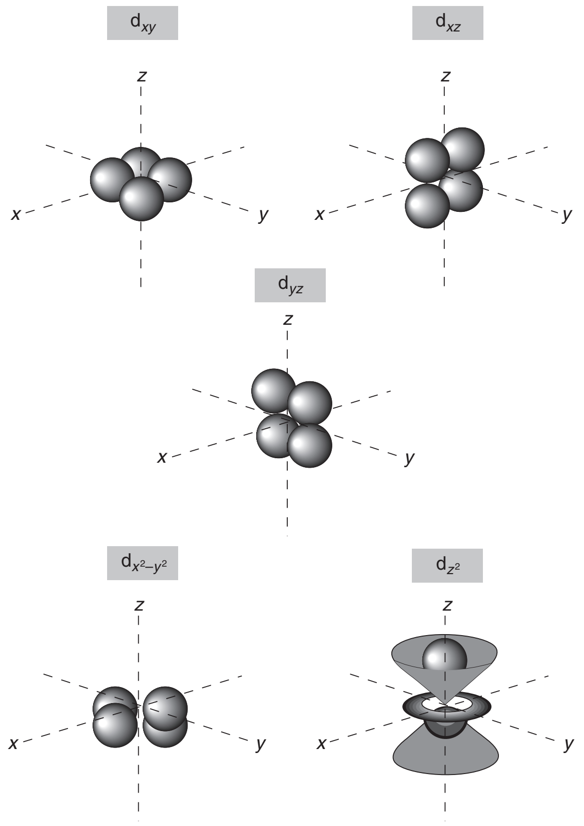
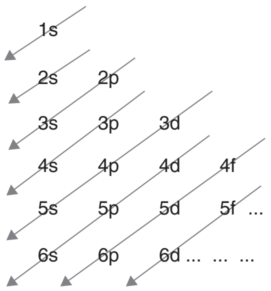
[5] SparkNotes Editors. "SparkNote on Atomic Structure." SparkNotes LLC. n.d. http://www.sparknotes.com/chemistry/fundamentals/atomicstructure/ (accessed January 14, 2014).

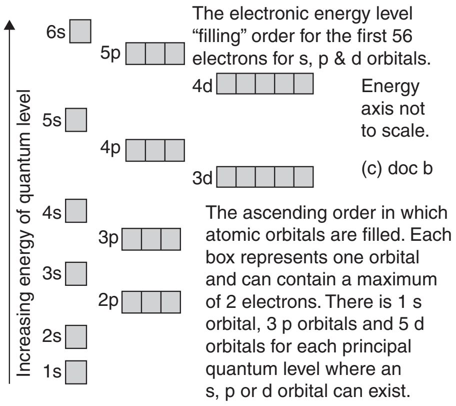
d-Orbitals. These orbitals come in five pairs. Note they have different shapes. You are not expected to remember the shapes, but if you are an HL candidate you will need to recall that there are three d-orbitals on the *x*, *y* and *z* axes and two that are not.



Where it gets interesting is that electrons in an atom fill up the orbitals in order of successive energy level, sometimes known as the Aufbau principle.



Building up



Either diagram can be used to help you write ground state configurations of atoms and ions. The trick is to remember to always follow the pattern and that the s-orbital before the d-orbital always has a lower principle quantum number.

So choose your model and practice the questions below! If you're ever stuck the best thing to do is to look at a periodic table. Memorize which part of the table is which "block," count the periods down (remember hydrogen and helium are in period 1. And work it through:
Sodium: Element 11, so it's:

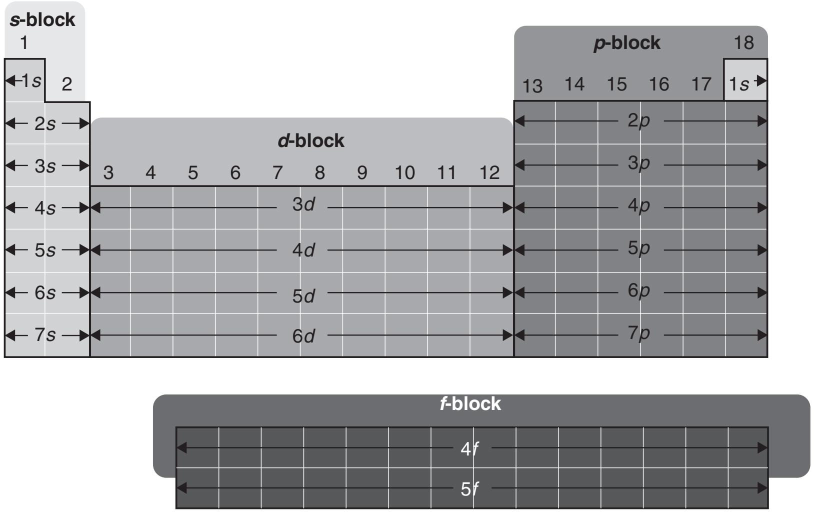
$1s^2\ 2s^2\ 2p^6\ 3s^1$

Bromine: Located below it is in the p-block, period 5, so it must end $5p^5$, all you have to do is work up to it from the start.

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^5$

Ions can also be shown:

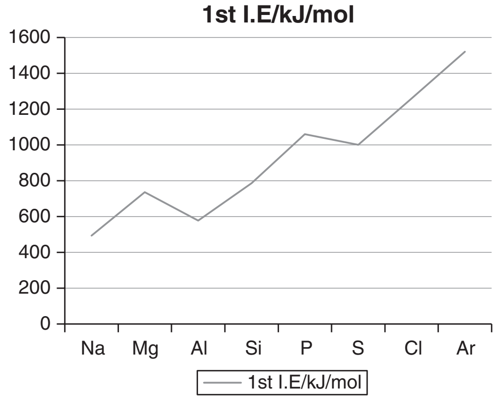
The Oxide ion has two more electrons than the oxygen atom.
Oxygen is $1s^2\ 2s^2\ 2p^4$
Oxide is $1s^2\ 2s^2\ 2p^6$



HL
SPREAD 6: Electrons in atoms

In an emission spectrum, the limit of convergence at higher frequency corresponds to the first ionization energy.

So, we've seen how successive ionization energies can show us the existence of general shells, but ionization energy can also show us the different s-, p- and d-orbitals. Look at the graph below:



You should be able to interpret this trend, but we will deal with this more in Chapter 3. At this stage look at the patterns: 2, 3, 3, suggesting an s-orbital and a p-orbital (putting the second electron into an orbital already occupied, orbital means there is a dip because the repulsion means the electron is easier to remove).

How do we actually calculate first ionization energy?

One of the great unanswered questions students often have about chemistry in this topic is how does ionization energy get calculated? The idea of an experiment with gaseous sodium atoms and knowing electrons off seems rather bizarre. The simple answer is that it isn't done this way. It's done using mathematics.

The link is this equation:

$E = hf$

Or sometimes:

$E = hc/\lambda$

Where:

E = energy
h is the Planck constant 6.6×10^{-34}
c is the speed of light 2.998×10^{8}

Both are in your data book.

Both can be used to work out ionization energy. The most likely scenario is to use data that gives you the convergence of the lines on a spectrum, which would constitute the ionization energy.

For example, the Lyman series with hydrogen can be used to work out the ionization energy of the hydrogen electron:

n	2	3	4	5	6	7	8	9	10	11	∞
Wavelength (nm)	121.6	102.6	97.3	95.0	93.8	93.1	92.6	92.3	92.1	91.9	91.18 (Lyman limit)

So the Lyman limit here is the wavelength of light corresponding to the removal of an electron.

So multiply Planck's constant by the speed of light/wavelength $\times 10^{-9}$ multiplied by Avogadro's number gives you the ionization energy.

Example:

$E = hc/\lambda$
$6.6 \times 10^{-34} \times 3 \times 10^{8}/91.18 \times 10^{-9}$
$= 1.98 \times 10^{25}/91.18 \times 10^{-9} = 2.12 \times 10^{-18}$
$2.12 \times 10^{-18} \times 6.02 \times 10^{23} = 1{,}307{,}260\ \text{Jmol}^{-1}$ or $1307\ \text{kJmol}^{-1}$

CHAPTER

4

Chemical bonding and structure

This chapter covers the material in Topics 4 and 14 of the IB DP syllabus.

CORE
SPREAD 1: Structure, an overview and metallic bonds

A metallic bond is the electrostatic attraction between a lattice of positive ions and delocalized electrons.

The strength of a metallic bond depends on the charge of the ions and the radius of the metal ion.

Alloys usually contain more than one metal and have enhanced properties.

Overview

Essentially this is a topic that is about covalent bonding, but before we get there we need to look at the bigger picture.

There are two types of structures:

Giant and molecular.

Giant structures are made of millions of atoms or ions held together in a giant lattice. To melt them you need to break every single bond in that lattice. This takes a lot of energy, and so melting points of giant structures have high melting points. Their chemical formula is the simplest ratio of atoms/ions in the lattice.

Molecular structures are finite, discreet structures that "stop." They have low melting points because when you melt a molecular substance you do not break the molecule down, but break the weak forces of attraction BETWEEN the molecules. These require much less energy to break. The formula of a molecule is the absolute number of each atom in the molecule.

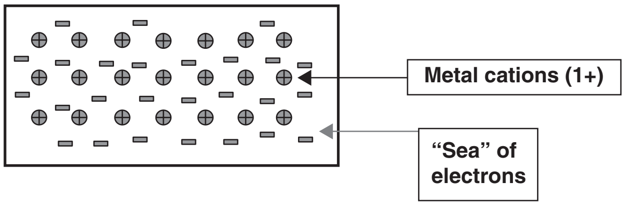
The two types of structure above have various types of bonds holding them together depending on the type of atom or ion the structure is composed of.

Introduction to bonding: Giant structure (1) the metallic bond

Metallic bonding occurs in metals and alloys (mixtures of metals). It is defined as metal cations surrounded by a sea of electrons. The valence (outer) shell electrons of metals are held less tightly than in non-metals. This allows them to delocalize and move through the lattice. The attraction is between these electrons and the metal ions left behind.

Often explanations ask for a diagram. An example is below. Try and get your metal cations in an ordered solid arrangement.

Metallic bonding is non-directional because the attraction is in all directions in the lattice.



Metals have a giant structure and have high melting points because of that. The melting point will depend on the nature of the metal cation. The smaller and higher the charge on the ion the higher the melting point. This is well illustrated by the first three metals of period 3:

Na Mg Al

Aluminum is a small 3^+ ion, so the attraction to the sea of electrons is much greater than the larger 1^+ ion of sodium. If you can't remember why aluminum ion is smaller than sodium an explanation is provided in the next chapter.

Properties of metals

Metals are very good conductors of electricity, because of the delocalized electrons. They can conduct electricity in any direction because the electron cloud is directionless.

Metals are malleable (easily bashed into another shape) because the delocalized electrons allow the layers of metal ions to slide over each other without destroying the metallic bonding. The cloud is still there.

Alloys

Alloys are mixtures of metals to get metals with better properties than the ones that naturally occur. Examples include various steels, which can make iron stronger or more resistant to corrosion, and brass (copper and zinc), which has many applications due to its similar look to gold, its acoustic properties (musical instruments) and its lack of friction (keys and pipes). It also doesn't produce sparks with friction, so it is popular for gas pipes. Solder is an alloy of tin and lead that is used for electric circuit joining. Alloys are often stronger than their component metals because the different sizes of the metal ions to each other disrupts the metallic bonding. Where metal ions of the same size can slide over each other, in alloys this is not the case. Electrical conductivity is less likely to be affected.

CORE
SPREAD 2: Ionic bonding and structure

Positive ions (cations) form by metals losing valence electrons.

Negative ions (anions) form by non-metals gaining electrons.

The number of electrons lost or gained is determined by the electron configuration of the atom.

The ionic bond is due to electrostatic attraction between oppositely charged ions.

Under normal conditions, ionic compounds are usually solids with lattice structures.

What are ions?

Let's just make sure we know what ions are. They are charged atoms, and they are formed when atoms gain or lose electrons. It is very easy to discuss this in simplistic terms gained from prior studies. You know atoms get happy when they have a full outer shell, so atoms "want" to gain or lose electrons to do this. Although this isn't a bad way of thinking about it you should avoid writing it down under exam conditions.

Positive ions have lost electrons and have the nearest noble gas electronic configuration. The fancy name for a positive ion is a cation (more about this in Chapter 10). Negative ions have gained electrons to reach the nearest noble gas configuration. The fancy name is an anion. The charge on the ion is dependent on how many electrons need to be gained or lost to get the noble gas configuration.

For example, aluminum has three electrons in its third shell; the aluminum ion loses three electrons to have the same electronic configuration as neon, so forming an Al^{3+} ion.

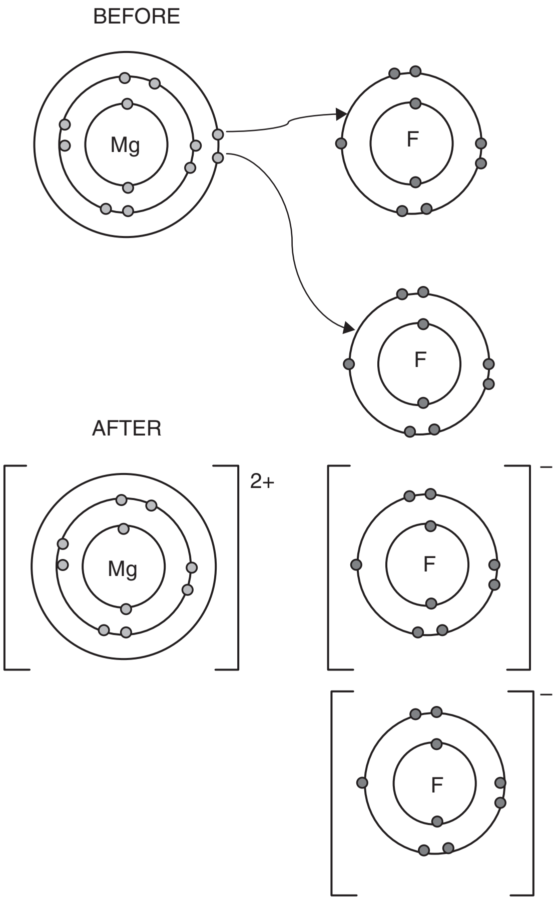
Ionic compounds

An ionic compound is formed with ions of opposite charges. The structure is held together by the electrostatic (means non-moving electric charges) attraction between these oppositely charged ions.

Given that ionic compounds have a giant lattice structure the melting point is very high (see table below). They also conduct electricity if melted or dissolved in water. For a substance to be able to conduct electricity it must have free moving charged particles. A giant ionic structure has charged particles (the oppositely charged ions) but they cannot move, so solids do not conduct electricity. However, once melted or dissolved the ions are free to move and so conduct electricity. Ionic bonds are known as non-directional because the ionic attraction is in all directions in the lattice.

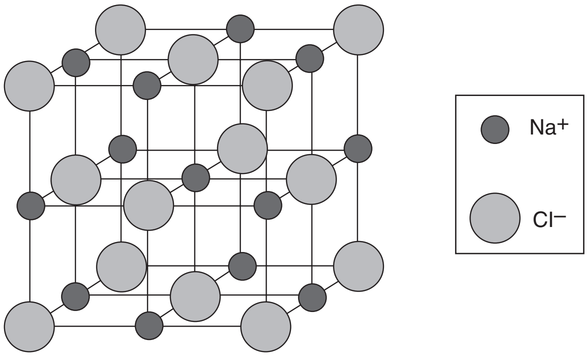
It is VITAL that any answer discussing the properties of ionic substances ONLY has the word IONS in it. Any mention of atoms or electrons in your explanation is likely to mean your answer gains no marks at all. The clue is in the name: ionic–ions.

You should be able to draw an ionic structure. A good example is magnesium fluoride:



The ionic lattice

Ionic bonding does not take place in isolation, and an ionic bond on its own doesn't exist. A giant ionic lattice consists of millions of ions all attracting and repelling each other. Look at the sodium chloride lattice example mentioned below.



CORE

SPREAD 3: Writing formulae from ions

You should be expected to work out the formula of an ionic compound given the ions in the structure. There is a simple trick to it (see below); however, you must also be familiar with the formulae of some polyatomic ions (ions with more than one atom). The ions mentioned in the syllabus are:

Ammonium	NH_4^+
Hydroxide	OH^-
Nitrate	NO_3^-
Hydrogen carbonate	HCO_3^-
Carbonate	CO_3^{2-}
Sulfate	SO_4^{2-}
Phosphate	PO_4^{3-}

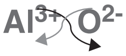
No short cuts, these need to be learned.

To work out the formula of ionic compounds you can simply swap the ion charges around:

So: Magnesium chloride

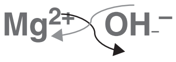
$$Mg\ Cl_2$$

Aluminum oxide



$$Al_2O_3$$

Magnesium hydroxide



$$Mg(OH)_2$$

And, the horrible ammonium sulfate

$$(NH_4)_2SO_4$$

Now practice with these examples

1 Sodium chloride
2 Sodium hydroxide
3 Sodium carbonate
4 Sodium sulfate
5 Sodium phosphate
6 Potassium chloride
7 Potassium bromide

8 Potassium iodide
9 Potassium hydrogen carbonate

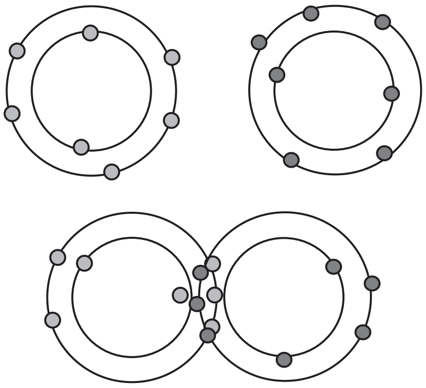
CORE
SPREAD 4: Covalent bonding

A covalent bond is formed by the electrostatic attraction between a shared pair of electrons and the positively charged nuclei. Lewis (electron dot) structures show all the valence electrons in a covalently bonded species. • The "octet rule" refers to the tendency of atoms to gain a valence shell with a total of eight electrons. • Some atoms, like Be and B, might form stable compounds with incomplete octets of electrons.

What is a covalent bond?

A covalent bond is formed by the electrostatic attraction between a shared pair of electrons and the positively charged nuclei. The crucial part of this is that the bond is formed from a SHARED **PAIR** OF ELECTRONS. Covalent bonds are directional because they do point specifically between the two nuclei of the covalent bond. Generally covalent bonds are found in non-metal structures.

The covalent bond should be drawn showing an overlap of the two valence electron clouds. A difficult example is N_2, a nitrogen molecule.



Properties of covalent bonds

Covalent bonds are usually found in molecules. These are discrete structures and stop. Covalent bonds are between atoms and can form single, double and triple covalent bonds involve one, two and three shared pairs of electrons respectively.

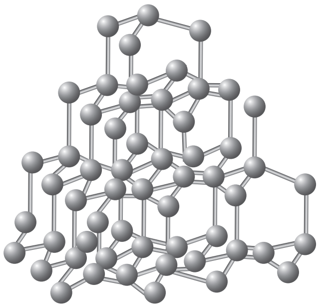
In general covalent compounds have low melting points, although there are few exceptions. The reason is that molecules are not giant structures and you DO NOT BREAK THE COVALENT BONDS. Instead you break the weak intermolecular forces between the molecules (see later on in this chapter). The best way to remember that is to think of water boiling. The steam is not hydrogen and oxygen is it? It's still water. Covalent substances do not conduct electricity because there are no charged particles.

The octet rule

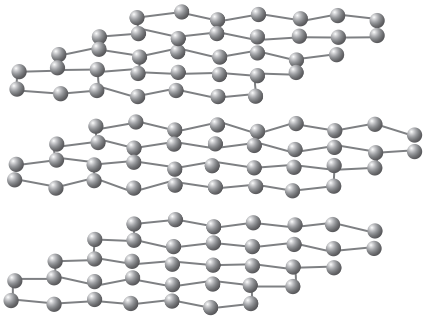
The "octet rule" refers to the tendency of atoms to gain a valence shell with a total of eight electrons. As a general rule it applies nicely but, as with many things in chemistry, the rule does have some exception. Some atoms, like Be and B, might form stable compounds with incomplete octets of electrons. Other elements like sulfur and phosphorus have vacant 3d orbitals that can be used in some circumstances. This means that phosphorus can form compounds like phosphorus pentachloride PCl_5. Here phosphorus has ten electrons in the outer shell, and we say that phosphorus has "expanded its octet."

CORE
SPREAD 5: Giant covalent structures

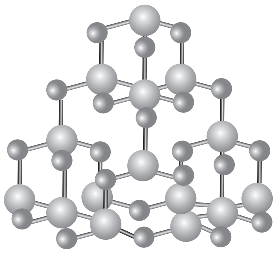
Carbon and silicon form giant covalent/network covalent structures.
There are (for the purposes of the IB syllabus) three covalent structures that are not molecular in structure. They have a giant structure. They have in common that they are group 4 elements. They are:



Diamond



Graphite



Silica

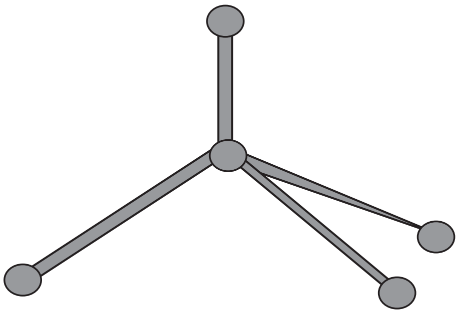
They have high melting points because in this giant structure you do have to break all the covalent bonds, which takes a lot of energy.

Allotropes of carbon

Diamond and graphite are allotropes of carbon. Allotropes are different versions of the same elements with a different structure. There are actually three allotropes:

Diamond

Diamond is a very hard, crystalline structure. The structure is very difficult to break down. Each carbon is bonded to four others in the classic tetrahedral shape (see the shape section of this chapter). You might be asked to draw the repeat unit. It looks like this:



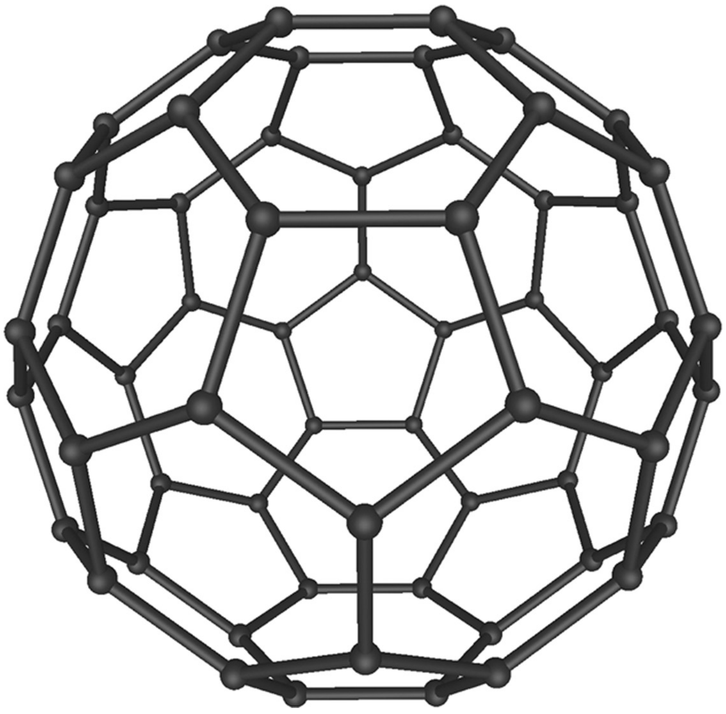
It combines together to form the lattice structure in the diagram above.

Graphite

Graphite is different. It is a series of sheets of carbon atoms in a hexagon arrangement. Each carbon here is joined to three others, despite there being four electrons available for bonding. This leaves one free (delocalized) electron. This electron can move along the sheets allowing the structure to conduct electricity along the plane of the hexagons. The hexagon layers are held apart by weak forces of attraction. This allows the layers to slide. Graphite is a good lubricant and is used in pencils. Again you should be able to draw the structure, so practice it.

Graphene

Graphene is the current name for the recently discovered MOLECULAR form of carbon. C60 has the shape of a soccer ball and is sometimes known as a Bucky ball. As a molecule it will have a lower melting point than the other two allotropes. The bonding is similar to graphite, with three bonds in a hexagonal structure, and a spare electron. This allows the molecule to conduct electricity within itself. It has been speculated that the spherical nature of the molecule allows it to have similar lubricant qualities as graphite.

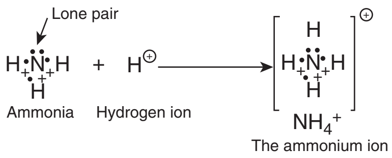


CORE
SPREAD 6: Dative covalent bonding and a summary of bond types

Dative covalent bonding

A dative covalent bond is one where the pair of electrons comes from the same atom:

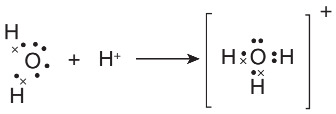
The most famous example is with the ammonium ion. As you can see from the diagram ammonia has a pair of electrons not used in bonding. This is known as a LONE PAIR. It can be used to form a dative covalent bond.



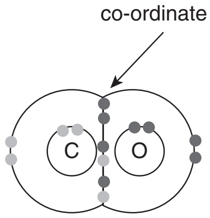
You need to ensure you use a dot and cross diagram properly to illustrate that you know the electron comes from the same atom.

Other examples of dative covalent compounds are:

H_3O^+: more of this in the acids and bases chapter.



Carbon monoxide (CO)



A summary of bond types and structures

Structure	**Giant**			**Molecular**
Bonding type	**Metallic**	**Ionic**	**Covalent**	**Covalent**
Definition	Metal cations in a sea of electrons	Electrostatic attraction between oppositely charged ions	Shared pair of electrons	Shared pair of electrons
Example	Iron	Sodium chloride	Diamond, graphite, silicon dioxide	Methane (CH_4)
Melting point	High melting point	High melting point	High melting point	Low melting point
Conduct electricity	Conduct electricity (free electrons)	Conduct electricity only when molten or dissolved (ions free to move)	Only graphite conducts (free electrons along the plane of the hexagon structure)	Do not conduct electricity
Strength	Malleable, ions can slide over	Brittle, ionic lattice has not leeway to move	Diamond: Hard, atoms held tightly Graphite can slide as layers slide over each other	
Solubility	Insoluble	Soluble in water	Insoluble in water	Soluble in non-polar solvents

CORE

SPREAD 7: Further covalent bonding

Single, double and triple covalent bonds involve one, two and three shared pairs of electrons respectively.

Bond length decreases and bond strength increases as the number of shared electrons increases.

Bond polarity results from the difference in electronegativities of the bonded atoms.
As stated earlier this topic is mainly about covalent bonding, so let's get stuck in.

Bond length and bond strength

This is simpler: Double bonds are stronger than single bonds, and triple bonds are stronger than double bonds, but the nature of the formation of these bonds means that the length of the covalent bond decreases as you increase the number of bonds:

Bond (Carbon)	**Bond enthalpy (kJmol^{-1})**	**Bond length (nm)**
C–C Single	348	0.154
C=C double	612	0.134
C≡C triple	837	0.120

You will have noted that the double bond is not twice as strong as the single. Again there are some good reasons for this in the HL section. At this stage though the TREND is all that matters.

Bond Polarity

As my old chemistry teacher used to say: chemistry isn't a black and white subject, it's mucky shades of grey. And never more is this true than with bonding, as we corrupt the covalent model, but there are incongruities to be addressed. One is that despite the lack of free charged particles in molecular covalent molecules some do conduct electricity: water being the obvious example.

The reason for this is because of an ELECTRONEGATIVITY difference.

Let's define electronegativity: "The ability of an atom to attract an electron pair in a bond." Depending on the effective strength of the nuclear charge some atoms are able to attract electron pairs. The effective nuclear charge will be high if the atom is small, has little shielding and has a high nuclear charge. See the next chapter for more on this. The most electronegative elements are in order:

FONClBrIS

A full list is in the data book.

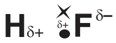
This is a nonsense word, but it's worth remembering. It is important that when you look at a molecule you know if one of these elements is in it, because if one is then it will make a difference.

An element with high electronegativity value will attract electron pairs better than other elements. At the extreme end a compound containing the most electronegative element (F) and the least electronegative (the one least good at attracting electrons [Cs]) will be ionic. In fact any compound with huge electronegativity values will be ionic. In covalent compounds an electronegativity difference can have a more subtle effect.

If there was no electronegativity difference a molecule like HF would have the bonding pair of electrons in the middle between the two atoms.

But because fluorine has a greater electronegativity value than hydrogen the pair of electrons is closer to the fluorine.

This causes a dipole to exist in the bond, and potentially across the molecule. This can be shown in a variety of ways:



This can also be represented as an arrow. The lower case delta simply means a small charge.

Any bond with an electronegativity difference will have a dipole. The bigger the electronegativity difference the bigger the dipole. A bond with a dipole like this is said to be polar.

CORE and HL
SPREAD 8: Shapes of molecules

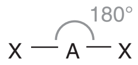
Shapes of species are determined by the repulsion of electron pairs according to VSEPR theory.

Valence shell electron pair repulsion theory

The shape of a covalent molecule depends on the number of electron domains around a central atom. Your teacher may have used the term "charge center," but the IB prefers electron domain. Essentially pairs of electrons repel, and trying to get as far away as possible from each other gives each molecule its own shape. Annoyingly the IB course puts some of the shapes in the core course and some in the HL course. This section will cover both, but if you are a standard level chemist do make a note of the ones you need to know.

Essentially there are five possible shapes for molecules and ten corruptions of these shapes because lone pairs repel more but aren't bonds, so creating new shapes:

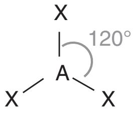
Two electron domains (two bond pairs)



AX_2
Linear

Examples are $BeCl_2$ and CO_2. Note that carbon dioxide has double bonds, but double (and triple) bonds repel the same as single bonds.

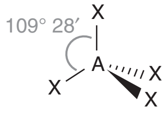
Three electron domains (three bond pairs)



AX_3
Trigonal planar

Bond angle reduces as more electron domains appear. Examples here include BCl_3 and alkenes where there is a double bond. Another classic example is the CO_3^{2-} (more on this later).

Four electron domains (four bond pairs)

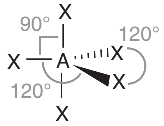


AX_4
Tetrahedral

In a 2-d world 90° would be the next shape, but molecules can go into 3-d and this is the result. The bond angle of 109.5 is very important to learn. Also practice drawing the tetrahedral shape with the correct wedges. Any single bonded organic molecule will be tetrahedral (so CH_4).

HL shapes

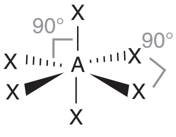
Five electron domains (five bond pairs)



AX_5
Trigonal bipyramidal

This one brings in the idea of two different bond angles in one molecule. Essentially it is trigonal planar with two electron domains on the *y* axis. PCl_5 is a common molecule with this shape.

Six electron domains (six bond pairs)



AX_6
Octahedral

The octahedral shape is seen with complex ions (see the next chapter). Also SF_6.

CORE and HL
SPREAD 9: How do lone pairs affect the shapes of molecules?

Lone pairs cause corruption of these basic shapes:

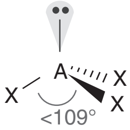
A simple truth is that lone pairs repel more than bond pairs, and this affects the shape in two ways. Firstly, the lone pairs repel just like any electron domain, but more so. Secondly, they also have no substance, so the shape is not the same.

Three electron domains (two bond pairs, one lone pair)

AX_2E_1
Bent or Angular

Here the third domain is a lone pair. It reduces the bond pair and has no presence, merely an influence. This gives us a shape known as "bent" or v-shaped. As a general rule lone pairs reduce the bond angle by 2°, so writing 118 for a bond angle here will be marked correct, although there is a lot of variation in molecules. The famous example is SO_2 (more below).

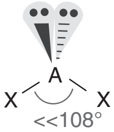
Four electron domains (three bond pairs, one lone pair)



AX_3E_1
Trigonal pyramidal

Again one lone pair electron domain decreases the bond angle and causes the shape to change to trigonal pyramidal. Subtracting 2° gets you 107. The classic molecule is ammonia.

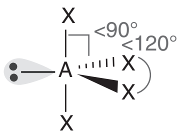
Four electron domains (two bond pairs, two lone pairs)



AX_2E_2
Bent or Angular

Two lone pairs cause over 4° worth of angle change, so the bond angle in this bent molecule is about 105°. This is also called bent, and water is the famous example.

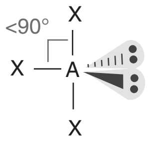
Five electron domains (four bond pairs, one lone pair)



AX_4E_1
Sawhorse or Seesaw

This one is called seesaw or distorted tetrahedral. SF_4 is the example.

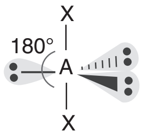
Five electron domains (three bond pairs, two lone pairs)



AX_3E_2
T-shape

This is called t-shaped and ClF_3 is your example.

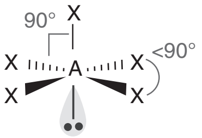
Five electron domains (two bond pairs, three lone pairs)



AX_2E_3
Linear

The examiners' favorite, the linear molecule here (XeF_2, I^{3+}, ICl^{2-}).

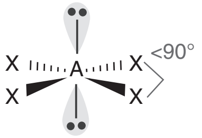
Six electron domains (five bond pairs, one lone pair)



AX_5E_1
Square pyramidal

BrF_5 this is known as square pyramidal. The 90° angle of the square down a few degrees from the 90.

Six electron domains (four bond pairs, two lone pairs)



AX_4E_2
Square planar

Square planar XeF_4.
CONFUSED? Look at the next spread.

CORE and HL
SPREAD 10: How to work out the shape of a molecule?

You will notice that it could get very easily lost with all the detail of shapes on the previous spreads. My advice is to remember the basic shapes, the names of the corrupted shapes and the −2 degree rule for lone pairs. Then use the method below to classify the molecule given to the right shape.

Easy example: Ammonia NH_3

1) What group is the central atom in? 5
2) How many bonds? (Look at the formula.) 3
   5 − 3 = 2.

This number gives you the number of spare electrons. 2 = 1 lone pair. So ammonia has three bond pairs and one lone pair: that is, trigonal pyramidal.

It also works for weirder examples:

ClF_3

Cl is in group 7.

There are three bonds.

7 − 3= 4: 2 lone pairs.

So 3 BP, 2 LP = T-shaped.

The method also works for ions:

ICl^{2-} ion

Iodine is in group 7. There are two bonds, 7 − 2 = 5, then add the extra electron from the—charge = 6 (3 LP).

Two bonds and three lone pairs = linear.

NH_4^+ nitrogen is in group 5 − 4 bonds = 1.

Remove the electron (as it is a positive ion) = 0 lone pairs.

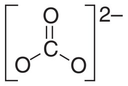
Tetrahedral.

Exceptions

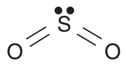
The IB likes to choose obscure molecules, and learning them all is impossible. The best things to do are to use this method but LEARN SOME EXCEPTIONS. They are mentioned below.

The exceptions are molecules with double or triple bonds. Some have been mentioned above:

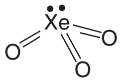
The carbonate ion has one double bond and is trigonal planar.



SO_2 has one double bond and is bent 118°.



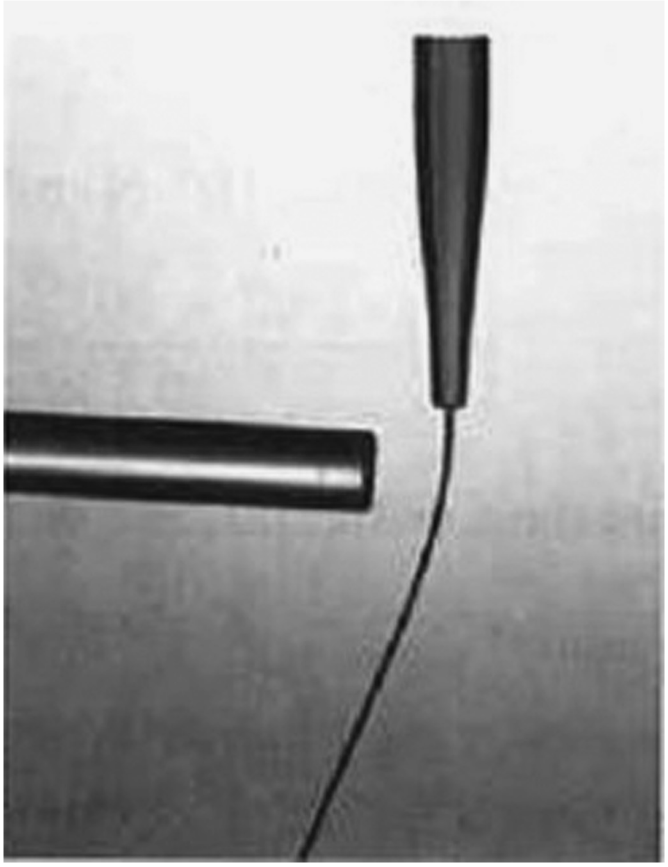
XeO_3, this has three double bonds and one lone pair, so four electron domains, one of which is a lone pair. It is trigonal pyramidal structure (107).



CORE
SPREAD 11: Molecular polarity

Bond polarity results from the difference in electronegativities of the bonded atoms.

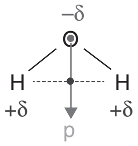
Molecular polarity



Your teacher may have demonstrated how a stream of some liquids from a burette can be deflected by a charged rod. This is a property of a polar molecule. We have seen that polarity in a BOND is due to a dipole moment caused by the electronegativity difference between the atoms in a bond. It is not the only factor however. The shape of the molecule is also a factor. If the shape of the molecule causes dipoles to cancel out then the molecule will not be polar.

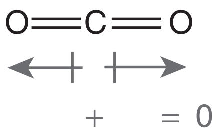
Examples:

Water



Water is bent; therefore, the dipoles do not cancel out. The molecule is polar.

Carbon dioxide



Here the molecule is linear; the two dipoles cancel out, and the molecule isn't polar despite the dipoles.

The best thing to do is always work out the shape of the molecule and check if the dipole applies to the whole molecule or not.

CORE
SPREAD 12: Intermolecular forces

Intermolecular forces include London (dispersion) forces, dipole–dipole forces and hydrogen bonding.

The relative strengths of these interactions are London (dispersion) forces < dipole–dipole forces < hydrogen bonds.

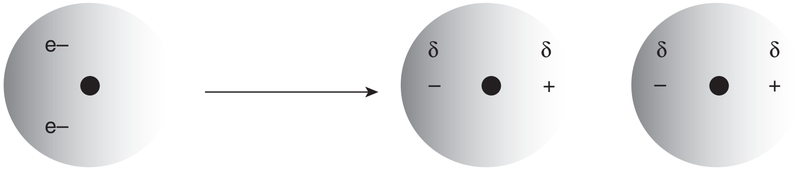
What are intermolecular forces?

In molecular structure (and a few giant structures) there are forces of attractions between the molecules. These are the glue that will bind the molecules to each other in solid structures. The strength and origin of these forces are detailed below.

London forces

Between structures made of unreactive atoms (like the noble gases) and molecules there are instantaneous induced dipole forces known as London forces. These have often been falsely taught as van der Waals forces, but these refer to many more forces than just these. The more correct term is London forces.

Below is a diagram of two atoms of helium (the simplest structure). At any stage the helium electrons could be on one side of the atom (diagram 2). When this happens there is a tiny dipole between the electron cloud and the nucleus. This tiny dipole could then induce a dipole in a neighboring helium atom. As you can imagine these forces of attraction are very weak, and helium has an extremely low melting point.



Instantaneous uneven distribution of electrons in He atom

Instantaneous dipole

Induced dipole on neighboring He atom. Resultant attractive force

However, London forces can become much stronger. The more electrons in the molecule the greater this induced dipole can be. The greater the London forces the stronger the forces of attraction between molecules and the greater the melting point.

A good example is with the melting/sublimation points of the halogens.

Halogen	Melting point (°C)	RMM
F_2	−220	38
Cl_2	−101	71
Br_2	−7	160
I_2	+114	254

As the RMM increases, along with the number of electrons so increases the melting point. This can also affect isomers of organic molecules (see Chapter 10 for more details).

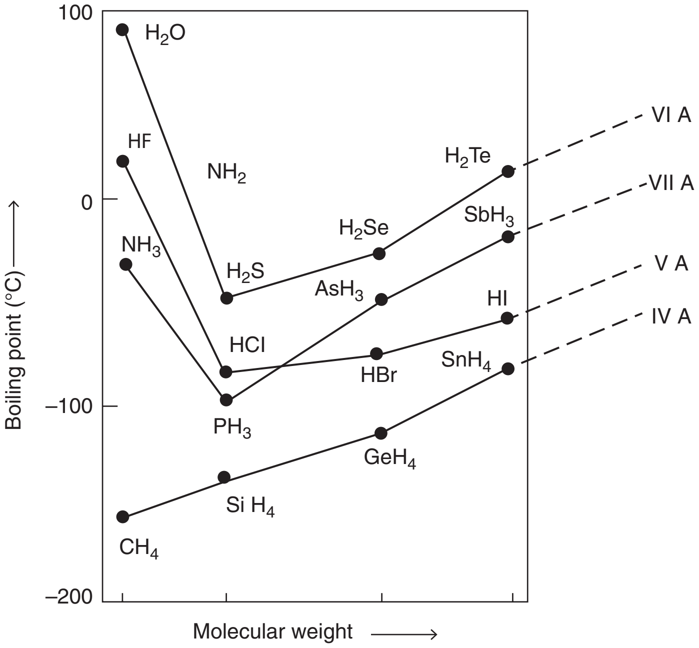
Dipole–dipole interactions

Dipole–dipole interactions are forces of attraction that also appear in molecules that are polar. In a polar molecule (example) there is a permanent dipole built into the molecule. This permanent dipole can have a more substantial attraction to a neighboring molecule. Dipole–dipole interaction molecules will have higher melting points than molecule with similar RMM with only London forces.

Look for a FONCIBrIS element attached to a molecule with lower electronegativity.

Hydrogen bonds

You'll have seen the graph below, but it is an important one.



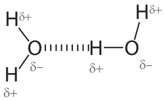
(b) Boiling point curves of hydrides of IV, V VI and VII group elements.

The general trend is of course upwards. This is because of the increased London forces as the molecular size increases. What London forces cannot explain are the very high melting points of the compounds NH_3, HF and H_2O, which have much higher boiling points. It illustrates the huge effect hydrogen bonds have on the melting points of covalent molecules.

A hydrogen bond is a special type of dipole–dipole interaction, a beefed up force of attraction if you prefer. For a molecule to display hydrogen bonding the molecule needs to have the following:

- The elements F, O or N.
- These elements must be joined to a hydrogen atom.
- There must be available lone pairs.

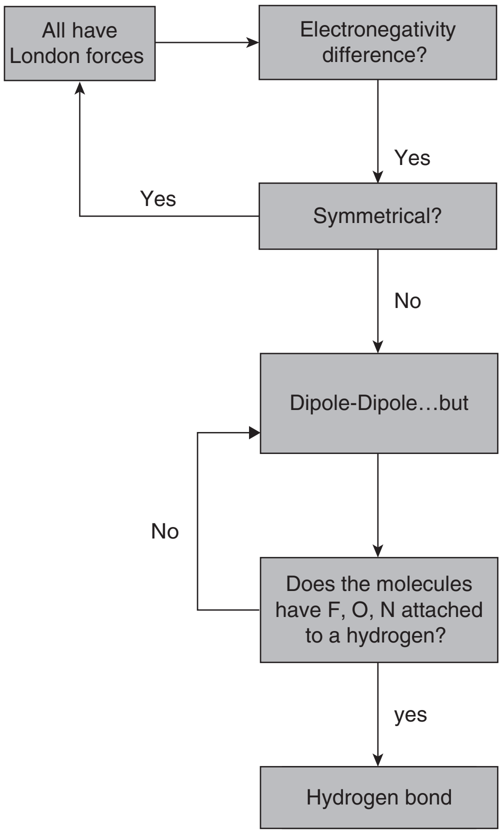
This produces the perfect storm for forces of attraction. Fluorine, oxygen and nitrogen are the three most electronegative elements. This causes the biggest dipole in a molecule. This big dipole causes the δ+ hydrogen to be very attracted to the lone pair on the F, O or N, causing a very strong attraction. See the diagram below.



When asked to illustrate a hydrogen bond make sure you have included the dipoles, the lone pair and the hydrogen bond, typically drawn with a dotted line, is in line with the lone pair and the covalent bond on the opposite molecule.

CORE
SPREAD 13: More on intermolecular forces

You will be expected to be able to identify the intermolecular forces in any molecule given to you.



Effect of intermolecular forces on physical properties

The strength of the intermolecular forces will affect various physical properties. They are detailed below:

Volatility

Volatile means turns into a gas easily and is a simple measure of the strength of the intermolecular forces. Those with only London forces will be more volatile than molecules of comparable RMM with stronger forces of attraction.

Electrical conductivity

Although I-M forces will not affect this, the molecule will conduct electricity if the molecule is polar, that is, it has a dipole and the shape allows the dipole to affect the whole molecule.

Solubility

In very simple terms: like dissolves like. So a substance with London forces will dissolve in a solvent with comparable forces. Hexane is a good solvent for such substances. Substances with hydrogen bonds will prefer to dissolve in a solvent with hydrogen bonds (water). This is because the forces of attraction involved with dissolving means that the forces of attraction must form between the solvent and the solute.

There are some exceptions, and it occurs in big molecules. This will be covered in more detail in the organic chemistry section, but for now a molecule containing the right ingredients for hydrogen bonding may not actually dissolve in water if the London forces overwhelm the hydrogen bond attraction. This is best illustrated with the alcohols homologous series.

CORE and HL
SPREAD 14: Resonance structures

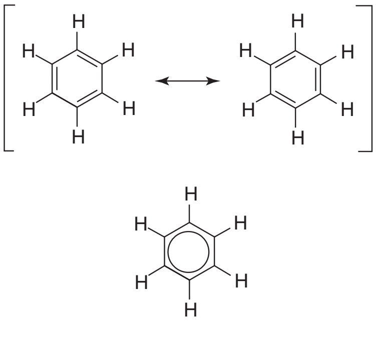
Covalent bonds result from the overlap of atomic orbitals. A sigma bond (σ) is formed by the direct head-on/end-to-end overlap of atomic orbitals, resulting in electron density concentrated between the nuclei of the bonding atoms. A pi bond (π) is formed by the sideways overlap of atomic orbitals, resulting in electron density above and below the plane of the nuclei of the bonding atoms.

Resonance involves using two or more Lewis (electron dot) structures to represent a particular molecule or ion. A resonance structure is one of two or more alternative Lewis (electron dot) structures for a molecule or ion that cannot be described fully with one Lewis (electron dot) structure alone.

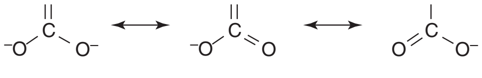
What is a resonance structure?

Resonance structures occur when there is more than one possible position for a double bond in a molecule. The most famous examples (and the ones given in the syllabus are):

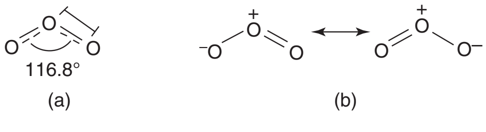
Benzene (diagram)



The carbonate ion



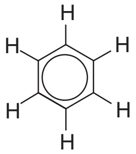
Ozone



You'll note by looking at the molecule the requirements for resonance structures. The molecule must have identical bonds, so the double bond could be in any position in the molecule without changing the structure. You will be expected to identify molecules that could exist in resonance form.

High level work

Resonance involves using two or more Lewis (electron dot) structures to represent a particular molecule or ion. A resonance structure is one of two or more alternative Lewis (electron dot) structures for a molecule or ion that cannot be described fully with one Lewis (electron dot) structure alone. Another way of describing this is delocalization. Delocalization involves electrons that are shared by/between all atoms in a molecule or ion as opposed to being localized between a pair of atoms. The IB discusses both.

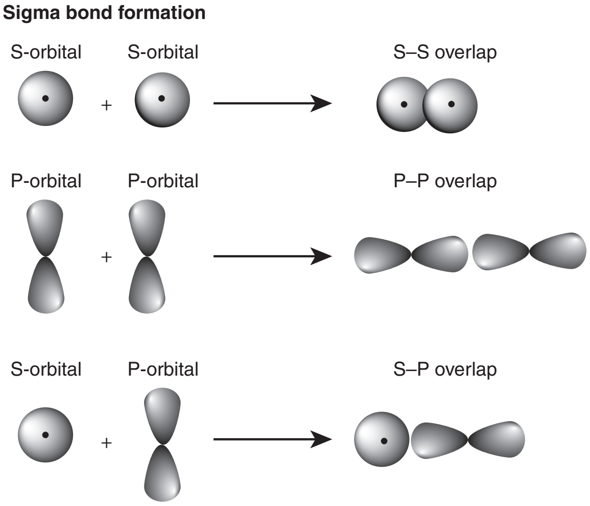


Sigma and pi bonding

The covalent bonds between atoms are more complicated than discussed in the core course. A little thought will make you realize that covalent bonds aren't just the sharing of electron pairs, These electrons were in s- or p-orbitals, and these orbitals must overlap to form the covalent bond.

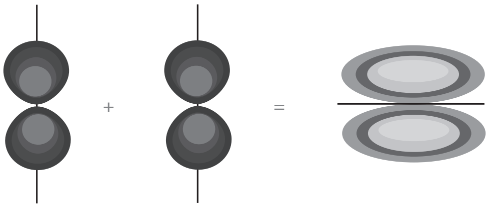
A sigma bond is the name given to a single covalent bond. It is formally defined as the end-to-end overlap of atomic orbitals. A sigma bond (σ) is formed by the direct head-on/end-to-end overlap of atomic orbitals, resulting in electron density concentrated between the nuclei of the bonding atoms.

See diagram below. It can be formed from s-orbitals or p-orbitals head on, although see the hybridization section below.



A pi bond (π) is formed by the sideways overlap of p-orbitals, resulting in electron density above and below the plane of the nuclei of the bonding atoms. See diagram below.

You would be expected to draw both types of bond and explain how they form.



The two P orbitals overlap sideways (laterally) to produce regions of election density above and below the axis joining the two nuclear centres. this is called a pi bond.

HL
SPREAD 15: Writing formulae

Exceptions to the octet rule include some species having incomplete octets and expanded octets.

Writing formulae

The HL syllabus specifies that you should be able to deduce the Lewis structures of molecules and ions showing all valence electrons for up to six electron pairs on each atom. Students can find it difficult for molecules with double bonds, or ions. Below are a few examples of how to work out any molecule. Let's start with a simple one H_2O:

First count all the valence electrons:

Each hydrogen has one, oxygen has six = 8.

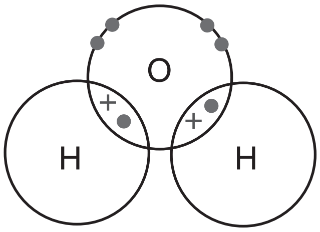
Next link the molecule with single bonds:

H–O–H

This uses up four electrons.

Finally add the rest of the electrons round the atoms, most electronegative first.

So we get:



Let's do a double bonded:

CO_2

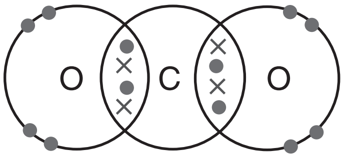
Count electrons: 4 + 6 + 6 = 16.

Link by single bonds.

O–C–O.
That uses up four.

Put the remaining 12 round the oxygen.

This doesn't work because carbon only has four around it, so use a pair from each oxygen to make double bonds.



Much Harder

The NO_3^- ion

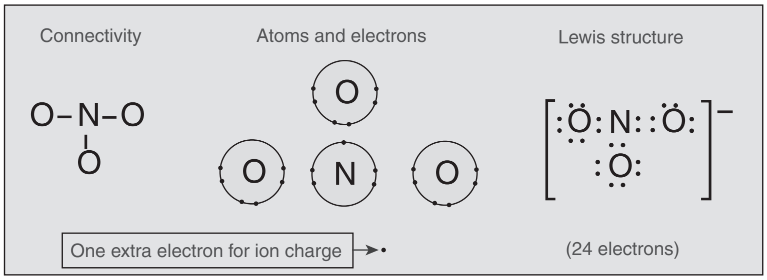
Total electrons: 5 + 18 + 1 = 24

Draw the molecule with single bonds.

INSERT BONDING NO_3 with three bonds.

NO_3 = 6 electrons

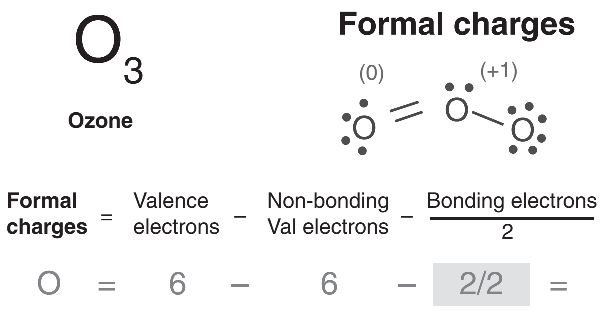
Eighteen left, put them round the oxygens. N only has three, so a double bond is created. The negative charge will complete its octet.



Ozone

O_3 = 18 electrons

O–O–O 14 left. Putting them around you run out before the last O, so there must be a double bond.



HL
SPREAD 16: Formal charge and exceptions to the octet

Formal charge (FC) can be used to decide which Lewis (electron dot) structure is preferred from several. The FC is the charge an atom would have if all atoms in the molecule had the same electronegativity. FC = (Number of valence electrons) – ½(Number of bonding electrons) – (Number of non-bonding electrons). The Lewis (electron dot) structure with the atoms having FC values closest to zero is preferred.

Formal charge

Formal charge (FC) can be used to decide which Lewis structure is preferred from several theoretical possibilities. The formal charge allows us to decide which structure is most stable and most likely.

The formal calculation is:

FC = (Number of valence electrons) – ½(number of bonding electrons) – (number of non-bonding electrons)

If you do this calculation the structure that produces the one with no formal charge is the one that is likely. Carbon dioxide is the most often quoted structure.

Assuming O=C=O

Oxygens

Valence electrons = 6. Number of bonding electrons ½ × 4 = 2. Lone pairs = 4

6 – 2 – 4 = 0

Carbon

Valence electrons = 4. Bonding electrons = ½ × 8 = 4. Lone pairs = 0

4 – 4 – 0 = 0

If this structure is proposed

Diagram

This time oxygen 1

Valence electrons = 6

Number of bonding electrons = ½ × 2 = 1

Number of lone pairs = 6

So 6 – 1 – 6 = −1

Oxygen 2

Valence electrons = 6

Bonding electrons =1/2 × 6 = 3

Number of lone pairs = 2

So 6 – 3 – 2 = +1

Carbon

Valence electrons = 4

Bonding electrons ½ × 8 = 4

Lone pairs = 0

4 – 4 – 0 = 0

Therefore the first option is the stable structure as it has all of its atoms with a formal charge of 0.

For example, in the FC there is the charge an atom would have if all atoms in the molecule had the same electronegativity. The Lewis (electron dot) structure with the atoms having FC values closest to zero is preferred.

HL
SPREAD 17: Ozone

Ozone's structure has been discussed above. It is a resonance structure. As it is allotropic to regular oxygen it is often known as trioxygen, and regular oxygen is dioxygen.

Ozone exists naturally in the atmosphere in the stratosphere. A natural equilibrium exists:

$O_2 \Leftrightarrow O_3$

The equilibrium runs by oxygen absorbing a photon of light of frequency of 242 nm. This is in the ultraviolet region.

This breaks up the dioxygen molecule.

$O_2 \Rightarrow 2O\cdot$

This is a photochemical reaction.

This can combine with other oxygen molecules to form the ozone.

$O. + O_2 \Rightarrow O_3$

The reverse is also true. The ozone can absorb the same radiation and for dioxygen.

The process is in perfect equilibrium, but other molecules that can get into the ozone layer can interrupt this process. CFCs are molecules that are good at cooling fridges. They produce a lot of chlorine or fluorine radicals (see Chapter 10).

$O_3 + Cl\cdot \Rightarrow O_2 + ClO\cdot$
$ClO + O\cdot \Rightarrow Cl\cdot + O_2$

Or

$ClO + O_3 \Rightarrow Cl\cdot + O_2$

Either way, the ozone depletes.

HL
SPREAD 18: Hybridization

A hybrid orbital results from the mixing of different types of atomic orbitals on the same atom.

Explanation of the formation of sp^3, sp^2 and sp hybrid orbitals in methane, ethene and ethyne.
Hybridization is the merging of atomic orbitals to form new orbitals. A hybrid orbital results from the mixing of different types of atomic orbitals on the same atom.

This is very difficult chemistry, and in my experience this is one of the parts that HL students find very difficult to get to grips with. Part of the problem is that teachers don't know how to simplify it and feel a moral obligation to explain it properly.

Below I will go through what you need to know in small chunks:

1) Know how they are formed.

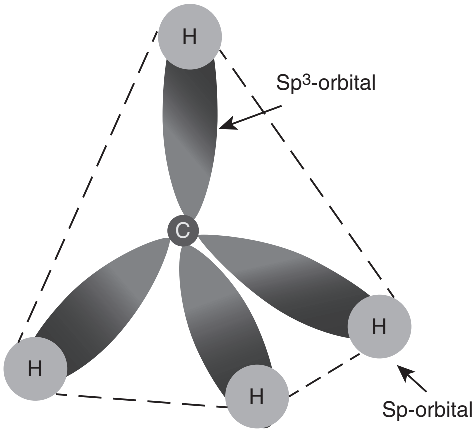
The problem with the whole topic is the issue with the taught shape of molecules, for example, methane is tetrahedral at 109.5°, and the shapes of s-and p-orbitals are covered in Topic 2, the p-orbitals where two of carbon's electrons are clearly at 90° to each other (go and remind yourself of the diagram in the previous chapter), not 109.5°.

Something ain't right.

That's because in molecules the orbitals merge and twist into new shapes to accommodate the required shape.

Example 1: Methane
Inset BONDING 3 Box diagram.

When carbon forms a methane molecule it promotes an electron from the 2s orbital to the vacant 2p orbital. We now don't have 1s orbital and 2p orbitals but one new merged hybrid of the old orbitals. It's called an sp^3 orbital (1s and 3p orbitals), and it is in the shape mentioned below.

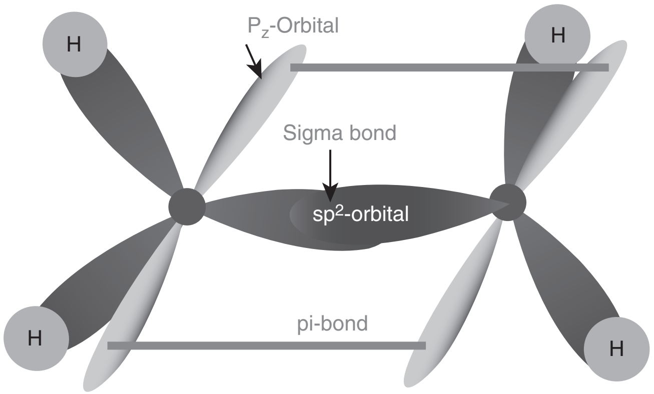


Orbital structure of methane

Note the 109.5° angle.

Example 2: Ethene
Ethene has a double bond. The same promotion of an electron from the s-orbital occurs.

This time one of the p-orbital electrons remains unhybridized and still in the old p-orbital. We get an sp^2 orbital (1s and 2p), and it looks like this:



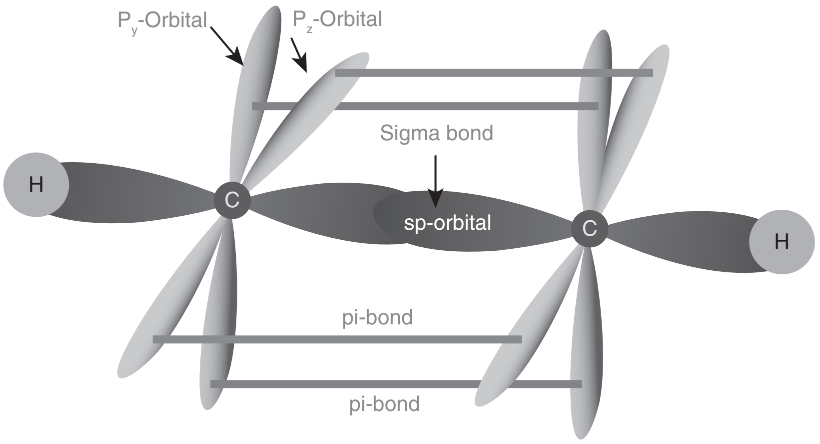
Orbital structure of ethene

The sp^2 is of course trigonal planar. The diagram above shows the two sp^2 orbitals in ethene combining. The unhybridized p electrons will form the pi bond.

Ethyne. H–C≡C–H

Same idea again but this time an sp orbital is formed. Two p-electrons form two pi bonds for the triple bond.

The hybridized orbital is:



Orbital structure of ethene

What do you need to do in an exam?

1) Know the hybridization found in a given molecule.

There are various ways of doing this:

Shape: if the molecule is based on the tetrahedral shape (which includes bent and trigonal pyramidal) then it is sp^3.

If it's based on the trigonal planar shape then it is sp^2.

If it's linear then it's sp^1.

Bonding: Single bonded = sp^1

Double bonded or any delocalized electrons = sp^2

Triple bonded = sp^3

Easy isn't it?

One final thing: the allotropes of carbons

Diamond, sp^3 = tetrahedral/single bonded

Graphite, sp^2 = trigonal planar/delocalized electrons.

CHAPTER

5

Periodicity

This chapter covers the material in Topics 3 and 13 of the IB syllabus.

CORE

SPREAD 1: The periodic table

The periodic table is arranged into four blocks associated with the four sub-levels—s, p, d and f.

The periodic table consists of groups (vertical columns) and periods (horizontal rows).

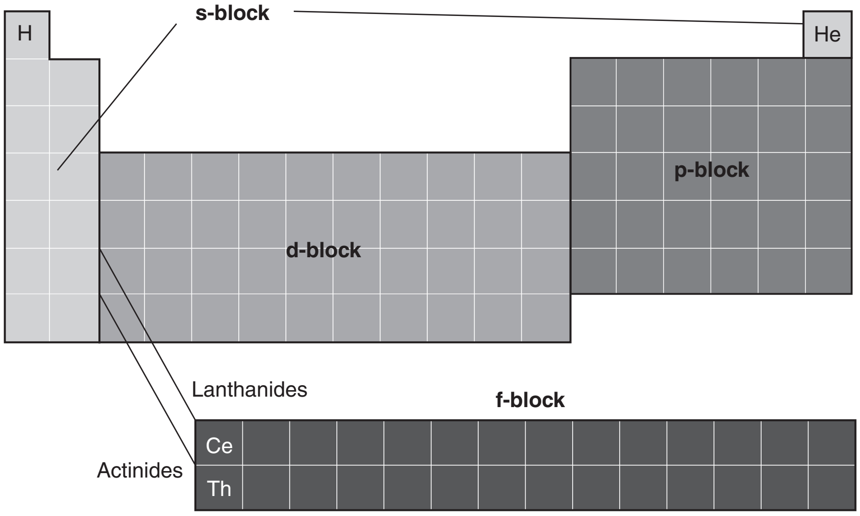
The period number (n) is the outer energy level that is occupied by electrons.

The number of the principal energy level and the number of the valence electrons in an atom can be deduced from its position on the periodic table.

The periodic table shows the positions of metals, non-metals and metalloids.

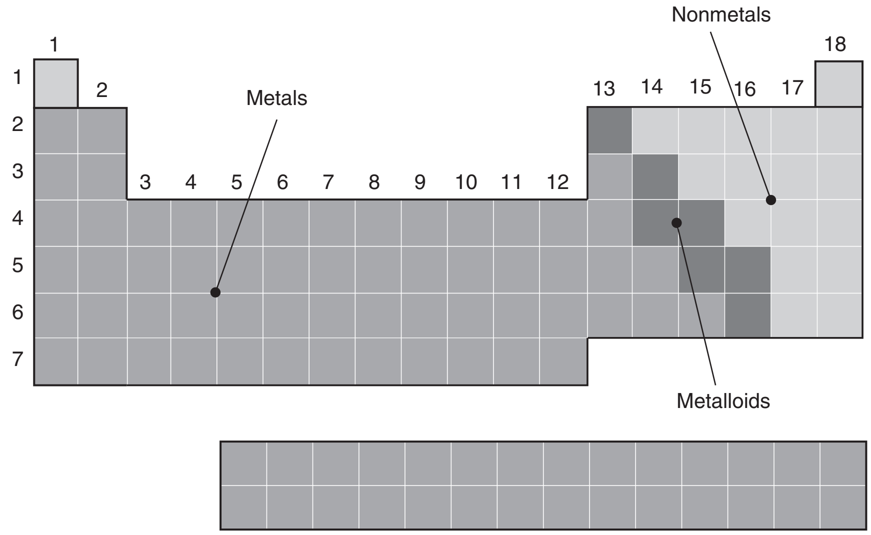
General background

The periodic table is, at its simplest, a list of the chemical elements in the order of their atomic number, but it's more than that. Its beauty is that if you do this and arrange them in groups of elements with similar chemical reactions, which by definition is the number of electrons in subshells, it gets really interesting. The periodic table is arranged into four blocks associated with the four sub-levels—s, p, d and f. The table below is the short form version of the table. The periodic table consists of groups (vertical columns) and periods (horizontal rows).



The periodic table is also a tool we can use to predict properties. Whether you are going down the group or along a period there are trends to be found, whether they are physical properties, or in their chemical reactions.

The periodic table also gives us a rough idea of the structure of elements:



CORE
SPREAD 2: Periodic trends—physical properties

Vertical and horizontal trends in the periodic table exist for atomic radius, ionic radius, ionization energy, electron affinity and electronegativity.

Physical properties

Physical properties means non-chemical reaction attributes. There are five worth considering here. For discussion of these physical properties, we will only look at group 1 (alkali metals) and group 17 (halogens) and period 3 Na ⇒ Ar.

All the data is available in the data book.

1) Atomic radius: The radius of an atom from its nucleus to its outer electron cloud.

Down groups—atomic radius INCREASES. Why? Because the number of electron orbitals increases as you go down the group.

Across periods—atomic radius DECREASES. Why? This is more counter-intuitive. As you go across the period the number of protons increases on the same outer shell. This increases the attraction to the electron cloud and the atom decreases in size.

2) Ionic radius: The radius from the center of the ion to its outer electron cloud.

In general the trend is the same but complicated by there being both positive and negative ions. So in group 1, for instance, the ions increase in size down the group, but of course the positive ion of the metal is smaller than the corresponding atom because it has lost its outer electron.

In group 17 the same is true but the ion is LARGER than the corresponding atom. This is because the ion is negative and adding an electron to an electron cloud will cause some repulsion.

3) Ionization energies

We have come across ionization energy before. Remember it is defined as the energy needed to remove an electron from one mole of gaseous atoms.

The size of the ionization energy is affected by three things colloquially known as the THREE HIT POINTS.

Ionization energy answers should always include the THREE HIT POINTS.

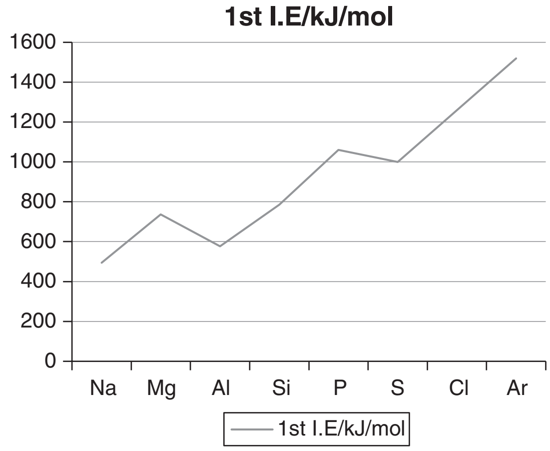
The hit points are :	Distance from the nucleus
	Shielding effect of inner shells
	Nuclear charge (number of protons)

While going down a group the ionization energy always DECREASES. Why?

Three hit points: The outer electron is further away (distance); there are more shells between the outer electron and the nucleus (which holds the electrons in place) (shielding), and this outweighs the effect of the increased nuclear charge.

Going across the group requires a bit more thought. In general the trend is for an INCREASE in ionization energy. As you go across the period the distance decreases (see atomic radius), the shielding is effectively the same and the nuclear charge increases. So there are more protons attracting the electrons that are getting closer.

It's a bit more complicated than that. Below is a reproduction of the graph of first ionization energies of period 3 from Chapter 2.



There is a drop in first ionization energy between Mg and Al. Why? The Al outer electron is in a 3p orbital. This is a little further out from the nucleus and shielded by the 3s orbital, so it is easier to remove.

There is also a drop between p and s. This is when the outer electron occupies an already occupied p orbital (draw). This causes repulsion, and it makes the electron easier to remove.

4) Electronegativity: This is defined as the ability of an atom to attract an electron pair in a bond. This a concept discussed in Chapter 4. If you need to familiarize yourself with this then do read ahead. As this is a revision guide hopefully you will know what it is.

Essentially: the order of electronegativity is:

FONC*l*BrIS

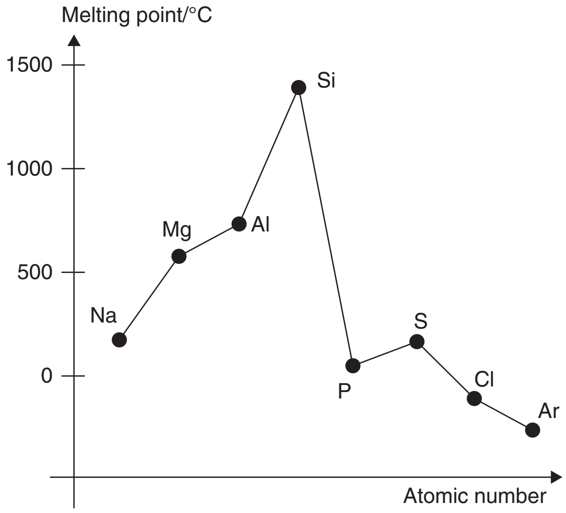
The electronegativity decreases away from fluorine. In other words it decreases down the groups and increases across the periods. As electronegativity is the ability to attract electron pairs in a bond, the strength of the nuclear charge is the most important thing. So the fewest shells between the nucleus and the outer shells will be more electronegative. Also the more the protons per shell the higher the electronegativity, hence fluorine being number 1.

Melting points: These of course depend on the strength of the bonding, or the intermolecular forces. Let's look at each part in turn.

Group 1: All metallic bonding—as the ions increase in size as we go down the group the charge density decreases, so the attraction between the ions and the electron cloud decreases. MELTING POINT DECREASES.

Group 17: All covalent molecules are held together by weak London forces. The forces increase as the size of the molecules increase. As I_2 has the largest RMM it has the highest "melting" point (although it actually sublimes). MELTING POINT INCREASES.

Period 3: It really depends on the bonding type. A plot is shown below:



The three metals have high-ish melting points. There is an increase because the ion size decreases, so the charge density increases. Silicon is a giant covalent substance, so the melting point is very high. The next three elements are all molecular covalent substances, held together by weak London forces; their melting points are very low. Sulfur is the highest because it exists as S_8 and has a higher RMM than the other two. Argon exists only as atoms, and the London forces are very weak.

HL
SPREAD 3: Chemical properties

Trends in metallic and non-metallic behavior are due to the trends above.

Oxides change from basic through amphoteric to acidic across a period.

There is almost infinite variety of chemistry on the periodic table. Our course it only focusses on group 1, group 17 and period 3.

Group 1: The alkali metals

You will have seen the alkali metals reacting with water. It is impossible to study chemistry without seeing them demonstrated. They all react violently, the metal fizzing in water producing an alkaline solution. The reactivity appears to increase as you go down the group, cesium being the most reactive (look on YouTube).

It is important that you appreciate the increase in reactivity:

Lithium fizzes.
Sodium melts into a ball.
Potassium lights itself and crackles.
Rubidium crackles and explodes.
Cesium really explodes.

You need to be able to write an equation for the reaction.

$$2Na_{(s)} + 2H_2O_{(l)} \Rightarrow 2NaOH_{(aq)} + H_{2(g)}$$

Don't forget that the equation is THE SAME for all of the elements of group 1, which is the point of periodicity.

$$2M_{(s)} + 2H_2O_{(l)} \Rightarrow 2MOH_{(aq)} + H_{2(g)}$$

So reactivity INCREASES down the group for similar reasons as to why ionization energy decreases. The outer electron is easier to remove, so the reactions become more reactive.

The halogens (group 17)

The halogens are the most studied non-metal group because it is the only group in the periodic table containing only non-metals that do any chemistry at all (the noble gases of group 18 are essentially unreactive). At first glance the elements don't seem to be particularly similar:

Fluorine	F	Pale yellow gas
Chlorine	Cl	Pale green gas
Bromine	Br	Red/brown liquid
Iodine	I	Grey solid/purple vapor
Astatine	At	Grey solid

Chemically of course they have similar outer electron configurations and react similarly. An explanation for increased melting point will be given in the next chapter.

The halogens' reactivity DECREASES down the group. This is related to filling the outer orbital. The greater the effective nuclear charge (number of protons related to shielding) the greater the attraction for an incoming electron.

This is usually illustrated by displacement reactions with compounds containing the halogens.

Halogen/compound	**Chlorine**	**Bromine**	**Iodine**
Potassium chloride (aq)		No reaction	No reaction
Potassium bromide (aq)	Brown color appears		No reaction
Potassium iodide (aq)	Yellow color appears	Yellow color appears	

The colors appearing are the colors of the displaced halogens in water (bromine—brown, iodine yellow).

Equations (both regular and ionic should be written for all the reactions that happen):

$$2KBr + Cl_2 \Rightarrow 2KCl + Br_2$$

Ionic:

$$2Br^-_{(aq)} + Cl_{2(aq)} \Rightarrow 2Cl^-_{(aq)} + Br_{2(aq)}$$

Note: These reactions are also REDOX reactions, but we will look at this terminology in Chapter 9.

CORE
SPREAD 4: More chemical trends

Combining groups 1 and 17

When alkali metals and halogens combine they form halide salts. All will combine relatively easily once lit, and the equations are identical no matter which elements you choose.

For example, the reaction between sodium and chlorine (the one you are most likely to have seen):

$$2Na_{(s)} + Cl_{2(g)} \Rightarrow 2NaCl_{(s)}$$

For reasons outlined above the most reactive combination will be one between a metal at the bottom of group 1 and the top of group 17. Don't ever mix fluorine with cesium!

Period 3 reactions

Unlike group chemistry the reactions across periods are not meant to be the same. The studies illustrate how things change across the periodic table as we go from metals to non-metals. This is best illustrated with the oxides of period 3.

First let's look at the reaction with the oxides when added to water.

THESE NEED TO BE LEARNED:

The metals:

Both sodium and magnesium oxide react with water to produce a hydroxide, which are strong bases:

$Na_2O + H_2O \Rightarrow 2NaOH$
$MgO + H_2O \Rightarrow Mg(OH)_2$

Aluminum oxide is amphoteric, which means it can act as an acid or a base. You do not need to learn equations.

Non-metal oxides produce ACIDIC oxides.

Phosphorus:

$P_4O_{10} + 6H_2O \Rightarrow 4H_3PO_4$
$SO_2 + H_2O \Rightarrow H_2SO_3$
$SO_3 + H_2O \Rightarrow H_2SO_4$

This illustrates nicely the trend in metal/non-metal behavior of the elements. Metals have oxides that are BASIC, and non-metal oxides are ACIDIC. Aluminum, in the area between metal and non-metal, which is a metal but has a lot of non-metal chemical reactions, does both.

Air pollution

The oxides of sulfur and nitrogen have been produced by the burning of fossil fuels. Sulfur is present in both oil and coal and if the coal or oil is not desulfured then the oxide can get into the atmosphere where the reactions above can occur. This can lead to acid rain. Remember acid rain nitrogen oxides are produced in engines where the normally inert nitrogen in the air can react with oxygen under the extreme conditions of the engine. Once again these oxides are toxic and can get into the atmosphere. Both problems have been addressed to some extent, with low sulfur gasoline being widely available and catalytic converters removing the NO_x before emission in cars. The syllabus also notes that you need to know the reaction with nitrogen oxides and water.

$N_2 + O_2 \Rightarrow NO_2$

Then:

$4NO_2 + 2H_2O + O_2 = 4HNO_3$

HL

SPREAD 5: The first-row d-block elements

Transition elements have variable oxidation states, form complex ions with ligands, have colored compounds and display catalytic and magnetic properties.

Zn is not considered to be a transition element as it does not form ions with incomplete d-orbitals.

Transition elements show an oxidation state of +2 when the s-electrons are removed.

The d-block consists of 30 elements, mentioned below. They are the middle block of the periodic table.

21 **Sc** 44.9559 Scandium	22 **Ti** 47.867 Titanium	23 **V** 50.9415 Vanadium	24 **Cr** 51.9961 Chromium	25 **Mn** 54.938 Manganese	26 **Fe** 55.845 Iron	27 **Co** 58.9332 Cobalt	28 **Ni** 58.6934 Nickel	29 **Cu** 63.546 Copper	30 **Zn** 65.4089 Zinc
39 **Y** 88.9058 Yitrium	40 **Zr** 91.224 Zirconium	41 **Nb** 92.9064 Niobium	42 **Mo** 85.94 Molybdenum	43 **Tc** 98 Technetium	44 **Ru** 101.07 Ruthenuim	45 **Rh** 102.9055 Rbodium	46 **Pd** 106.42 Palladium	47 **Ag** 107.8682 Silver	48 **Cd** 112.411 Cadmium
71 **Lu** 174.967 Lutetium	72 **Hf** 178.49 Hafnium	73 **Ta** 180.9497 Tantalum	74 **W** 183.84 Tungsten	75 **Re** 186.207 Rhenium	76 **Os** 190.23 Osmium	77 **Ir** 192.217 Iridium	78 **Pt** 195.084 Platinum	79 **Au** 196.9666 Gold	80 **Hg** 200.59 Mercury

If your teacher is wise then this was one of the last things you studied in the course, because it contains concepts from all over the syllabus and ties things up nicely. You need to know the following six things:

- Definitions and ground state configurations.
- Oxidation states.
- Complex ions.
- Colored compounds.
- Catalytic and magnetic behavior.

Definitions and ground state configurations

The ground state electronic configurations of d-block elements require some thought:

Up until electron 18 everything is as normal: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$.

The next lowest energy level is the 4s, not the 3d, so they are filled in next, followed by the 3d.

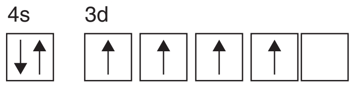
So scandium, element number 21 is:

$[Ar]\ 4s^2\ 3d^1$

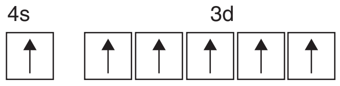
Titanium is $[Ar]\ 4s^2\ 3d^2$, and vanadium is $[Ar]\ 4s^2\ 3d^3$.

Chromium breaks the pattern:

If you look at this as a series of orbitals chromium could be $[Ar]\ 4s^2\ 3d^4$.



But chromium finds better stability by having a half-filled d-orbital, so it promotes a 4s electron:



So chromium is actually $[Ar]\ 4s^1\ 3d^5$.

Copper pulls the same trick.

Instead of being $4s^2\ 3d^9$, it takes the option having a more stable full 3d orbital and promotes an electron from the 4s.

So copper is $[Ar]\ 4s^1\ 3d^{10}$.

There is no really easy way to remember these two anomalies; if cobalt didn't begin with C then it would be the only two elements beginning with C, but life isn't that kind.

The d-block elements form ions in a different way as well. Instead of losing electrons from the 3d orbital first they lose their 4s electrons first, which explains the frequency by which the 2+ ion appears in the d-block. Other ions are possible, but we will get to that in a moment.

The term "d-block" and transition metal are often used, but they are not totally interchangeable. The elements we know as transition elements have all the properties below, but not all the d-block elements are transition metals. The definition of transition elements are that they are elements that have at least one ion that contains an incomplete d-orbital (i.e., with at least one electron in it, but not full). This may seem a strange definition, but it explains things beautifully.

Running this definition through the first row of the d-block elements we find two elements that do not fit the definition:

Scandium: $4s^2\ 3d^1$. It forms only the Sc^{3+} ion: which removes both the 4s and the $3d^1$ electron, so it is empty.

Zinc: $4s^2\ 3d^{10}$. It only forms a 2+ ion, leaving a complete 3d orbital. It is not a transition element either. The importance of this will be seen further down this section.

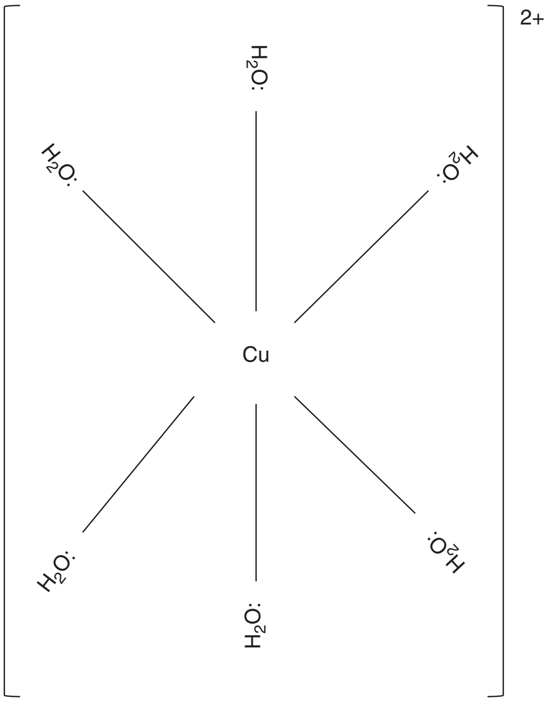
Note, copper forms both a Cu^+ and a Cu^{2+} ion. The Cu^{2+} ion leaves you with a $3d^9$ orbital, which is fine, but the Cu^+ ion leaves you with a complete d orbital.

HL
SPREAD 6: More transition metals

Complex ions

Transition metals can form **complex ions**. This is where small molecules use lone pairs or negative charges to form a dative covalent bond to the metal cation.

For example, this copper/water complex:



The lone pairs form the covalent bonds to the small highly charged metal cation. The formula for this complex ion is $[Cu(H_2O)_6]^{2+}$.

The molecule or ion is known as a ligand.

Variable oxidation states

The transition metals display a variety of oxidation states. The most common ones are listed in your data book. It is also mentioned below. You do not need to know these; however, the 2+ ion must be known.

Sc	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
	+2	**+2**	**+2**	**+2**	**+2**	**+2**	**+2**	**+2**	**+2**
+3		**+3**	**+3**		**+3**	**+3**			
	+4	**+4**		**+4**					
		+5							
			+6						
				+7					

The reason transition metals have many oxidation states is usually explained by the relative successive ionization energies. If you compare transition metals to its nearest neighbor calcium the point is illustrated well. We'll use iron.

Calcium			
1st	2nd	3rd	4th
590	1945	4912	6491
Iron			
1st	2nd	3rd	4th
762	1560	2960	5400

The 2+ ion is easy to form, the 2nd ionization energy isn't too high, yet look at the huge jump in calcium as the next electron is taken from the 3p orbital—much harder to remove. The third electron from iron is from the 3d orbital, and it isn't particularly high in comparison.

Catalytic behavior

Transition metals are good catalyst because of their variable oxidation states. They can be oxidized and reduced thus allowing alternate pathways for the reaction to follow, which may have a lower activation energy. This is the definition of catalytic behavior.

Magnetic behavior

Unpaired electrons possess a magnetic moment associated with the electron "spinning." This causes transition metals with unpaired electrons to be paramagnetic. The more unpaired electrons the more strong the attraction. Iron, nickel and cobalt that have the most unpaired electrons and are noticeably magnetic.

HL

SPREAD 7: Colored compounds

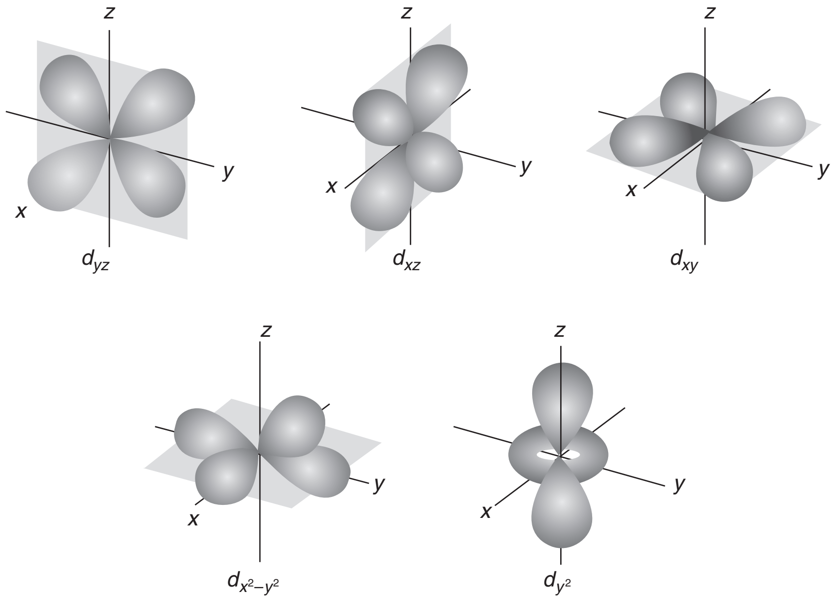
The most striking aspect of transition metal compounds is the wide variety of colors displayed by transition metals. You need to understand quite a lot about this:

Origin of the color:

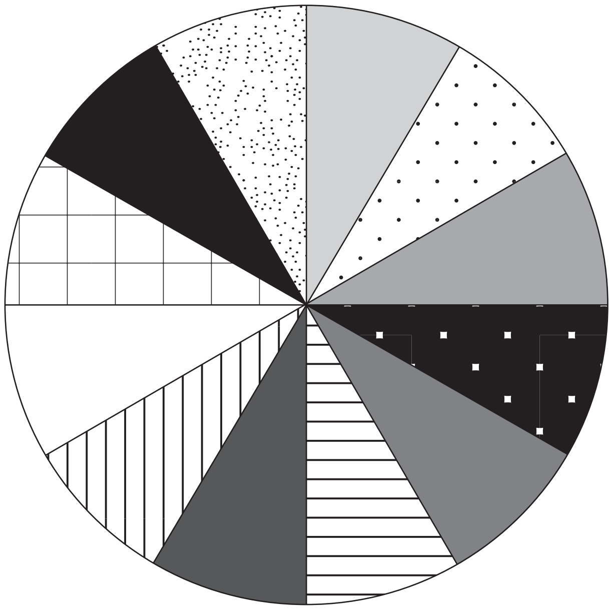
Depending on your teacher you may have a very complicated explanation for this. You do not necessarily need to regurgitate the complicated explanation, especially as a detailed explanation goes beyond the scope of the course (but you still need to explain it—go figure) and you can skip to that bit below if you like.

Complicated explanation:

Essentially the d-orbitals (see below) have five different shapes:



You'll notice that two of the orbital shapes cut along the *x*, *y* and *z* axes and three don't. Now cast your minds back up to the ligand diagram above. You'll notice the ligands attach to the metal ion in an octahedral direction (i.e., along the *x*, *y* and *z* axes). So the incoming ligands cause some repulsion to any electrons in these orbitals. This causes a split in the d-orbitals, three have a higher energy level than the other two. The fancy word for this is that orbitals are non-degenerate. The gap between the two sets of non-degenerate orbitals corresponds to a frequency of light necessary to cause an electron to jump from one orbital to another. The frequency of light is absorbed, so the color seen will be complementary to the absorbed light, that is, on the other side of a color wheel (there is one in your data book).



For those who want to know what to write in an exam. It is this:

- The d-orbital sub-level splits into two sets of orbitals of different energy in a complex ion.
- Complexes of d-block elements are colored, as light is absorbed when an electron is excited between the d-orbitals.
- The color absorbed is complementary to the color observed.

Some examples to illustrate this:

Copper sulfate is blue because the energy gap is equivalent to orange light. The complementary color is blue.

Note also that zinc and scandium compounds are white because there are either no electrons or a full d-orbital so that no transitions are possible.

What affects the color?

Three things affect the color:

- The metal ion in the complex: The number of protons/the nuclear charge will also affect the energy gap, which can explain why elements with similar electronic configurations have different colors.
- The oxidation number of the metal ion: Different oxidation numbers of a metal ion will cause different amounts of splitting; therefore, the color absorbed and seen will vary.
- The identity of the ligand: The ligand's relationship with the d-orbital will also affect the gap, and this will affect the energy absorbed.

CHAPTER

6 Energetics and thermochemistry

This chapter covers the material in Topics 5 and 15 of the IB syllabus.

CORE
SPREAD 1: Energy changes

Heat is a form of energy.

Temperature is a measure of the average kinetic energy of the particles.

Total energy is conserved in chemical reactions.

Chemical reactions that involve transfer of heat between the system and the surroundings are described as endothermic or exothermic.

The enthalpy change (ΔH) *for chemical reactions is indicated in* $kJmol^{-1}$.

ΔH *values are usually expressed under standard conditions, given by* $\Delta H°$, *including standard states.*

Measuring energy changes

This topic is very experimental. Many chemical reactions involve a temperature change as they occur. As heat is a form of energy there is clearly an energy exchange going on. As energy cannot be created or destroyed but can be converted from one form to another the energy exchange has to involve the chemical reagents in some way. In other words energy is conserved. Temperature and heat energy by the way are not the same thing, and this misunderstanding can cause confusion. Heat energy, like all energy, is measured in joules. Temperature (in scientific circles and everywhere except the USA) is measured in °C. The temperature something has is actually a measure of the average kinetic energy of the particles. When there is a change in temperature then there has been a change in energy.

You will have studied the two types of reaction that involve heat energy exchange:

Exothermic—when reactions release heat energy into the surroundings (they usually see an increase in temperature).

Classic example: combustion of a fuel (methane)

$$CH_4 + 2O_2 \Rightarrow CO_2 + 2H_2O$$

Exothermic reactions often continue spontaneously until the limiting reagent has run out.

Endothermic—when reactions take in heat from the surroundings (these can but not always see a drop in the temperature of the surroundings, but other sorts require a constant input of heat energy from the surroundings to make them happen).

An example of the first sort would be obscure, although one often demonstrated is between ammonium carbonate and ethanoic acid.

The second is much more common and is also known as thermal decomposition.

For example,

$$CaCO_3 \Rightarrow CaO + CO_2$$

The calcium carbonate will only decompose to the two oxides when considerable heat energy is supplied, and stops when the source of energy is withdrawn.

Enthalpy change

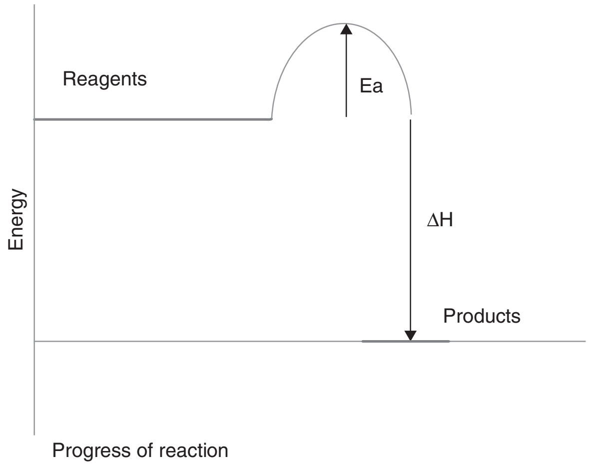
The first part of this topic is concerned with working out the energy change for chemical reactions by experiment. You will always be calculating the ENTHALPY CHANGE (ΔH). Enthalpy change is essentially the energy of a chemical reaction, and as it will be quantity related it has the units of $kJmol^{-1}$. Data book–quoted examples of enthalpy change values will often have this sign next to them: θ.

This tells the reader that the reaction was carried out under standard conditions. These are:

- Using the normal, most pure stable state of a substance.
- At a pressure of 100 kPa. Your teacher may have referred to this as 1 atmosphere. They are interchangeable (sort of) although 100 kPa is perhaps more correct.
- Temperature is not a part of the definition of standard state, but 298 K is commonly given as the temperature, which is considered room temperature in many parts of the world. Technically as long as you have stated a temperature for the reaction, you are covered. Note 298 K = 25°C. 1 K = 1°C.
- If using a solution then a 1 $moldm^{-3}$ solution is used.

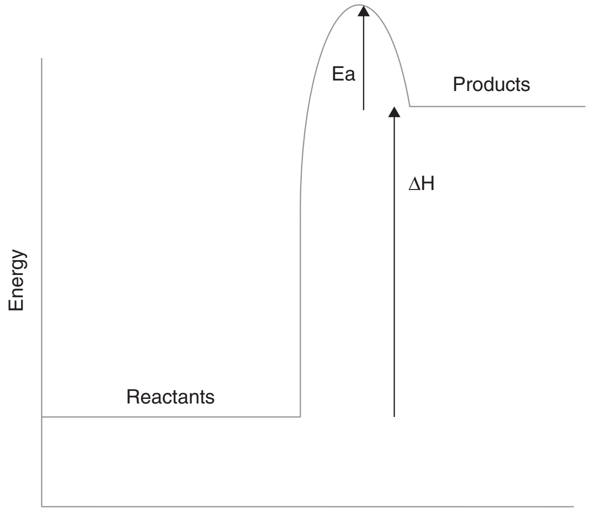
More detail on exothermic and endothermic reactions

An exothermic reaction can be represented by an energy profile diagram.



This shows that as a chemical exothermic reaction happens the products have less energy than the reactants and must release energy to the surroundings. The value of ΔH is negative because the energy has left the chemical system and gone to the surroundings. The E_a labelled is the activation energy. More on that in Chapter 7.

There is also an energy profile diagram for an endothermic reaction.



This time the reaction takes in energy, so the products have more energy than the reactants did. ΔH is positive and has a + value in front of the value.

There can be a lot of confusion with the + and − values for ΔH. Usually the calculation you are doing calculates whether the answer is + or −. The exception is the real calorimetry experiment calculations in the first section where you have to decide for yourself. It's not difficult but you must remember to do it.

Finally, before we spend the rest of this chapter with our calculators out remember SUS:

Signs

Units

Significant figures.

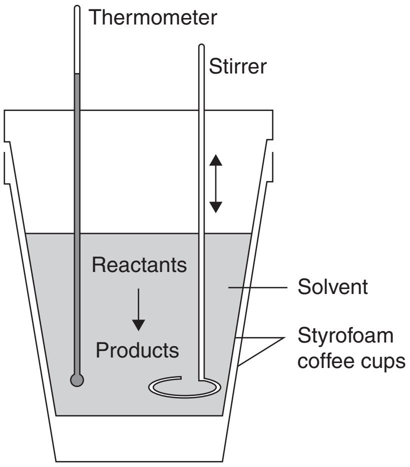
All three are very important in this chapter, in particular.

CORE
SPREAD 2: Calculating the enthalpy change for a chemical reaction

Calorimetry

You have no doubt carried out some experiments to calculate the enthalpy change of a chemical reaction. They are worth knowing in a lot of detail because they are very popular with examiners for the Paper 3 experimental question, because of the large sources of error associated with them.

An insulating calorimeter



When the chemical reaction is possible by mixing the reagents together where one is in solution you can carry out the experiment in an insulating calorimeter, often a Styrofoam cup. The cup prevents the energy exchange being affected too much, as it will prevent heat loss. These calculations are relatively straight forward:

$$Q = mc\Delta T$$

Where Q = the heat exchange
m = the mass of the liquid experiencing the heat exchange (usually water)
c = the specific heat capacity of the liquid experiencing the heat exchange (usually water). This value is 4.18 $\text{J}\text{g}^{-1}\text{K}^{-1}$ and is in your data book, although to be honest you probably know it.
ΔT = the temperature change.

Calculating this gives us the heat exchange in joules, but this is **not** the enthalpy change. To calculate this you need to divide this value by the moles of the LIMITING REAGENT. Then convert to kJmol^{-1} and give the value a sign.

Easy example

A 50.0 cm^3 of 1 $moldm^{-3}$ copper sulfate solution was put into a calorimeter. The temperature was noted. A total 0.65 g of zinc was added, and the mixture was stirred until there was no further temperature change. The temperature change was 52.0°C. Calculate ΔH.

$CuSO_4 + Zn \Rightarrow ZnSO_4 + Cu$

1) First let's do the Q:
   $m = 50$, $c = 4.18$, $\Delta T = 52$

Remember m = the mass of the liquid getting warm, in this case the copper sulfate solution. As it is mainly water we assume the mass is the same as the volume. Same logic for the SHC, which is for water.

$50 \times 4.18 \times 52 = 10{,}868$ J

2) Now the "per mole" bit. We need the limiting reagent:
   $50/1000 \times 1 = 0.05$ mole $CuSO_4$
   $0.65/65 = 0.10$ moles of zinc
   The limiting reagent is copper sulfate.
3) Work out enthalpy change:
   $10{,}868/0.05 = 217{,}360$ $Jmol^{-1}$
   Conventionally -217 $kJmol^{-1}$

Note, I have converted to kJ by dividing by 1000 and added the sign because I know it is exothermic. SF are correct to the 3sf used in the question.

Challenging example

Part of the problem with these calculations is that it is easy to make silly mistakes in your calculation. I give this example to all my students to show them how easy it is to get the wrong answer. Usually in a class of 10, 9 good students will get the wrong answer.

A 50 cm^3 of 1 $moldm^{-3}$ HCl is added to 50 cm^3 of 1 $moldm^{-3}$ NaOH solution in a calorimeter. The mixture was stirred until no further temperature change, which was 7.0°C.

1) Calculate ΔH
   Now do this calculation. There are a few traps in this for the unwary.

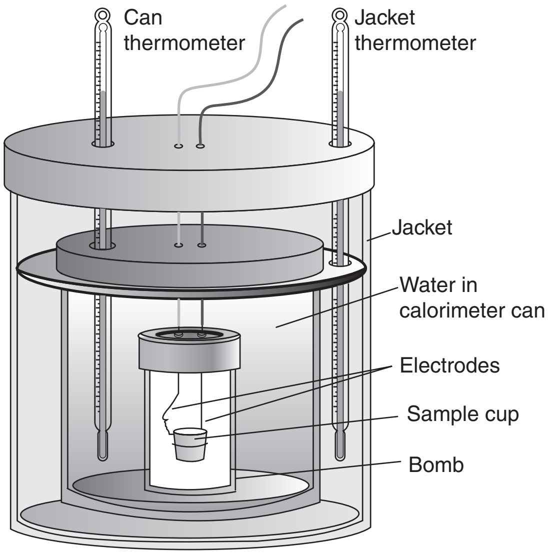
You should award yourself three marks if you have got as an answer exactly -58.5 $kJmol^{-1}$.

If you haven't then ask yourself these questions: in order of most likely mistakes.

What is your "m" value? If you haven't got 100, then look again, and work out why. What is your moles value? Make sure you have calculated it correctly.

CORE
SPREAD 3: Using a conducting calorimeter

The calculations outlined above get more complicated if you are using a copper calorimeter, or similar. In this sort of experiment a fuel of some sort is burned and the heat produced is used to heat water inside the calorimeter. This means the calorimeter must be a good conductor rather than a good insulator. They can be complicated like the bomb calorimeter below:



The calculation is essentially the same:

Example 1:

A methanol spirit burner is placed beneath a copper calorimeter containing 50 cm^3 of water. A total 0.57 g of methanol was burned and the temperature rise of the water was 29°C. Work out the enthalpy change.

$Q = mc\Delta T$
$m = 50$ (the water in the calorimeter)
$c = 4.18$
$T = 29$
$= 6061$ J

The moles is calculated from the mass change (RMM of methanol is 32 $gmol^{-1}$):

0.57/32 = 0.0178 mol

So the enthalpy change is:

6061/0.0178 = −340 $kJmol^{-1}$

Note, as usual I have worked out the reaction is exothermic and given it the right sign.

This is a long way from the true answer of −726 $kJmol^{-1}$. This will be due to at least four reasons, all of which you need to consider.

Reason 1: reaction may not have been at standard conditions (good answer if you can't think of a better one)
Reason 2: incomplete combustion. The true answer was calculated assuming 100% combustion to CO_2 and H_2O. Any soot on the bottom of your calorimeter will mean this is not the case.
Reason 3: Heat loss (1): drafts blowing the flame, the air heating, not the water, heat loss from the heated water to the air will all mean an answer some way from the true answer.
Reason 4: Heat loss (2): heat loss to the calorimeter itself. The copper calorimeter is a good conductor and will let a lot of the heat through to the water, but not all of it. A really good answer ought to allow you to calculate the heat capacity of the calorimeter.

$Q = mc\Delta T$ of the water + specific heat capacity of the calorimeter × the temperature rise

Often the problems make life easier by simply telling the overall specific heat capacity for the calorimeter and the water. In which case you simply multiply by this value.

CORE
SPREAD 4: Bond enthalpies

Bond-forming releases energy and bond-breaking requires energy.

Average bond enthalpy is the energy needed to break one mole of a bond in a gaseous molecule averaged over similar compounds.

Everybody thinks they can do bond enthalpy calculations, but they are one of the places where students drop a lot of marks. Let's start by getting some points clarified first.

The IB data book contains a list of average bond energies for a series of covalent bonds. Note the "average"; these are not necessarily specific to the bond in the molecule you are working out. It is defined as "the energy needed to break one mole of a bond in a gaseous molecule averaged over similar compounds."

In addition the energy quoted is for gaseous species, and therefore do not take into consideration any intermolecular forces. This means that the answer you calculate will not be an exact answer to the enthalpy change for the reaction given.

Secondly, it's important to understand the relationship between enthalpy and bond breaking and making. Breaking bonds always requires you to supply energy (endothermic). Making bonds releases energy. In a chemical reaction the magnitude of both breaking all the reactant bonds and making all the product bonds will decide whether the reaction itself is exothermic or endothermic.

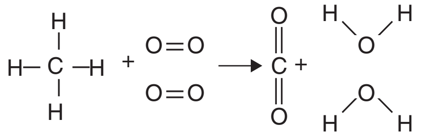
A simple way to remember this is the nonsense word MEXOBENDO

Making bonds is
Exothermic
Breaking bonds is
Endothermic

We'll look at a simple example then look at two that can cause problems:

Work out using bond enthalpy values the enthalpy change for the complete combustion of methane.

- Write out the equation, but draw everything in displayed form so you can see the bonds:



$CH_4 + 2O_2 \Rightarrow CO_2 + 2H_2O$

- Draw a table under your displayed equation and list the bonds and their number.

Breaking	**Making**
4 × C–H bonds 4 × 413 = 1652	2 × C=O bonds 2 × 746 = 1492
2 × O=O bonds 2 × 498 = 996	4 × O–H bonds 4 × 464 = 1856
Total = 2648	Total = 3348

You can see that the product value is higher than the reactants, so the reaction will be EXOTHERMIC because making bonds is exothermic. To find the answer simply subtract product from reactant values.

$2648 - 3348 = -700$ kJ mol^{-1}

Not difficult:

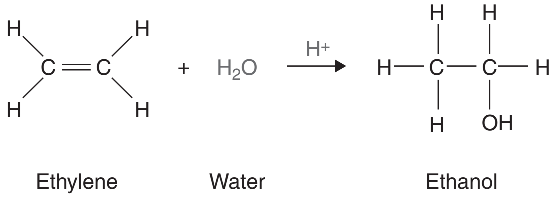
Where mistakes can be made:

Choosing the wrong bond energy values. The IB examiners know where you make mistakes and will guide you to the table in your data book, then try and get you to write the wrong value. A classic example is:

$N_2 + 3H_2 \Rightarrow 2NH_3$

The unthinking IB student immediately looks up the N–N bond angle as 158 and gets it wrong, because (of course) a quick think about the nature of the N–N bond will make you realize that it will be an N≡N bond.

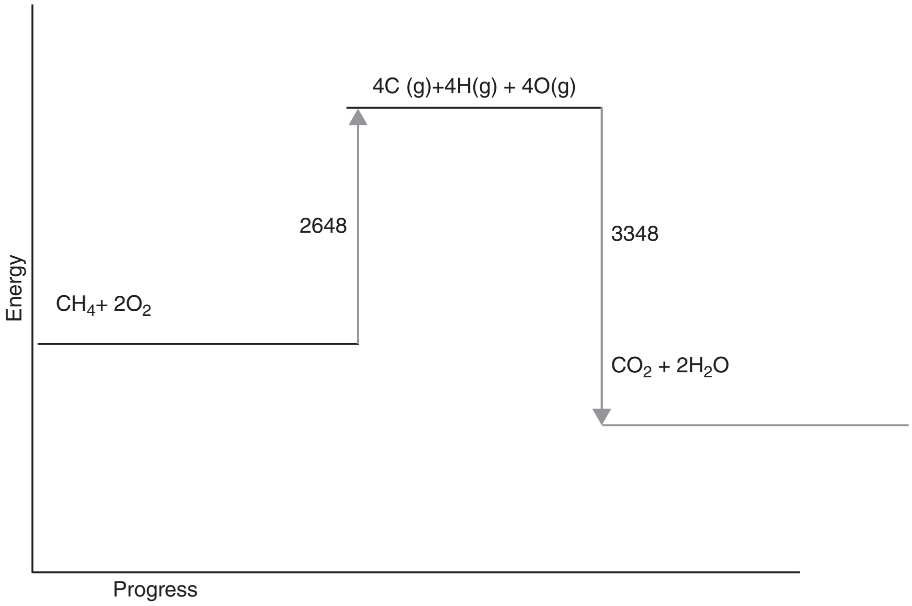
The other common mistake is in a more complicated setup, see below.



The overenthusiastic, mistake-prone IB student will miss the C–C bond in the ethanol as he/she works around the outside of the molecule. We've all done it; try to bear in mind the IB knows this and is trying to get you to do it!

CORE
SPREAD 5: Potential energy diagrams and ozone

These are similar to the enthalpy profile diagrams sketched above but with the transitional state for the unbonded atoms added in. Below is the one for the combustion of methane above.



In this sort of diagram the products are said to be thermodynamically more stable than the reactants because they have less energy for the reactants. This is true for all exothermic reactions. Conversely in an endothermic reaction the products have more energy than the reactants, so it is said to be thermodynamically unstable.

Ozone

Ozone has been discussed before as a resonating allotrope of oxygen. It contains O–O bonds that are neither single nor double but somewhere in between. The actual value is around 445 kJmol^{-1}, less than the typical O=O bond (498). This weakness means it is easily broken down in the atmosphere by pollutant chemicals such as CFCs and oxides of nitrogen. This weakness has caused a chain reaction that has led to a severe depletion in the ozone layer in our upper atmosphere.

CORE
SPREAD 6: Hess's Law

The enthalpy change for a reaction that is carried out in a series of steps is equal to the sum of the enthalpy changes for the individual steps.

Application of Hess's Law to calculate enthalpy changes.

Calculation of ΔH reactions using ΔHf^{θ} data.

Determination of the enthalpy change of a reaction that is the sum of multiple reactions with known enthalpy changes.

So far we have concentrated on working out the enthalpy changes for reactions that really happen. But sometimes it is impossible to calculate an enthalpy of reaction because:

The reaction is too fast, too dangerous, too slow or the products may not be formed as you would wish, or the reaction doesn't happen at all.

When this happens all is not lost, as we can use HESS'S LAW.

This states that the enthalpy change of a reaction is the same no matter which pathway you take. In other words the enthalpy change of your target reaction can be worked out by taking another route, usually using one intermediary step.

The most popular way to view this principle is to form a Hess's cycle to show the reaction you wish to investigate.

There are three types of cycles commonly employed:

Using standard enthalpy of formation data (ΔH^{θ}_{f}):

Standard enthalpy of formation is defined as "the energy exchanged when one mole of a compound is formed from its elements under standard conditions." As the definition suggests it uses the elements as the alternative pathway for the reaction.

Worked example:

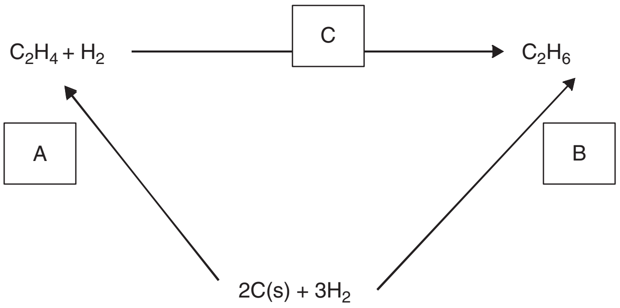
Work out the enthalpy change for the hydration of ethane:

$C_2H_4 + H_2 \Rightarrow C_2H_6$

Data:

ΔH^{θ}_{f} Ethene = +52 kJmol^{-1}
ΔH^{θ}_{f} Ethane = −52 kJmol^{-1}

Method 1—using vectors, with a Hess's cycle



You can see that the enthalpy of formation data has allowed the elements to be the intermediary. To work out the enthalpy change you simply follow the alternate pathway, remembering that if you go against the arrow the sign is reversed.

Note, that the enthalpy change of formation of hydrogen is zero because it's an element.

So to work out C we need to −A + B:

= −52 + −85 = −137 kJmol^{-1}

Things to remember: if you are using this method you need to remember that for formation data the arrows go UP

If the equation has a coefficient, then you will need to change your value for ΔH_f because this is for forming one mole!

Method 2: Algebraic

This is the faster and more common method. If you are using formation data then:

ΔH reaction = $\Sigma(\Delta H^{\theta}_f$ products$) - \Sigma(\Delta H^{\theta}_f$ reactants$)$

Which makes the above sum = $-85 - +52 = -137$ kJmol^{-1}

Both methods work, the second method is easier, but requires you apply it to formation only. The top method is more flexible, as we shall see.

CORE
SPREAD 7: Using enthalpy of combustion data (ΔH^{θ}_c)

Enthalpy of combustion is defined as "the energy released when one mole of a compound is completely burned in oxygen." This time the intermediate step will be the products of combustion, and with organic compounds this will be carbon dioxide and water vapor.

Example: Work out the enthalpy change for the reaction below:

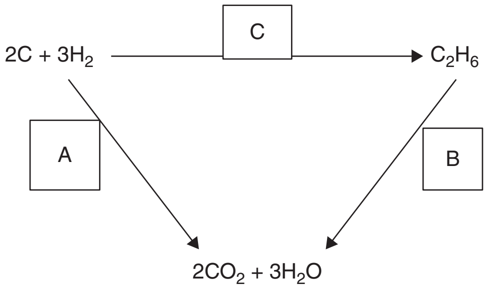
$2C + 3H_2 \Rightarrow C_2H_6$

Data:

$\Delta H^{\theta}c$ $C_{(s)} = -393$ kJmol^{-1}
ΔH^{θ}_c $H_{2(g)} = -286$ kJmol^{-1}
ΔH^{θ}_c $C_2H_{6(g)} = -1560$ kJmol^{-1}

The first thing to notice is that this is an enthalpy of formation equation. Enthalpies of formation are difficult to calculate experimentally because combining carbon and hydrogen will give a variety of hydrocarbons, not just the one you want. Values are often calculated by looking at enthalpies of combustion.

Method one: Hess's cycle



This time the arrows go down to the products, so:

$c = a - b$
$A = 2 \times -393 + 3 \times -286 = -1644$
So $C = -1644 - (-1560) = -84$ kJmol^{-1}

Method 2: Algebraic

This time the way to remember is enthalpy change = Sum of reactants – products

So the calculation is the same as in the cycle above.

Using a different intermediate

When you have a different intermediate it will not be as clear as which way the arrows go. In that case the best advice is to draw a cycle so you can see what the pathway is. They are rare though.

Things to watch out for:

Coefficients: be careful and remember to do to your values what the coefficient in the equation requires.

Using the right cycle: Look very carefully at the DATA if given to see if it's ΔH_f or ΔH_c. Sometimes the IB will try and muddy the water, so read the question carefully. If they don't state what the data is (often in multiple choice papers where you can't use the data book) look at the equation and work out if it's enthalpy of combustion or formation. If all the reactants are elements then it's enthalpy of formation and so on.

Disguised enthalpy values: The IB enjoys trying to put you off the scent. Remember that the enthalpy of formation of CO_2 is the same as the enthalpy of combustion of carbon! We're just looking at it from different perspectives. Armed with this sometimes you can make the data work for you.

HL
SPREAD 8: Born–Haber cycles

Representative equations (e.g., $M^+_{(g)} \Rightarrow M^+_{(aq)}$) can be used for enthalpy/energy of hydration, ionization, atomization, electron affinity, lattice, covalent bond and solution.

Calculation of enthalpy changes from Born–Haber or dissolution energy cycles.

Relate size and charge of ions to lattice and hydration enthalpies.

Born–Haber cycles are used primarily to work out lattice enthalpies of ionic compounds. Lattice enthalpy is defined as: "Energy released when one mole of a solid crystal lattice is formed from its constituent gaseous ions."

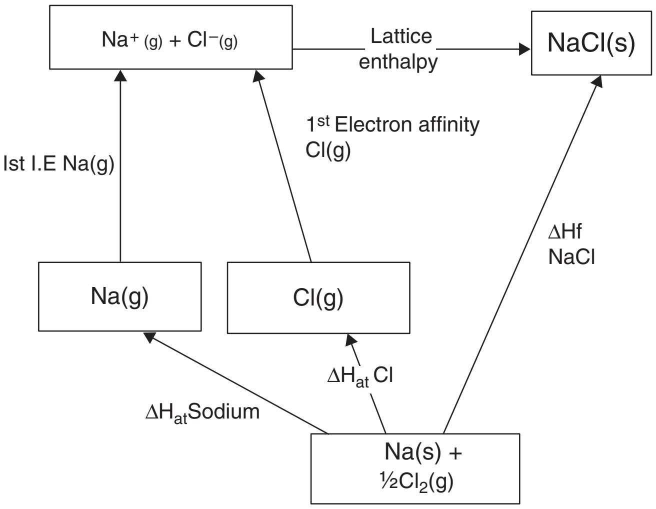
As you are making bonds the value is always exothermic. It can also be defined the other way round but then the sign will be opposite.

As an equation it is:

$$M^+_{(g)} + X^-_{(g)} \Rightarrow MX_{(s)}$$

Born–Haber cycles are multi-step Hess's cycles, which increases the complication, but they are much more predictable.

Example 1:
Calculate the lattice enthalpy of sodium chloride given the data below:



There is a lot of detail in this cycle, but it is very logical.

The cycle is set up with elements on the bottom with the regular enthalpy of formation of the compound on the RHS. The left hand side needs to create the gaseous ions.

The first step is to atomize the elements. For molecules that involves breaking the covalent bonds to form isolated gaseous atoms (so the value is half the value for the same for the average bond enthalpy for the relevant covalent bond in the data book). Metal atomization energies are not in the data book:

Definition is for forming one mole of isolated gaseous atoms.

Summary of equations for the cycle above:

Enthalpy of atomization: Energy required to form one mole of isolated gaseous ions: ΔH_{at}

$Na_{(s)} \Rightarrow Na_{(g)}$
$½Cl_2 \Rightarrow Cl_{(g)}$

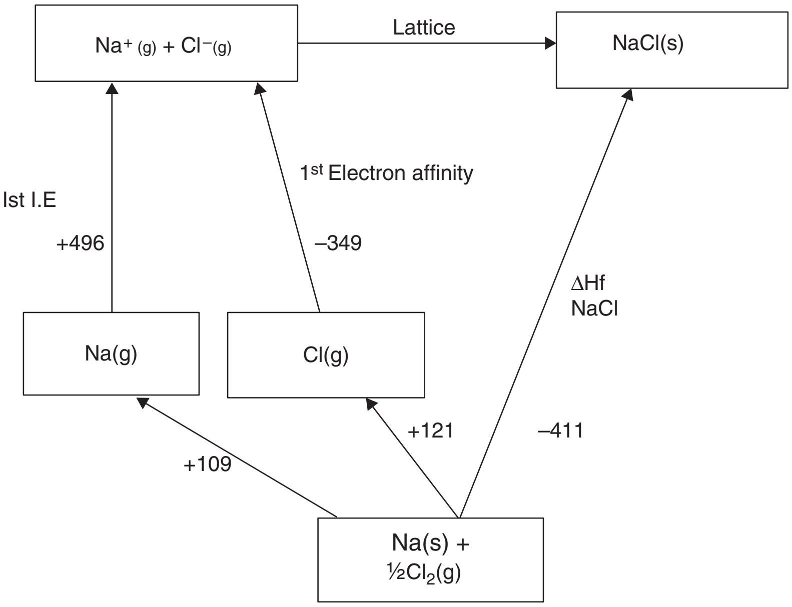
Once we have the gaseous atoms we need to ionize them. For metals this is simply the first ionization energy (see Chapters 2 and 4), although if you need a 2^+ ion (and so on) you need to use the second or third as well.

$Na_{(g)} \Rightarrow Na^+_{(g)} + e^-$

To get a negative ion you need to use the electron AFFINITY. This is the energy exchanged when an electron is added to one mole of gaseous atoms.

$Cl_{(g)} + e^- \Rightarrow Cl^-_{(g)}$

Once you have added all the values you get:



Then it is simply Sum of products – reactants

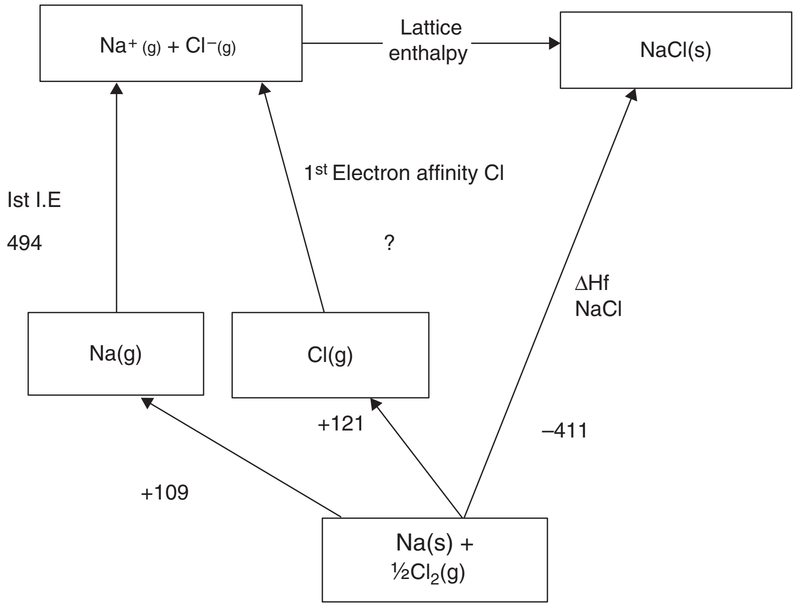
$-411 - (109 + 121 - 349 + 496) = -788\ kJmol^{-1}$

Marks are often available for a well-drawn, fully labelled Born–Haber cycle, so make sure you get all the state symbols correct and know what each section has. Practice some of the examples below. The syllabus suggests that any group 1 or 2 oxide or chloride is a fair game.

5.9 Where things get harder.

Sometimes the question will ask you to work out something else from the cycle, like the electron affinity. If so you have to solve using algebra. Let's use the example above.

Work out the first electron affinity of chlorine given in the data.



LE = Products − minus reactants, letting x be electron affinity

$$-788 = -411 - (109 + 121 + x + 494)$$
$$-788 + 411 = -(724 + x)$$
$$-377 = -724 - x$$
$$-377 + 724 = -x$$
$$x = -347 \text{ kJmol}^{-1}$$

In essence try and remember it's simply algebra you do in math class for fun.

HL

SPREAD 9: Enthalpy of solution cycle

Enthalpy of solution, hydration enthalpy and lattice enthalpy are related in an energy cycle.

Construction of Born–Haber cycles for group 1 and 2 oxides and chlorides.

Construction of energy cycles from hydration, lattice and solution enthalpy. For example, dissolution of solid NaOH or NH_4Cl *in water.*

The solubility of ionic compounds is dependent on the size of the lattice enthalpy. Water being a polar molecule is attracted to the ions in the lattice. As the water molecules approach ions in a lattice the positive end of the water molecule is attracted to negative ions and the negative end is attracted to positive ions. This attraction causes a release of energy. This is known as the enthalpy of hydration (ΔH_{hyd}) and is more formally defined below. If the hydration enthalpy of each ion can compare to the size of the lattice enthalpy then the ionic compound will dissolve in water.

When an ionic compound does dissolve in water, the enthalpy change accompanying this is known as the enthalpy change of solution ΔH_{sol}.

A similar Born–Haber cycle relates lattice enthalpy, enthalpy of solution and enthalpy of hydration.

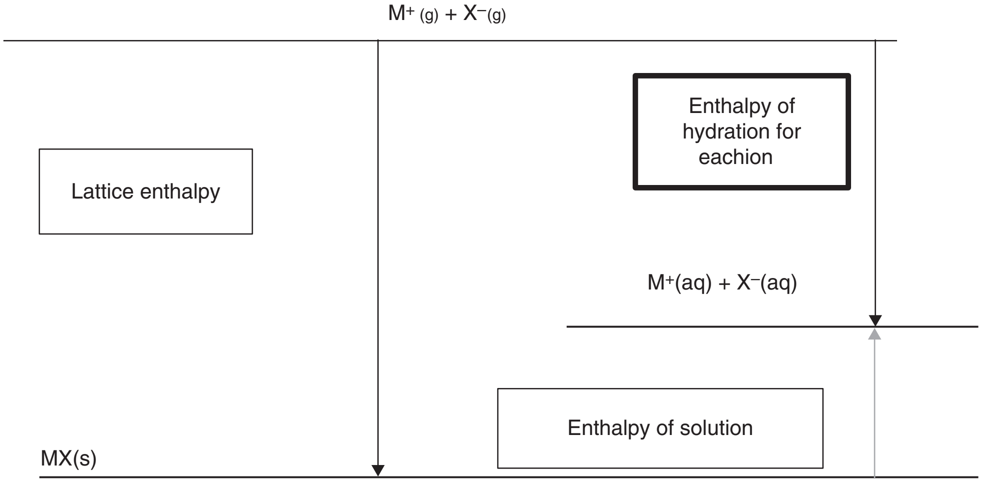
Enthalpy of hydration is the enthalpy change when one mole of gaseous ions is dissolved in large excess of water: this value is always exothermic.

$$M^+_{(g)} \Rightarrow M^+_{(aq)}$$

Enthalpy of solution is the enthalpy change accompanying one mole of a solute being dissolved in an infinite amount of water.

$MX_{(s)} \Rightarrow M^+_{(aq)} + X^-_{(aq)}$

This is difficult to do experimentally, so a cycle is set up to relate the three:



Again, working around the cycle is needed to get the answer, for example,

Calculate the enthalpy of solution of silver fluoride, if lattice enthalpy is −958

Enthalpy of hydration of silver ions −510 and fluoride −483

So working round the arrows and remembering to reverse the sign if we go against the arrow

Solution = −lattice enthalpy + hydration enthalpy
$= -(-958) + (-510) + (-483) = -35\ \text{kJmol}^{-1}$

Again be careful with formulae. Something like Na_2O will require you to double the hydration enthalpy for sodium value.

As a rule of thumb enthalpy of solution values will tell you if an ionic solid is soluble in water. Essentially any negative value will be soluble in water but also most substances with a slightly positive value.

HL
SPREAD 10: The magnitude of lattice enthalpy

Consider the following lattice enthalpies from the data book, quoted as positive values for breaking the lattice:

LiF	1049	LiF	1049	NaF	930
NaF	930	LiCl	864	MgF_2	2957
KF	829	LiBr	820	AlF_3	5215

The first and second column show a clear trend as you increase the size of the cation and anion respectively: they both decrease. This is because the size of the ion decreases the influence of the charge. This is also known as charge density. The bigger the ion the lower charge density, so the weaker attraction to oppositely charged ions. The third column shows how increasing the charge (and also decreasing size as a consequence) greatly increases the lattice enthalpy. This shows how the charge density increases as the charge increases:

So, a small highly charged ion will have a greater charge than a large ion with a small charge. Compounds with two ions of high charge density will have a greater lattice enthalpy.

This is a classic multiple choice question:

Value for lattice enthalpies (Topic 18), enthalpies of aqueous solutions (Topic 19) and enthalpies of hydration (Topic 20) are given in the data booklet.

HL
SPREAD 11: Entropy and spontaneity

Entropy (S) refers to the distribution of available energy among the particles. The more ways the energy can be distributed the higher the entropy.

Gibbs free energy (G) relates the energy that can be obtained from a chemical reaction to the change in enthalpy (ΔH), change in entropy (ΔS) and absolute temperature (T).

Entropy of gas > liquid > solid under the same conditions.

In a roundabout way this whole chapter has been about spontaneity: whether a reaction "goes" or doesn't. There are various factors we've met so far that appear to contribute:

The enthalpy change of reaction.
The temperature the reaction happens at.

Although both are factors, neither gives us the definitive "yes" or "no" answer we're looking for. This section looks at a third factor and leads us to a formula for definitively working out the spontaneity of a reaction.

Entropy is the third factor. Entropy (*S*) of a substance refers to the distribution of available energy among the particles. The more ways the energy can be distributed the higher the entropy. By this token a substance has more energy in the gaseous phase than in the solid phase. The units of entropy are $JK^{-1}mol^{-1}$.

In multiple choice questions there are simple questions that test your understanding of entropy. Any chemical reaction where gases are produced from solids (increase in disorder) will lead to an increase in entropy. See the three examples below:

Examples:

$ZnCO_{3(s)} \Rightarrow ZnO_{(s)} + CO_{2(g)}$

Here there is an increase in entropy because there are more moles of gas on the right hand side. Gases are more disordered, so the entropy change is positive.

$N_{2(g)} + 3H_{2(g)} \Rightarrow 2NH_{3(g)}$

Here the entropy change is negative because there were four moles of gas on the left and only two on the right. The system gets less ordered.

Calculating entropy change

For this course the entropy of a reaction can be calculated using the formula below:

$\Delta S_{(\text{reaction})} = \Delta S_{(\text{products})} - \Delta S_{(\text{reactants})}$

The IB does not publish entropy values in their data book, so all values must be given in the question. The calculation is clearly one of the simpler ones and is usually given in tandem with other work (see ammonia question below). If you calculate the value remember:

A positive value means an INCREASE in entropy.
A negative value means a DECREASE in entropy.

A positive value for entropy should be quite a factor in whether a reaction is spontaneous but (again) it's not the definitive answer. For example,

Magnesium burning in oxygen is a well-known and clearly spontaneous reaction but just looking at the state symbols tells you the entropy DECREASES.

$Mg_{(s)} + 2O_{2(g)} \Rightarrow 2MgO_{(s)}$

HL
SPREAD 12: Gibbs free energy

As we have seen, ΔH, ΔS and temperature all provide clues to the spontaneity puzzle but aren't the whole answer. Gibbs free energy (ΔG) does provide the answer.

The derivation of this goes beyond the scope of the entropy explanation on the syllabus, but it is usually shown as an equation.

$$\Delta G^{\theta} = \Delta H^{\theta} - T\Delta S^{\theta}$$

This is in the data book.

Units are kJmol^{-1}.

And all three factors are linked together to give us an answer, which is:

If ΔG is negative then the reaction IS spontaneous.

If ΔG is positive then the reaction IS not spontaneous.

Again, the calculation isn't too onerous and is often linked to a three-part question (see below). The mistakes are to use the temperature given in Celsius not Kelvin and to forget that entropy has different units (JK^{-1}mol^{-1}), which means the value must be divided by 1000. This is why you often see the formula written

$$\Delta G^{\theta} = \Delta H - T(\Delta S/1000)$$

Other uses of ΔG

Ready reckoner for predicting ΔG without a calculator

It is important to have a feel for whether a reaction is spontaneous or not just from the signs of the enthalpy and the entropy. The table below is worth learning.

Enthalpy (DH)	**Entropy (DS)**	**ΔG**	**Spontaneity**
Exothermic (–)	Positive	Always negative	Always spontaneous
Endothermic (+)	Positive	Depends on temperature	Spontaneous at high temperature
Exothermic (–)	Negative	Depends on temperature	Spontaneous at low temperature
Endothermic (+)	Negative	Always positive	Never spontaneous

The second and third conditions in the table note that spontaneity depends on temperature. Sometimes you can be asked to work out the temperature that the reaction becomes spontaneous. To do this you need to manipulate the ΔG equation so $\Delta G = 0$.

That is, $T = \Delta H/\Delta S$

Don't forget to divide entropy by 1000 and also remember the value is in Kelvin, so subtract 273 to get the value in Celsius.

CHAPTER

7 Chemical kinetics

This chapter covers material from Topics 6 and 16 of the IB syllabus.

CORE
SPREAD 1: Collision theory and rates of reaction

Species react as a result of collisions of sufficient energy and proper orientation.

The rate of reaction is expressed as the change in concentration of a particular reactant/product per unit time.

Concentration changes in a reaction can be followed indirectly by monitoring changes in mass, volume and color.

Introduction

Chemical reactions occur: we know that, but one of the truths of all chemical reaction is that we can have some influence in how quickly the reaction goes.

Kinetics is a topic that has almost certainly been met in studying chemistry on prior courses and this book will not dwell on the basics, although there are essentially five ways in which this can be sped up:

- Increasing the concentration of one or more of the reagents.
- Increasing the temperature at which the experiment is carried out.
- Increasing the pressure exerted on gaseous reagents.
- Increasing the surface area of solid reactants.
- Adding a suitable catalyst.

Students would not be expected to recall these but might be expected to recall why they affect reaction rate.

For a chemical reaction to occur reactant particles (which could be atoms, molecules, ions or radicals) must collide in the right orientation and with sufficient energy. All chemical reactions have an activation energy that is uniquely associated with it (see previous chapter); this must be overcome if the collision is to be successful. The orientation is related to precisely where the collision occurs on each molecule. This is less relevant for ions, which are often spherical but for complicated organic molecules only one small part of the molecule might actually be "reactive" to the other reagent.

What is rate of reaction?

Students often get confused as to what reaction rate actually is, confusing it with time. Reaction rate is the speed of the chemical reaction, and it is usually expressed as the change in concentration of a particular reactant/product per unit time:

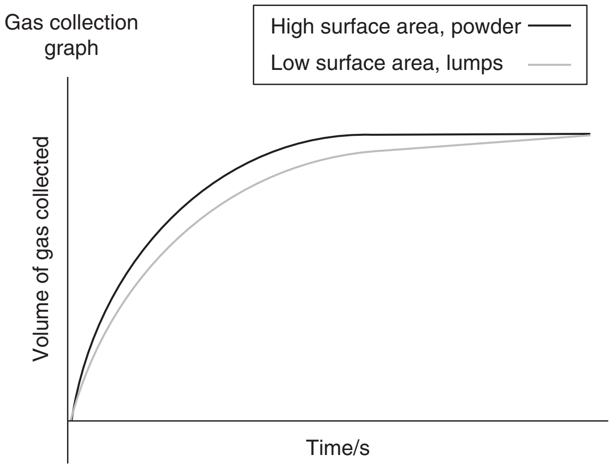
For example, $\text{moldm}^{-3}\text{s}^{-1}$

However if a reaction is particularly slow this could be changed to be per minute, or even per hour. Another confusion is precisely how this is measured. Often reaction rate is measured by color changes, volume of gas collected, mass loss as a gas is created, or other visual changes. These may not be directly related to the concentration of a reagent or product, and so some extrapolation may have to be done.

Any answer relating to how these factors affect reaction rate must relate to how the change has "increased the chances of successful collisions." Activation energy (E_a) is the minimum energy that colliding molecules need in order to have successful collisions. The following sections look at each factor that affects rate:

Surface area

In simple terms a powder reacts faster than a lump. This is because crushing a lump into a powder allows all the reagents inside the lump to be exposed and able to react.

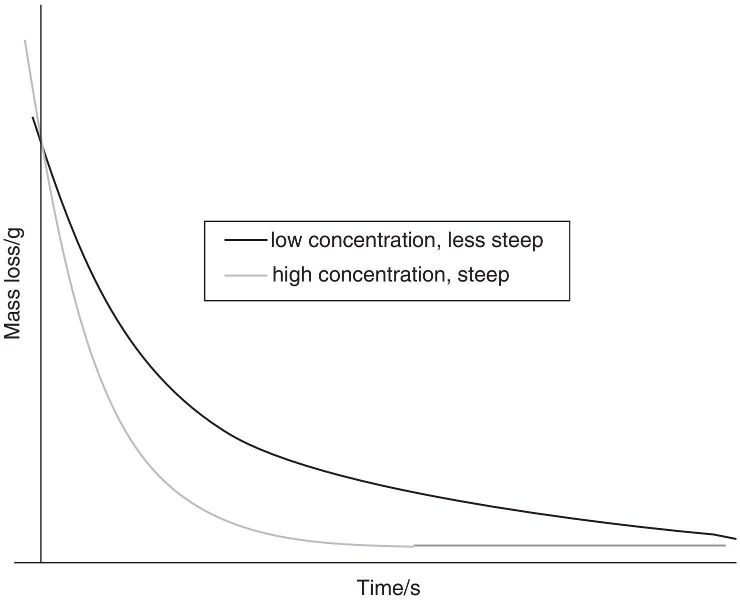


As you can see the steeper the curve the faster the rate of reaction. In fact taking a tangent and working out the gradient will give a value for the rate of reaction at that particular time. Two other points to note: (1) the graph flattens out as one of the reagents runs out, (2) both graphs finish at the same point because the same amount of reagent was used.

If the graph is related to measuring concentration change then the graph is the other way round.

Concentration

Very simple, increasing concentration increases the amount of reactant particles in a given volume, therefore increasing the probability of a successful collision. With a plot of such a reaction be careful of changing the quantity of a reagent. If you increase the concentration and keep the volume the same then you will increase the molar quantity of the reaction, so the graph will not finish at the same place.



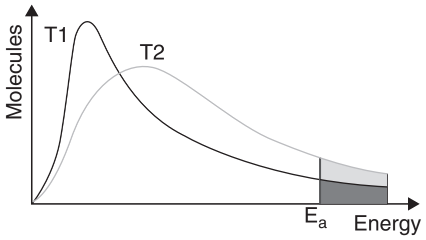
Here the grey line is with a higher concentration. The line is steeper, and as the concentration has increased the quantity the graph finishes at a lower level.

CORE
SPREAD 2: How do temperature and catalysts affect rate of reaction?

Activation energy (E_a) is the minimum energy that colliding molecules need in order to have successful collisions leading to a reaction.

By decreasing E_a, a catalyst increases the rate of a chemical reaction, without itself being permanently chemically changed.

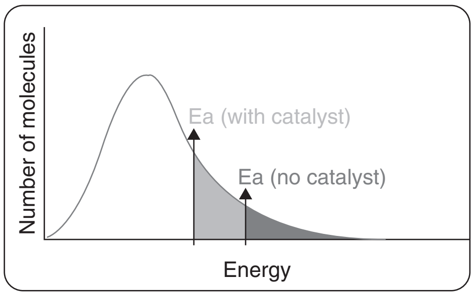
Temperature has a minor effect on the frequency of collisions but has much more of an effect on the quality of the collision. Temperature is a measure of the average kinetic energy of the particles, so increasing the temperature increases the energy of the collision, which can allow more molecules to collide with the required activation energy. This is often explained using a Maxwell–Boltzmann distribution curve: see below.



The distributions show the area under the line as all the reactant particles. T1 is the lower temperature, and most particles have the energy where the peak is. Very few particles are past the "winning post" of the activation energy, therefore few collisions are successful and the reaction is slow. Increasing the temperature to T2 increases the average kinetic energy of the particles, and the curve peak shifts to the right and gets less steep. This has the effect of shifting more particles past the winning post, which means more successful collisions occur. Activation energy is fixed. The higher the temperature the flatter and further to the right becomes the curve and the faster the reaction will be.

Catalysts

It's easy to think of a catalyst in simple terms, in that it speeds up a reaction without being used up. Even a very superficial thought will soon realize how wrong that must be. Catalysts do get involved forming intermediaries, and they regenerate at the end of the reaction. It is better to say catalysts speed up reactions by using a different reaction pathway with a lower activation energy. In Maxwell–Boltzmann terms it looks like this:



You can see that activation energy with the catalyst is much lower, which allows more particles to react successfully, which brings us to the other fundamental misunderstanding with catalysts: namely that we do not use them to speed up reactions per se. We add catalysts to carry out reactions at lower temperature, so we can save on the costs of energy. Simply heating something up is much easier than searching for the exact catalyst for a particular reaction.

HL
SPREAD 3: The rate expression

The order of a reaction can be either integer or fractional in nature. The order of a reaction can describe, with respect to a reactant, the number of particles taking part in the rate-determining step.

Rate equations can only be determined experimentally.

The value of the rate constant (k) is affected by temperature, and its units are determined from the overall order of the reaction.

Catalysts alter a reaction mechanism, introducing a step with lower activation energy.

As is often the case the HL material here puts numbers on the theories. The first aspect to look at is the rate expression. This is a relationship between the concentrations of the reagents and the rate of reaction.

In general terms the rate of reaction is directly proportional to the concentrations of the reagents:

Rate $\propto$ Concentration

We remove the proportionality sign by adding a constant so we get

Rate = k × concentrations of reagents

k is known as the RATE CONSTANT

Each reagent is listed as below:

Rate = $k\,[A]^x\,[B]^y$

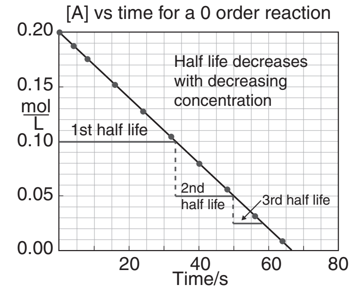
The x and y are the orders of the reaction and are defined as the power to which the concentrations are raised in the rate expression. Essentially they nail down how the reagent in question affects rate and can only be determined from experiments.

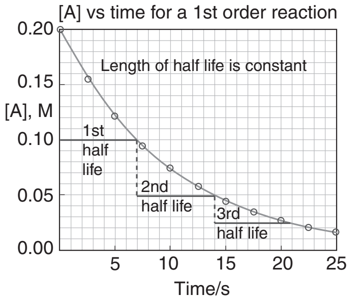
The three possibilities are:

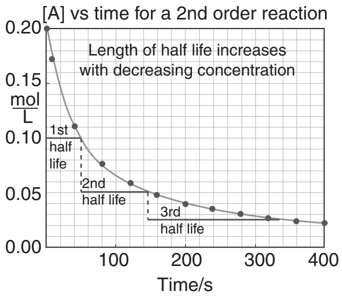
Zero order: no effect on rate.
First order: if concentration doubles then rate is doubled.
Second order: if concentration doubles the rate is quadrupled.

What you would be expected to be able to do:

1) Determine order of reaction from a graph.
2) Look at the graphs below; they show a series of concentration versus time graphs for zero order, first order and second order reactions. The most important one is the first order graph. It is exponential, and it has a constant half-life. If presented with a graph in an exam the easiest way of proving the order is first to check the half-life, as illustrated below.



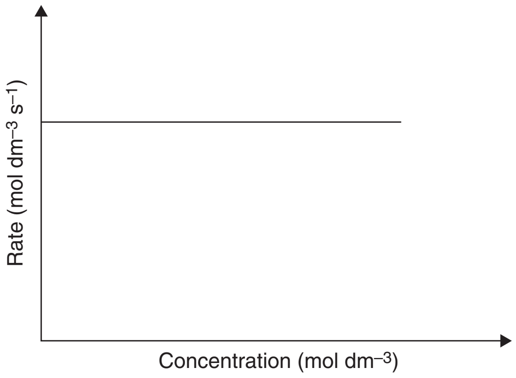


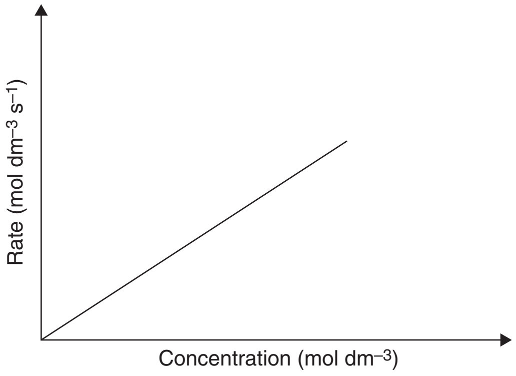


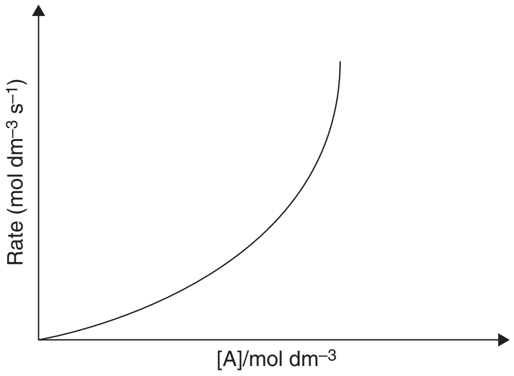
As you can see there is a clear half-life for first order reactions. In reality, given the stress of an exam any graph given to you will almost certainly be a first order with constant half-life. To prove it you will need to show it as you see in the graphs.

You can also work out the rate by taking a tangent at any point along the line.

Rate concentration graphs are equally easy to interpret. See the three below. First order will be exponential, and second will deviate from the straight line.







HL
SPREAD 4: Initial rates data

A more common way of expressing data from rates experiments is to use initial rates data. This requires an experiment where concentrations are changed and experiments performed. Graphs are plotted, as above, but the tangent is taken at the top of the curve to work out the initial rate.

As is often the way, looking at an example is the best way forward.

Example:
Given the following data, determine the rate for the reaction of nitrogen monoxide reacting with hydrogen forming nitrogen and water.

$2NO_{(g)} + 2H_{2(g)}\ N_{2(g)} + 2H_2O$

Experiment	Moles NO	Moles H_2	Initial rate (m/s)
1	0.10	0.10	1.23×10^{-3}
2	0.10	0.20	2.46×10^{-3}
3	0.20	0.10	4.92×10^{-3}

You work it out by comparing the experiments:

In experiments 1 and 3 the concentration of NO doubles. How does this affect the rate?
Answer: It quadruples it. This means that the order with respect to NO is 2.
In experiments 1 and 2 the concentration of H_2 is doubled and the rate doubled. This shows the order with respect to hydrogen is 1.

Rate expression:

$\text{Rate} = k[NO]^2[H_2]$

Overall order = 3

Next you might be asked to work out the value of the rate constant (*k*)

Put the numbers in (from any of the rows in the table—it won't matter—it's a constant) and raise by the order of reaction.

Taking the top row NO = 0.10 moldm^{-3} H_2 = 0.1 moldm^{-3}. Rate 1.23×10^{-3} $\text{molm}^{-3}\text{s}^{-1}$

Rearrange the rate expression

$k = \text{Rate}/[NO]^2[H_2]$

So $1.23 \times 10^{-3}/0.1^2 \times 0.1 = 1.23$ units $\text{moldm}^{-3}\text{s}^{-1}/\text{moldm}^{-3}\ \text{moldm}^{-3}\ \text{moldm}^{-3}$

So the units are $1/\text{mol}^2\text{dm}^{-6}$

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

More on the units for *k*

The value of *k* should have units, and they are worked out from the other things in the relationship.

$\text{Rate} = k\,[A]^1[B]^2$

So:

$$k = \text{Rate} / [A]^1[B]^2 \text{ or in units} = \frac{\text{moldm}^{-3}\text{s}^{-1}}{\text{moldm}^{-3}\ \text{moldm}^{-3}\ \text{moldm}^{-3}}$$

There are two ways of working it out:

1) Using indices we can add across and subtract down

Across first—add them up:

$$\frac{\text{moldm}^{-3}\text{s}^{-1}}{\text{mol}^3\text{dm}^{-9}}$$

Then subtract down:

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

2) By cancelling out

$$\frac{\cancel{moldm^{-3}}\ \cancel{s^{-1}}}{moldm^{-3}\ moldm^{-3}\ \cancel{moldm^{-3}}}$$

This leaves nothing on top and two underneath. This is mathematically:

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

This is the inverse, so the units are $mol^{-2}dm^{6}$.

It is worth practicing this. There are quicker ways of doing this, but this method is great for those who want to be sure they are getting it right.

The rate constant is a constant and does not change for a particular experiment and a particular temperature. It WILL change with temperature, however, and the higher the temperature the higher the value of the rate constant.

HL
SPREAD 5: Mechanisms

Reactions may occur by more than one step and the slowest step determines the rate of reaction (rate determining step/RDS).

The molecularity of an elementary step is the number of reactant particles taking part in that step.

How do chemical reactions really work?

It is easy to imagine that chemical reactions happen as if by magic. In fact they can work in far more complicated ways than the simplistic collision model outlined on the core course. In truth chemical reactions can occur in a series of steps. Chemists spend a lot of time working out the precise nature of these steps. Evidence from kinetics experiments and the orders of reaction can give us clues to how the reaction happens. The steps are known as mechanisms. You will meet a lot of them in the Chapter 11 of the book.

Mechanisms in more detail

Consider a simple task: sorting out some papers into order groups, and stapling them together. We only have one stapler, so if we wanted to speed up the task where could we assign more people? Well as there is only one person putting two people onto the stapler wouldn't speed it up. Therefore putting more people onto the sorting out task would make the difference. This is the RATE DETERMINING STEP, because changing things here changes the rate of reaction. The same is true in chemical reactions: there will always be a step that can be speeded up. This could be written as "the slow step, or the rate determining step." Either way, it's crucial.

How can we find the rate determining step?

Easy, the rate determining step is the one in the mechanism that up to and including it includes everything mentioned in the rate expression.

The best way of explaining it is to look at a classic example: the reaction between nitrogen monoxide and hydrogen:

Chemical equation:

$$2NO + 2H_2 \Rightarrow N_2 + 2H_2O$$

A series of experiments could be carried out, and it was found that the order with respect to NO is second order and the order with respect to H_2 is first order.

$$\text{Rate} = k\,[NO]^2[H_2]^1$$

Below is a proposed mechanism for this reaction; below it are the justifications. Reaction intermediates are in italics. Reaction intermediates are sometimes known as activated complexes and do not exist in real terms, only as a stepping stone.

Step 1: $NO + NO \Rightarrow N_2O_2$
Step 2: $N_2O_2 + H_2 \Rightarrow N_2O + H_2O$ (slow step, the rate determining step)
Step 3: $N_2O + H_2 \Rightarrow N_2 + H_2O$

We can be confident of this mechanism because:

- The mechanism works stoichiometrically. The equation balances for number of moles of reactants and products, as in the CHEMICAL EQUATION: 2NO, $2H_2$ on the left side, one nitrogen molecule and two waters on the right hand side.
- The mechanism works with respect to the rate expression. The rate expression says NO is second order. This means two NO molecules must appear UP TO AND INCLUDING THE RATE DETERMINING STEP. This is true (both in step 1).
- The order with respect to hydrogen is one. And one hydrogen appears in the mechanism UP TO AND INCLUDING THE RATE DETERMINING STEP.

There may be other possibilities that satisfy both the stoichiometric chemical equation and the rate expression.

This one below does, but it can't possibly happen.

Step 1: $NO + NO + H_2 \Rightarrow N_2O_2H_2$ (slow, rate determining step)
Step 2: $N_2O_2H_2 + H_2 \Rightarrow 2H_2O + N_2$

Although the rate expression and chemical equation criteria are fulfilled this falls down on practicality. The mechanism required three particles to collide perfectly at the same time. This is very unlikely.

You might be expected to look at a mechanism and work out the rate determining step from the rate expression. Or comment on the proposed mechanism for whether the RDS is the right one or its practicality. You might also be asked to propose a mechanism. If asked to do this remember that the intermediates don't matter; just make sure the reagents and products balance and the rate expression data is used.

Single step mechanisms

Single step mechanisms are possible of course, but they need to fulfil specific criteria of the rate expression. The overall order of the reaction must be two, and there can only be two moles of reagents. This is because all steps can only involve two particles colliding so if the orders in the rate expression add up to more than that then there must be more molecules to collide.

Molecularity

This is the name given to the number of particles in a particular step. Specifically it is usually associated with the rate determining step. So in the example above with three steps the molecularity refers to the slowest step. The molecularity is two.

Molecularity can have some subdivisions. Unimolecular refers to one species molecularity. This is where a big molecule breaks down (as there is only one species in the step). Bimolecular is where two species collide.

HL
SPREAD 6: Activation energy

The final task in this topic is to be able to work out activation energy.

There is a simple relationship between temperature/activation energy and the rate constant. It is known as the Arrhenius equation.

It is:

$$\ln k = E_a/RT + \ln A$$

Where $\ln k$ is the natural log of the rate constant:

E_a = activation energy
R = gas constant (8.314)
T = temperature in Kelvin

$\ln A$ = the steric factor, a numerical value for the orientational importance of the collision

This expression is in your data book. Various versions of it exist, but this version allows things to be clearer. Because when you look at this closely it resembles:

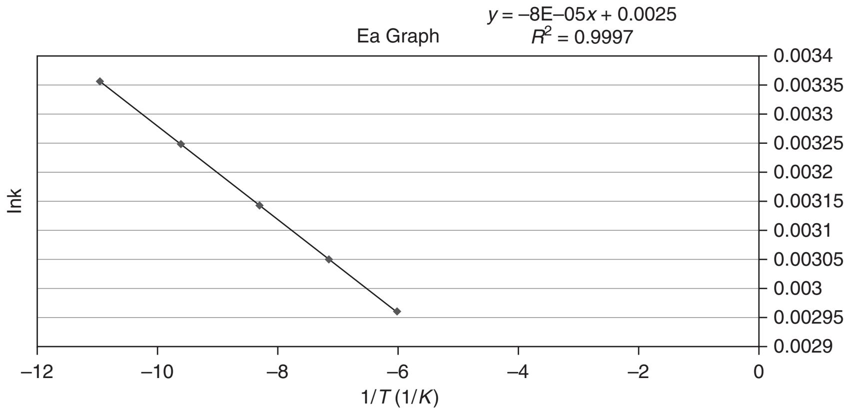
$Y = mx + c$—the general equation for a straight line on graph.

So if you plot A graph of $1/T$ against $\ln k$ is a linear plot with gradient $-E_a/R$ and intercept, $\ln A$.

You get a straight line and the gradient will = $-E_a/R$.

A bit of manipulation and you can work out E_a.

Example below:



You would not be expected to fully plot a graph as this (that would be too easy!), but you might be given a graph and would be expected to work out the gradient of the line. A multiple choice question would be more interested in if you know what the x and y axes would be.

The frequency factor is the c in the equation and, therefore, would be the value of the intercept on the y axis.

To work out the activation energy you need to find the gradient of the straight line. This equals $-E_a/R$

Multiplying by the gas constant 8.314 and you have the activation energy in joules. It should be endothermic.

CHAPTER

8 Equilibrium

This chapter's contents refer to the material covered in Topics 7 and 17 of the IB Chemistry Specification.

CORE
SPREAD 1: What is equilibrium?

The characteristics of chemical and physical systems in a state of equilibrium.

A state of equilibrium is reached in a closed system when the rates of the forward and reverse reactions are equal.

What is equilibrium?

If there is a loose theme to this middle part of the IB DP chemistry course it is about exploring the nature of what it takes to make a chemical reaction happen. In Chapter 6 it was all about whether reactions actually happened or not, and how we know for sure by doing some mathematics. The last chapter was about how we can control the speed at which the reactions go. This chapter looks at those reactions that get stuck somewhere between "going" and "not going." You probably know them better as reversible reactions, or reactions that are at equilibrium.

You can tell if you have an equilibrium system because of the sign:

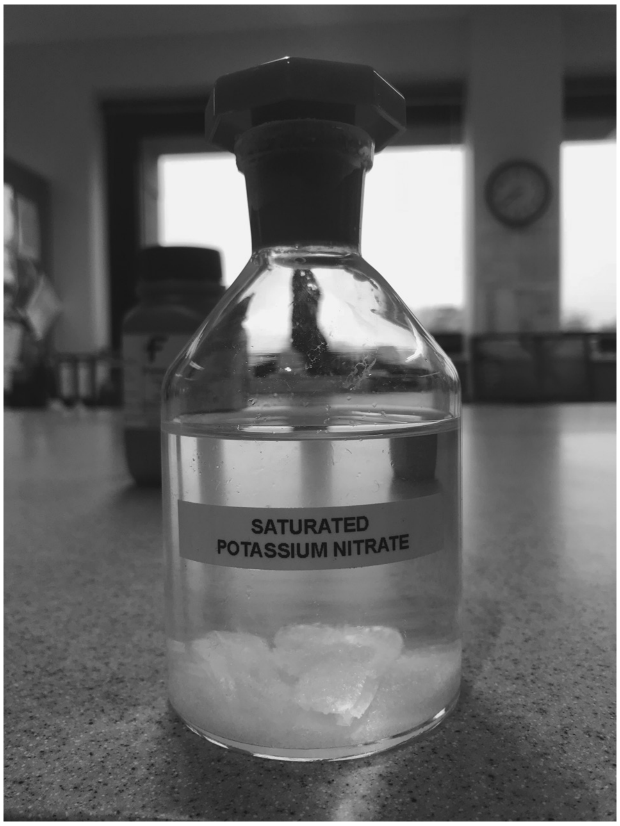
$\rightleftharpoons$

This section is really all about getting to understand what we mean by equilibrium. I'll start with an everyday analogy and then get to the science.

Essentially a reaction is at equilibrium when the forward and backward reaction are happening at the same rate. This is a bit of weird idea, so the best way is to think about a down escalator.

Imagine a person walking up the down escalator like in the picture. If they can get their pace right to the observer some distance away it might look like the person wasn't moving, when in fact both escalator and person are going quite quickly but in opposite directions. We can of course change the position of the person, but that involves changing the conditions. The same is true in chemical reactions.

A more scientific example is a sealed saturated solution.



This will not change it composition because the lid is on. There will always be the same amount of undissolved solute and solution. Again we could ruin this perfect equilibrium between solid and solution in a number of ways, and we'll come to that on the next few pages, but if the conditions do not change the reaction will remain the same forever.

EQUILIBRIUM IS ACHIEVED WHEN THE FORWARD AND BACKWARD REACTION ARE HAPPENING AT THE SAME RATE.

So let's sort out the four principles of a system at equilibrium.

1) Equilibrium is dynamic. Constantly moving, as said above, the forward and backward reactions are happening at the same rate.
2) At equilibrium the quantities of the reactants and products remain constant (up to a microscopic point).
3) Equilibrium must happen is a closed system. Otherwise gas or water would evaporate. Nothing can escape, or it's not going to stay in equilibrium.
4) Equilibrium can be approached from either direction. It doesn't matter whether you start with reactants or products; ultimately, at the temperature carried out you will always reach the same equilibrium.

Learning these pillars of wisdom are crucial to understanding an equilibrium question—and the examiners can ask about them too!

CORE
SPREAD 2: Changing the position of equilibrium

The effects of temperature, pressure, concentration and catalyst on the position of equilibrium.

Le Chatelier's principle

Apart from buffer solutions in your body and the ozone–dioxygen equilibrium in the atmosphere that both stop us from dying most equilibrium systems are annoying to chemists! We want reactions to go to completion, or certainly produce products in good quantities when we mix the chemicals together.

Let's be clear about this. This is not the same as speeding up the reaction; it is about making the reaction go in the direction you want it to: this is often summarized as "how far," rather than "how fast." The problems start because the factors that will speed up a reaction will often also push an equilibrium system in various directions. This is why you need to be careful to look at the question to see what they are asking.

Essentially if you see this:

$\leftrightarrows$

Then give your answer a bit of thought.

Let's define Le Chatelier's principle first. It is that "when a change is done to a system at equilibrium the system will adjust to negate that change." And let's also be clear the answer to a question in an exam is never "because of Le Chatelier's principle"! In fact it's better never to mention it by name, simply state what change happens because of the change you make.

Try and use language like the equilibrium shifts left/right too.

Conditions

Concentration

This is the easy one (although it returns with a vengeance in the next chapter). Look at the system below:

$$\underset{x}{CH_3COOH} + H_2O \rightleftharpoons \underset{y}{CH_3COO^-} + H_3O^+$$

It is fairly easy to see that increasing the concentration of the x will shift the equilibrium to the right. You have added more of x; the only way to remove that is to turn some of that into y, therefore the equilibrium shifts right.

Let's note the opposite too. Let's say we remove one of the reagents (x); this time the system will shift left to create more of the removed reagent.

Removing a reagent seems weird, but if it wasn't a closed system and the reagent was a gas it would remove itself on its own accord. Concentration examples are very easy and are usually not examined.

Pressure

To work out how an increase in pressure affects the position of equilibrium you need to do a bit more work.

Pressure is effectively the number of gas particles in a given space, and pressure will affect all gas particles whether reactants or products.

Let's look at the famous example below:

Ammonia

$$N_{2(g)} + 3H_{2(g)} \leftrightarrows 2NH_{3(g)}$$

You can see there are four moles of gas on the left hand side (LHS) and 2 on the right hand side (RHS). If you increase pressure the system will want to relieve the pressure. It can't physically turn off the pressure (!) so it has to lower the pressure by lowering the "amount of particles in a given space." It therefore shifts to the side of fewest moles, in this case the RHS.

If you lower the pressure in the example above it will shift to the LHS to increase the number of particles in a given volume.

What about this example?

$$2HI_{(g)} \leftrightarrows H_{2(g)} + I_{2(g)}$$

Well spotted! Both sides have the same number of moles, so an increase in pressure will have no effect on the POSITION of equilibrium. Although from a rate perspective it will get there faster.

Temperature

This one requires additional information. You need to know the enthalpy change for the reaction.

Ammonia

$$N_{2(g)} + 3H_{2(g)} \leftrightarrows 2NH_{3(g)} \quad \Delta H = -95\ \text{kJmol}^{-1}$$

The enthalpy change quoted is for the forward reaction, the reverse is the opposite.

It is best to always consider the ENDOTHERMIC direction first. What do endothermic reactions need? Heat energy. Therefore any increase in temperature will ALWAYS favor the endothermic reaction. So in the example above a change of temperature would shift the equilibrium to the left.

So how do we make exothermic reactions shift in the direction we want? Answer: we don't encourage the endothermic reaction: that is, cool them down. (It can sometimes be misleading to think exothermic reactions need to be cold. They don't; we just don't want to encourage the endothermic.)

Look at the example below:

$$2SO_{2(g)} + O_{2(g)} \leftrightarrows 2SO_{3(g)} \quad \Delta H = -395.2\ \text{kJmol}^{-1}$$

To make more SO_3 you need to do either of the following:

Raise the pressure: it would shift the equilibrium to the right (fewer moles).

Lower the temperature: the reaction is exothermic so it favors the RHS.

Catalyst

A catalyst will speed up both directions of an equilibrium reaction and therefore has no effect on the QUANTITY of products made. They always ask: make sure you remember it does not affect the position of equilibrium.

CORE
SPREAD 3: The equilibrium constant, K_c

The equilibrium law describes how the equilibrium constant (K_c) can be determined for a particular chemical reaction.

The magnitude of the equilibrium constant indicates the extent of a reaction at equilibrium and is temperature dependent.

At equilibrium there is a relationship between the concentrations of the products and the concentrations of reactants. Essentially the concentration of the products to the power of their coefficients divided by the reactants will provide a constant at any given temperature. This constant is known as the equilibrium constant (K_c).

So for the reaction:

$$wA + xB \leftrightarrows yC + zD$$

$$K_c = \frac{[C]_y[D]_z}{[A]_w[B]_x}$$

(The square brackets are shorthand for concentration.)

The value of K_c can be worked out if the concentrations are known.

Example:
Calculate K_c for the reaction below:

$H_2 + I_2 \leftrightarrows 2HI$

Given that $[H_2] = 0.2$ moldm^{-3}, $[HI] = 1.38$ moldm^{-3} and $[I_2] = 0.3$ moldm^{-3}

First write out the K_c expression:

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

Then add the numbers in:

$K_c = 1.38^2/0.2 \times 0.3 = 54$

Working out the units:

The units of K_c depend on the structure of the K_c expression, like we did for rates. Here we have

$$\frac{\cancel{\text{moldm}}^{-3}\ \cancel{\text{moldm}}^{-3}}{\cancel{\text{moldm}}^{-3}\ \cancel{\text{moldm}}^{-3}}$$

All units cancel so the number has no units, or is “dimensionless.”

What affects K_c?

The value K_c is unaffected by changes in concentration and pressure but does vary with temperature.

Essentially K_c is a fraction. When temperature changes the position of equilibrium it will affect the size of the denominator and the numerator:

$$\frac{\text{Numerator}}{\text{Denominator}}$$

If the denominator increases then the fraction gets smaller, so K_c decreases. The denominator is the reactants.

If the numerator increases the fraction gets larger and K_c increases. The numerator is the products.

Consider:

$A + B \leftrightarrows C + D$

$$K_c = \frac{[C][D]}{[A][B]}$$

As the temperature increases this happens:

Temperature (°C)	K_c
25	1
35	5
45	9
55	14

As temperature increases K_c increases. This means the top of the fraction must be getting bigger, which means the products are increasing, so the equilibrium *must* have shifted to the right. This must be the endothermic direction.

In summary, changes in K_c with temperature allow us to work out whether the reaction is exothermic or endothermic. The trick is to think through what the change to K_c means to the fraction.

CORE
SPREAD 4: What does the value of K_c tell us?

The magnitude of the equilibrium constant indicates the extent of a reaction at equilibrium and is temperature dependent.

The reaction quotient (Q) measures the relative amount of products and reactants present during a reaction at a particular point in time.

A large value K_c means the equilibrium lies to the right, and the reaction nearly goes to completion. A very small value of K_c means the reaction lies to the left and very little product is made. Think of the number as a fraction, if it helps.

The reaction quotient

The reaction quotient (Q) measures the relative amount of products and reactants present during a reaction at a particular point in time. It can be used to help us work out what the change you have made to the equilibrium will do to the equilibrium.

K_c is constant for a system at equilibrium. Therefore, at equilibrium $K_c = Q$.

However if you change the conditions this will affect the concentrations temporarily, so Q_c will be different from K_c.

If Q_c is greater than K_c then the reaction favors the reactants and the reaction will shift left.

If Q_c is less than K_c then reaction favors the products and the reaction will shift right.

If $Q_c = K_c$ then the reaction **is** at equilibrium and no shift takes place. The position of the equilibrium changes with changes in concentration, pressure and temperature.

HL
SPREAD 5: The equilibrium law

The position of equilibrium can be quantified by the equilibrium law. The equilibrium constant for a particular reaction only depends on the temperature.

Solution of homogeneous equilibrium problems using the expression for K_c.

The HL course demands that you work out the equilibrium concentration for a reaction when you do not know all the quantities of the components of the equilibrium. This can be a tricky bit of work.

Worked example

Consider the equilibrium between:

$2HI_{(g)} \leftrightarrows H_{2(g)} + I_{2(g)}$

Two moles of HI were left in a sealed container of 2 dm³ volume. The system was allowed to reach equilibrium, and it was found that at equilibrium 0.4 moles of HI remained. Calculate K_c.

Step 1: Draw a table

$2HI \leftrightarrows H_2 + I_2$

Moles at the start (from the question)	2	0	0
Moles at equilibrium (from the question	0.4		
Concentration			

You can see how this is set up. Now we need to fill in the gaps. We can see that we started with 2.0 moles of HI and at equilibrium we have 0.4 moles; therefore, we have used up 1.6 moles. Therefore according to the equation we make half that amount of each of the products.

$2HI \leftrightarrows H_2 + I_2$

Moles at start	2 − 1.6	0 + 0.8	+0.8
Moles at equilibrium	0.4	0.8	0.8
Concentration (2 moles as given in question)	0.4/2 = 0.2	0.8/2 = 0.4	0.8/2 = 0.4

So $K_c = 0.2^2/0.4 \times 0.4$
$= 0.25$ (no units)

Other examples can be more complicated, but stick to the table method to ensure you pick up marks. Practice the examples given.

HL
SPREAD 6: K_c, free energy and entropy

The relationship between ΔG and the equilibrium constant.

Calculations using the equation $\Delta G = -RT \ln K$.

Although K_c values have no say in the rate of the reaction there is a relationship between K_c and the feasibility of reaction, as measured by ΔG. It is known as the van't Hoff equation.

$\Delta G = -RT\ln K_c$

This is given in the data book, and you would be expected to work out things using it.

Example

Consider the equilibrium below:

Work out K_c for the reaction below at 298 K

$2NO_2 \leftrightarrows N_2O_4 \qquad \Delta G = -6\ kJmol^{-1}$

Step 1: You must convert ΔG to joules as the gas equation is in joules:

−6000 J

Step 2: Work through:

$-6000 = -8.314.\ 298.\ \ln K_c$
$\ln K_c = -6000\ (-8.314.\ 298) = -6.2466.57$
$\ln K_c = 2.42$
$K_c = e^{2.42} = 11.26$

Note that e^x is the anti ln button on your calculator.

In more general terms if a reaction goes, that is, ΔG is negative then this suggests the equilibrium lies to the right, so $K_c > 1$. If ΔG is positive then the equilibrium lies to the left and K_c is less than one. This is summarized in the table below.

ΔG	**lnK_c**	**K_c**
Negative	Positive	>1
Zero	Zero	=1
Positive	Negative	<1

This is useful for learning of the multiple choice questions.

Entropy considerations

How can the entropy of an equilibrium system be positive in both directions? In truth it's more of a spectrum of feasibility. In general terms if the entropy range is +200 $JK^{-1}mol^{-1}$ for the forward and −200 for the backward then you can safely say this reaction goes to completion in the positive direction (it is not in equilibrium). If the entropy is between +40 and −40 $JK^{-1}mol^{-1}$ then the reaction is said to be in equilibrium. So the equilibrium position is dictated by the most negative ΔG and the most positive ΔS.

CHAPTER

9

Acids and bases

This chapter covers the IB syllabus content in Sections 8 and 18.

SPREAD 1: What is an acid?

A Brønsted–Lowry acid is a proton/H^+ donor and a Brønsted–Lowry base is a proton/H^+ acceptor.

Introduction

Acids and bases have been known about since ancient times, although defining precisely what an acid and a base is perhaps a little harder.

The most useful definition of an acid for IB students is the Brønsted–Lowry definition:

An acid is a **proton donor**. By proton here we mean a hydrogen ion (H^+) that consists only of a proton.

A base is a **proton acceptor**. By this we usually mean a compound that contains hydroxide ions (OH^-) that can accept a proton to form water.

In more simple terms an acid is a compound that releases hydrogen ions when dissolved in water. The technical term for this is DISSOCIATION.

It is often easier to see this in terms of equations:

$\mathbf{H}Cl + Na\mathbf{OH} \Rightarrow NaCl + \mathbf{H_2O}$

The HCl donates its proton to the OH^- ion in the base to form water.

As an ionic equation:

$H^+_{(aq)} + OH^-_{(aq)} \Rightarrow H_2O_{(l)}$

More complicated examples of acid–base behavior still fit the same, simple, logical ionic equation. For example, in the generation of an electrophile for benzene in the organic section (Chapter 11).

$\mathbf{H}_2SO4 + HNO_3 \Rightarrow HSO_4^- + \mathbf{H}_2NO_3^+$

Here the sulfuric acid acts as an acid and the nitric acid acts as the base! The donated proton is shown in bold.

Products of neutralization

Reactions involving acids and bases produce compounds called "salts." Such reactions are known as neutralization reactions. Salts are more properly defined as "compounds where the H^+ of an acid has been replaced by another positive ion."

An alkali is a subgroup of bases that are soluble in water.

Some typical acids

The three common mineral acids are:

Hydrochloric acid (HCl)
Sulfuric acid (H_2SO_4)
Nitric acid (HNO_3)

Knowing the formulas of these three acids is considered absolutely essential for any chemistry course.

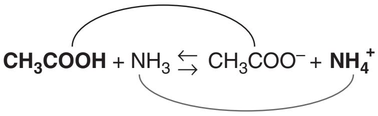
There are thousands of weak acids. Their structures and reactions will be looked at in more detail in the organic chemistry course, but it is important that when writing equations with such acids you show exactly which hydrogen is donated.

Ethanoic acid CH_3COOH (Draw it) ⇒ $H^+ + CH_3COO^-$

CORE and HL
SPREAD 2: Conjugate acid–base pairs and Lewis acids

- *A pair of species differing by a single proton is called a conjugate acid–base pair.*
- *Amphiprotic species can act as both Brønsted–Lowry acids and bases.*

Many reactions involving acids and bases are equilibrium reactions. The acid donates the proton to the base. The products can simply return back to the original. You might be asked to identify the conjugate acid–base pairs. The trick is to always find the things that DONATE PROTONS. In the tricky example below these acids are in bold.



$$\mathbf{CH_3COOH} + NH_3 \leftrightarrows CH_3COO^- + \mathbf{NH_4^+}$$

On the left the ammonium ion can donate a proton to form ammonia. The ethanoate ion can accept a proton to form ethanoic acid.

Therefore the conjugate acid–base pairs are:

CH_3COOH and CH_3COO^- (acid and conjugate base)
NH_3 and NH_4^+ (base and conjugate acid)

The hydroxonium ion

The use of H^+ to describe the ion responsible for acidity is a simplification. In truth an acid in water donates its proton to the water.

$HCl + H_2O \leftrightarrows H_3O^+ + Cl^-$

The H_3O^+ ion is known as the hydroxonium ion. You should be able to use this ion instead of the H^+ in some examples.

Amphoteric or amphiprotic?

Beware of confusion between these two terms in relation to acid–base behavior. We've met amphoteric before. It means a substance that can behave either as an acid or a base depending on what it is reacting with.

Amphiprotic is a more refined definition, as it is in terms of protons rather than chemistry. An amphiprotic substance can either accept or donate PROTONS depending on what it is reacting with, water being a classic example, as it accepts protons from acids and donates protons with bases.

All amphiprotic substances are also amphoteric, However NOT ALL amphoteric substances are amphiprotic, as not all acids donate protons. See the HL section on Lewis acids for more on this (below).

HL Lewis acids and bases

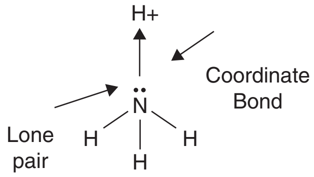
A Lewis acid is a lone pair acceptor and a Lewis base is a lone pair donor.
When a Lewis base reacts with a Lewis acid a coordinate bond is formed.
A nucleophile is a Lewis base and an electrophile is a Lewis acid.

It was noted above that there are many different definitions of what an acid or a base is, and some substances that display acid–base behavior don't fit the Brønsted–Lowry definition. Fortunately for us these are fairly uncommon, so we don't have to dwell on them for too long.

A look at ammonia chemistry helps us here:

$HNO_3 + NH_3 \leftrightarrows NH_4^+ + NO_3^-$

As you can see the nitric acid has donated a proton to the ammonia to form ammonium nitrate. The ammonia has accepted the proton to form the ammonium ion. How has this happened? The lone pair on the ammonia molecule has formed a coordinate bond with the electron-deficient proton.



This is the Lewis definition:

An acid is an electron pair acceptor.
A base is an electron pair donor.

So if you are asked to identify the Lewis acid from a list of Brønsted–Lowry acids, then look for the electron deficient molecule.

Boron trifluoride (BF_3) is a good place to start.

A Lewis base has a lone pair of electrons and is easier to spot.

CORE
SPREAD 3: Properties of acids and bases

Most acids have observable characteristic chemical reactions with reactive metals, metal oxides, metal hydroxides, hydrogen carbonates and carbonates.

Salt and water are produced in exothermic neutralization reactions.

The general reaction for acids and alkalis isn't often summed up by the following:

Acid + base ⇒ Salt + water

The ionic equation being:

$H^+ + OH^- \Rightarrow H_2O$

There are some variations to this though depending on the base/reagent the acid is reacting with.

Any neutralization reaction of this type is exothermic.

Neutralization

Here are some examples of neutralization reactions. You must complete the word equations by giving the products.

Remember :	Hydrochloric acid gives chloride salts
	Sulfuric acid gives sulfate salts
	Nitric acid gives nitrate salts
	Phosphoric acid gives phosphate salts
Etc.	

The general reactions are:

1) Acid + base ⇒ Salt + water

   $H_2SO_4 + NaOH \Rightarrow Na_2SO_4 + H_2O$
   $H_2SO_4 + 2NH_3 \Rightarrow (NH_4)_2SO_4$
   $CH_3COOH + NaOH \Rightarrow CH_3COO\ Na + H_2O$

2) Acid + metal ⇒ Salt + hydrogen

   $HNO_3 + Mg \Rightarrow Mg(NO_3)_2 + H_2$*
   $2CH_3COOH + Ca \Rightarrow (CH_3COO)_2Mg + H_2$

3) Acid + metal oxide ⇒ Salt + water

   $HCl + Na_2O \Rightarrow 2NaCl + H_2O$
   $2CH_3COOH + MgO \Rightarrow Mg(CH_3COO)_2 + H_2O$

4) Acid + metal carbonate ⇒ Salt + water + carbon dioxide

   $CuCO_3 + H_2SO_4 \Rightarrow CuSO_4 + H_2O + CO_2$
   $Na_2CO_3 + 2CH_3COOH \Rightarrow 2CH_3COONa + CO_2 + H_2O$

5) Acid + hydrogen carbonate ⇒ Salt + water + carbon dioxide

   $HNO_3 + NaHCO_3 \Rightarrow NaNO_3 + H_2O$
   $CH_3COOH + NaHCO_3 \Rightarrow CH_3COONa + H_2O + CO_2$

Titrations

Titration, as mentioned in Chapter 1, is a common way of neutralizing acids and bases. You should be familiar with the technique. Indicator colors are given in the data book, and you wouldn't be expected to memorize them.

CORE
SPREAD 4: Strong and weak acids and indicators

Strong and weak acids and bases differ in the extent of ionization.

Strong acids and bases of equal concentrations have higher conductivities than weak acids and bases.

A strong acid is a good proton donor and has a weak conjugate base.

A strong base is a good proton acceptor and has a weak conjugate acid.

If we take the Brønsted–Lowry definition of an acid as our truth then acids donate protons: but, to what extent do they donate them?

Let's take a hypothetical acid HA. The equation for the dissociation/ionization is below:

$$HA + H_2O \Rightarrow H_3O^+ + A^-$$

Which is simplified to:

$$HA \Rightarrow H^+ + A^-$$

---

* This isn't a neutralization in the strictest sense, although the acid is neutralized. It's probably more correctly a redox reaction.

In this example it is assumed that all the acid molecules fully break open (dissociate) when added to water. In truth very few do. Those where 100% dissociation occurs are called STRONG ACIDS and there are very few. They are:

HCl, H_2SO_4 and HNO_3

Most acids are weak acids, and the equation above is modified with an equilibrium sign.

$$HA \leftrightarrows H^+ + A^-$$

As few molecules dissociate the equilibrium lies firmly to the left.

These are weak acids because they do not fully dissociate. There are fewer H^+ ions in the resulting solution so the pH is lower, as we will see.

The same is true of strong and weak bases. Strong bases all accept a proton. In weak bases very few molecules accept the proton.

$$XOH + H^+ \Rightarrow H_2O + X^+$$

Or, for weak bases:

$$XOH + H^+ \leftrightarrows H_2O + X^+$$

The differences between strong and weak acids and bases

What experiments can we do to decide if an acid is strong or weak?

1) Ionization

Strong and weak acids and bases differ in the extent of ionization.

2) Electrical conductivity

Strong acids donate all their protons producing a solution with large amounts of ions compared to a solution of similar concentration of a weak acid. Therefore as ions can conduct electricity strong acids and bases of equal concentrations have higher conductivities than weak acids and bases.

3) Reactivity

In terms of general chemical reaction strong acids will react more vigorously with bases, carbonates and reactive metals than weak acids of comparable concentration. This may manifest itself in more bubbles in reactions that produce gases.

More technical statements

A strong acid is a good proton donor and has a weak conjugate base. In other words equilibrium lies COMPLETELY on the right.

A strong base is a good proton acceptor and has a weak conjugate acid.

CORE
SPREAD 5: What is pH?

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

A change of one pH unit represents a 10-fold change in the hydrogen ion concentration $[H^+]$.

pH values distinguish between acidic, neutral and alkaline solutions.

The ionic product constant, $K_w = [H^+][OH^-] = 10^{-14}$ *at 298 K.*

Simple pH

Once we are clear that acids can have different strengths depending on how well they split up in water, it doesn't take a great leap to see that we could look at the strength of acids quantitatively and put a number to this value. There are two problems with this:

- The concentration of hydrogen ions might be a very small number meaning the value is difficult to use, especially for young students.
- Given that we can quantify acid strength we also need a measure of the strength of bases, and they don't have a concentration of hydrogen ions in the same way that acids do.

The first problem is solved by converting hydrogen ions into the pH scale. The pH scale usually runs from 0 to 14 and gives the strength of acids and bases—1 being a strong acid, 7 being neutral and 14 being a strong base. The pH scale takes the negative logarithm of the concentration of hydrogen ions to give a nice numerical scale. This can then be measured with a pH meter or universal indicator paper.

$$\mathrm{pH} = -\log_{10}[\mathrm{H^+}]$$

So the pH of 0.02 moldm^{-3} HCl is

$$-\log[0.02] = 1.7$$

This is an easy calculation but watch out for a few traps (below):

- The pH of 8 moldm^{-3} HCl is –0.9! Don't worry about negative pH values. It is just a number.
- What is the pH of 0.01 moldm^{-3} H_2SO_4? Well it's not 2! There are two moles of hydrogen ions per mole of H_2SO_4 (look at the formula) therefore you need to double the concentration of H^+ ions, so it is

$$-\log[2 \times 0.01] = 1.69$$

Most acids are monoprotic (have one H^+ ion per molecule) but be careful.

Working out pH without a calculator

On multiple choice papers there are often questions asking you to work out the pH without a calculator. These are quite simple once you recall that the logarithm is essentially the order of magnitude of the number.

So the pH of a 0.1 moldm^{-3} strong acid is 1,

0.01 is 2,

0.001 is 3 and so on.

With this in mind you can also work out the relative concentrations of acids. An acid with a pH of 1 has 10 times more hydrogen ions in it than an acid of pH 2, and 100 times more than an acid of pH 3.

Working out concentration of hydrogen ions from pH

To work out the concentration of the acid from a pH requires you to reverse the process used to work out pH. You need the anti-log button on your calculator.

$[H^+] = 10^{-pH}$

So an acid with a pH of 3.5 = $10^{-3.5} = 3.16 \times 10^{-4}$ moldm^{-3}

Working out the pH of bases

Clearly it is impossible based on the above to work out the pH of bases but equally clearly bases have pHs! Where do the hydrogen ions come from?

The answer is: the water constant

When a base is in water it interacts with the water a bit. Water dissociates a tiny amount too.

$H_2O \leftrightarrows H^+ + OH^-$

Working out K_c for this is simple.

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

The water concentration is so large that it is effectively constant, so we can make a new constant on the left.

$K_c[H_2O] = [H^+][OH^-]$
$K_w = [H^+][OH^-]$

We call this water constant and at 298 K it is 1×10^{-14} moldm^{-3}. It's in the data book.

The water constant can be used to work out the pH of bases because:

pK_w = pH + pOH. The pK_w would be 14.
Or: $K_w = [H^+]/[OH^-]$

So, to work out the pH of a base, first work out the pOH.

What is the pH of a 0.025 moldm^{-3} solution of NaOH?

pOH = $-\log[0.025] = 1.60$
pH = pK_w – pOH $14 - 1.60 = 12.4$

Or, using the concentrations method:

$[H^+] = [OH^-]/K_w$
$0.025/1 \times 10^{-14} = 2.5 \times 10^{-12}$
$-\log 2.5 \times 10^{-12} = 12.4$

Either method is acceptable. It will depend on your own ability to do mathematics.

CORE
SPREAD 6: Acid deposition

Rain is naturally acidic because of dissolved CO_2 and has a pH of 5.6. Acid deposition has a pH below 5.6.

Acid deposition is formed when nitrogen or sulfur oxides dissolve in water to form

HNO_3, HNO_2, H_2SO_4 *and* H_2SO_3.

The chemistry of rain

Rain water isn't pure. It contains a variety of dissolved gases and perhaps pollutants. One of these will be carbon dioxide. As carbon dioxide is an acidic oxide it will dissolve in the rain water producing a solution of pH 5.6. In principle the product is carbonic acid. The equations are below:

$H_2O + CO_2 \Rightarrow H_2CO_3$

Carbonic acid is unstable and this decomposes to HCO_3^- ions and the hydroxonium ion H_3O^+.

$H_2CO_3 \Rightarrow HCO_3^- + H_3O^+$

Acid deposition

Acid deposition is more colloquially known as acid rain, and in the context of a person on the street it means polluted rain, not the naturally acidic rain discussed above. The two main causes of natural rainwater to be more acidic are dissolved oxides of sulfur and nitrogen. Both are formed from the combustion of these elements, precisely which is summarized below.

Oxides of nitrogen

Types of oxide:
NO = nitrogen monoxide
N_2O = dinitrogen monoxide
NO_2 = nitrogen dioxide

Collectively these are often known as NO_x.

Natural sources: Forest fires, volcanic activity, electrical storms and denitrifying activity of some bacteria.

Man-made sources: By-product of burning fossil fuels. As air is required to burn these and nitrogen is present in air the extreme conditions of an engine allows nitrogen to react where it wouldn't under normal conditions.

Reactions

$N_2 + O_2 \Rightarrow 2NO$

This can further oxidize in the atmosphere to NO_2.

$2NO + O_2 \Rightarrow 2NO_2$

In the clouds the NO_x combine with water to form acid rain.

$2NO + H_2O \Rightarrow 2HNO_3$

The reaction is more complicated than this, but this will suffice.

Oxides of sulfur

There are two oxides of sulfur:

Sulfur dioxide SO_2
Sulfur trioxide SO_3

Natural sources: Volcanic activity.

Man-made sources: Burning of oil-based hydrocarbons and coal, both sources naturally contain sulfur which will burn readily in air.

$S + O_2 \Rightarrow SO_2$

SO_2 will react further with oxygen.

$2SO_2 + O_2 \Rightarrow 2SO_3$

When these oxides hit the water vapor in clouds they react to form various forms of sulfuric acid:

$SO_2 + H_2O \Rightarrow H_2SO_3$
$SO_3 + H_2O \Rightarrow H_2SO_4$

Consequences of acid deposition

1) It affects pH of rivers and lakes. If the acid rain has a pH less than 5.6 then any marine life that cannot live in such conditions will be at great risk. It may not affect the organism itself but could affect the process of eggs hatching.
2) Affects soil nutrients. Soils contain metal ions useful to many plants. Acid rain can cause these metals to react with forming soluble compounds that wash away. You might be asked to write an equation for such a reaction.
3) Affects trees and other land-based plants, often in the form of damaging leaf chlorophyll and thus affecting photosynthesis.
4) Affects limestone buildings. Obviously limestone being calcium carbonate will react with acid rain. See carbonate reactions on a previous spread.

Ways of reducing the impact of acid rain

Nitrogen oxides from vehicles have now been very effectively reduced by the addition of catalytic converters to cars. Any oxides of nitrogen produced in an engine are now emitted as nitrogen gas.

Sulfur oxides are trickier. In power stations you can remove it by fluidized bed combustion or flue gas desulfurization. In both cases limestone is used to react with the acidic gases to form stable calcium sulfate compounds. The first involves a gaseous reaction, and the second involves bubbling the gases through a suspension of calcium carbonate.

$CaCO_3 \Rightarrow CaO + CO_2$

The basic oxide is able to react with the oxides of sulfur.

HL
SPREAD 7: Calculations involving acids and bases

The expression for the dissociation constant of a weak acid (K_a) *and a weak base* (K_b).

For a conjugate acid–base pair, $K_a \times K_b = K_w$.

The relationship between K_a *and* pK_a *is* ($pK_a = -\log K_a$)*, and between* K_b *and* pK_b *is* ($pK_b = -\log K_b$).

The pH of weak acids and the K_a expression

Weak acids partially dissociate, so working out the pH from the concentration isn't possible, because the concentration of hydrogen ions will not be the same as the concentration of the acid, it's in equilibrium.

$HA \leftrightarrows H^+ + A^-$

As weak acids are in equilibrium you can write an equilibrium expression for them:

For example, ethanoic acid:

$CH_3COOH \leftrightarrows CH_3COO^- + H^+$

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

As the equilibrium constant for acids are so important it is given a special symbol, K_a, so:

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

The units will always be moldm^{-3}.

The K_a expression is crucial to understanding weak acids, and various forms of it will apply in this section. Unlike K_c expressions the K_a always has the same structure, two products over the undissociated acid.

pK_a values

K_a values can tell us a lot about an acid. Put simply the bigger the value of K_a the further to the right the equilibrium lies, so the acid further dissociates and is stronger.

As the values are always small numbers they are often listed in data books (like your IB data book) as pK_a values.

pK_a values relate to K_a values in the same way that pH relates to $[H^+]$

$$pK_a = -\log_{10} K_a$$

As your data book lists acid values as pK_a values your first job is always to convert them into a K_a value.

$K_a = 10^{-pKa}$ (or the 10^x button on your calculator again)

Example

The pK_a of pyruvic acid is 2.39, what is its K_a value?

$$10^{-2.39} = 4.07 \times 10^{-3} \text{ moldm}^{-3}$$

HL
SPREAD 8: Using the K_a expression to work out the pH of a weak acid

Using the K_a expression to work out pH is a simple case of manipulating the equation to isolate the H^+ ions. Because weak acids dissociate equally the value of the H^+ concentration is always the same as the conjugate base, which makes the calculation a lot easier.

The simplest way to look at these calculations is to do a few.

1) Working out pH given the K_a value and the concentration:

What is the pH of a 0.6 moldm^{-3} solution of pyruvic acid (K_a 4.07×10^{-3} moldm^{-3})?

$$CH_3COCOOH \leftrightarrows H^+ + CH_3COCOO^-$$

$$K_a = \frac{[H^+][CH_3COCOO^-]}{[CH_3COCOOH]}$$

Substitute in the known values:

$$4.07 \times 10^{-3} = \frac{[H^+][CH^3COCOO^{-1}]}{0.6}$$

$$\Rightarrow [H^+][CH_3COCOO^-] = 4.07 \times 10^{-3} \times 0.6 = 2.44 \times 10^{-3}$$

As the concentration of H^+ is always the same as the concentration of the conjugate base we can write:

$2.44 \times 10^{-3} = [H^+]^2$
So $[H^+] = \sqrt{2.44 \times 10^{-3}} \Rightarrow [H^+] = 0.49$ moldm^{-3}
So pH $= -\log 0.49 = 1.31$

Working the other way:

Work out the pK_a of acid HA of concentration 0.4 moldm^{-3} and pH 3.7.

Step 1: work out the concentration of hydrogen ions:

$$10^{-3.7} = 1.99 \times 10^{-4}$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

As $[H^+]$ always equals $[A^-]$ we can square the H^+ concentration:

$$(1.99 \times 10^{-4})^2 = 3.98 \times 10^{-8} \text{ moldm}^{-3}$$

Now divide by the concentration to get K_a:

$3.98 \times 10^{-8}/0.4 = 9.95 \times 10^{-8} = 6.63 \times 10^{-8}$ moldm^{-3}
p$K_a = -\log 6.63 \times 10^{-8} = 7.17$

Assumptions

This calculation makes some assumptions; this may seem like a flaw in the calculation, but working at the sensible, significant figures means it won't unduly affect the answer.

Assumption 1: the concentration of the acid at equilibrium is the same as at the start. Well, this clearly cannot be true as we have some hydrogen ions and so some of the acid must have reacted. However the dissociation is so small that it makes no difference to our answer.

Assumption 2: we ignore the contribution of water. As we have seen water dissociates a little and some of the hydrogen ions in the solution may have originated from water. Again, if you recall, this is around the 10^{-7} region which will not affect our answer unduly.

HL
SPREAD 9: Working out pH of bases and temperature changes

Solution of problems involving $[H^+_{(aq)}]$, $[OH^-_{(aq)}]$, *pH, pOH,* K_a, pK_a, K_b *and* pK_b.

Discussion of the relative strengths of acids and bases using values of K_a, pK_a, K_b *and* pK_b.

Working out pH for weak bases is similar to working out the pH of strong bases on the core course, and applying the same principles to working out pH from a K_a value.

All weak bases have K_b or pK_b values just like acids and are derived the same way:

For example, ammonia:

$$NH_4OH \leftrightarrows NH_3 + H_2O$$
$$K_b = \frac{[OH^-][NH_3]}{[NH_4OH]}$$

With such an expression set up it is simple to work out pH or K_b, as we did before.

Example

Calculate the pH of a 0.3 moldm^{-3} solution of ammonia. $pK_b = 4.74$

Step 1: Work out K_b.

$$10^{-4.74} = 1.81 \times 10^{-5}$$

Step 2: Isolate the top.

$$K_b = \frac{[OH^-][NH_3]}{[NH_4OH]}$$
$$1.81\times10^{-5} = \frac{[OH^-][NH_3]}{0.3}$$
$$1.81 \times 10^{-5} \times 0.3 = 5.4 \times 10^{-6}$$

Step 3: Root the value to get concentration of hydroxide ions.

$$5.4 \times 10^{-6} = [OH^-]^2$$
$$[OH^-] \Rightarrow \sqrt{}5.4 \times 10^{-6} = 2.33 \times 10^{-3}$$

Step 4: Work out pOH.

$$pOH^- -\log = 2.631$$

Step 5: Work out pH.

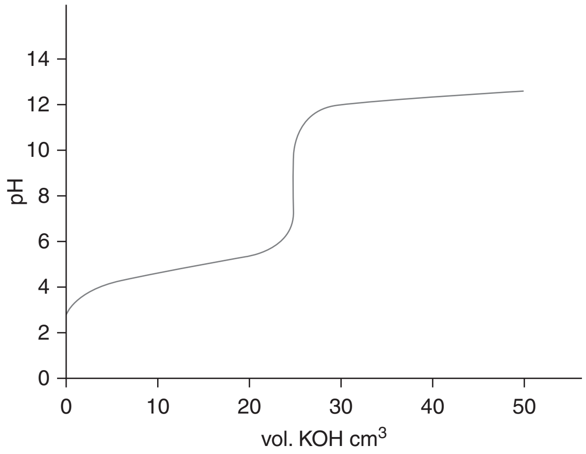
$$14 - 2.631 = 11.36$$

HL
SPREAD 10: pH curves

The characteristics of the pH curves produced by the different combinations of strong and weak acids and bases.

Introduction

When an acid is added to a base the pH does not change in a linear manner. In fact adding base to an acid (or vice versa) will seemingly have no effect on the pH at all. Then, at the point of neutralization where the H^+ ions exactly equal the OH^- ions the pH will change rapidly, see below.



Points to note on the pH curve:

The flattish part at the start is known as the buffer zone; see the buffer section on the opposite page.

The vertical section is important. This is where the pH changes rapidly. Any indicator used must change within this vertical value. The reason titrations work is because the rapid change in pH happens with the addition of one drop.

The midway point of the vertical is called the inflexion point, or the equivalence point. The pH of the salt produced by the reaction can be read from this point. In this example it is around 9. It will not necessarily be 7.

You can use the curve to work out pK_a value. The half equivalence point marked on the curve can be extrapolated and where it crosses the pH line this is the pK_a.

Different curves for different systems

The curve above is for a strong acid, strong base reaction. You can tell this because the pH starts low and ends high.

The curves for different systems are subtly different. They are below:

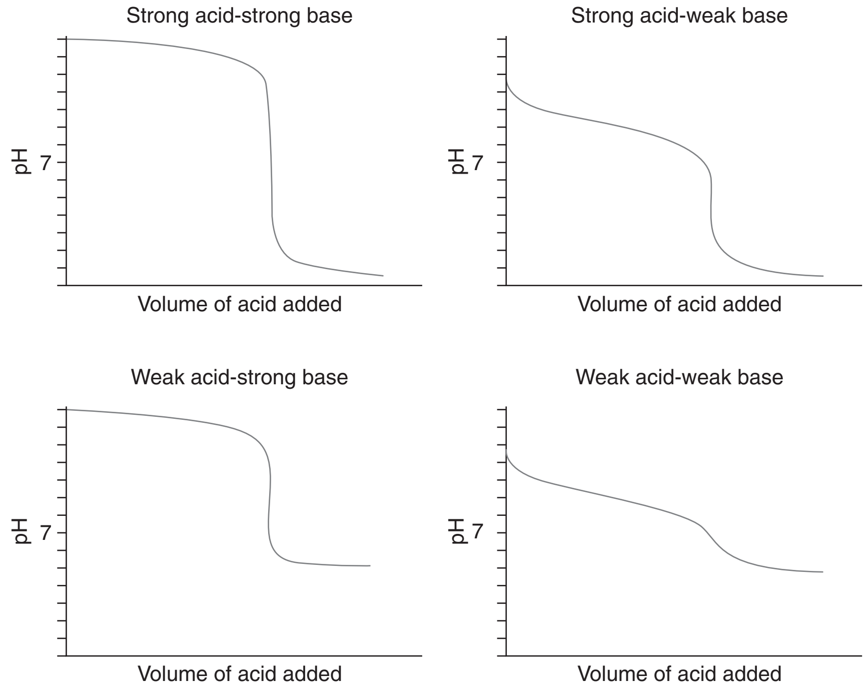
Strong acid, strong base. The curve starts low and ends high. The vertical point is long and straight. The inflexion point is at seven.

Strong acid, weak base. The curve starts low and finishes low. The vertical point is shorter and the inflexion point is below seven.

Weak acid, strong base. The curve starts high and finishes high. The vertical point is shorter and the inflexion point is above seven.

Weak acid, weak base. There isn't really a vertical part at all. In fact titrations are impossible with such combinations, and there is no vertical point to allow an indicator to change.

These need to be reversed.



HL
SPREAD 11: Buffer solutions and indicators

An acid–base indicator is a weak acid or a weak base where the components of the conjugate acid–base pair have different colors.

Understanding the relationship between the pH range of an acid–base indicator, which is a weak acid, and its pK_a *value.*

The buffer region on the pH curve represents the region where small additions of acid or base result in little or no change in pH.

What are buffer solutions?

As we saw in the last spread there is a buffer zone in neutralization when the pH doesn't change significantly as base is added to acid. Buffer solutions are defined as "solutions that resist changes in pH when small amounts of acid or base are added."

Making a buffer solution

Buffer solutions must consist of a WEAK ACID and the salt of a weak acid, for example, something like ethanoic acid and sodium ethanoate.

CH_3COOH and $NaCH_3COO$

Salts of weak acids are not necessarily standard lab reagents, but it is easy to make them in situ by adding to the weak acid half the amount of a strong base. This will turn half the acid into the salt.

$$CH_3COOH + \tfrac{1}{2}NaOH \Rightarrow \tfrac{1}{2}NaCH_3COO + \tfrac{1}{2}CH_3COOH + \tfrac{1}{2}H_2O$$

Both methods are equally valid, and you must be familiar with both.

For a base buffer solution the opposite is true: you need a weak base and the salt of a weak base, for example, ammonia and ammonium chloride.

NH_3 and NH_4Cl

Or, if ammonium chloride is not available then half the amount of acid is added to the base:

$NH_3 + \frac{1}{2}HCl \Rightarrow \frac{1}{2}NH_4Cl + \frac{1}{2}NH_3$

How do buffer solutions work?

This is one of the trickiest concepts to master. It brings in both acid/base work, as well as equilibrium.

Assuming an ethanoic acid/sodium ethanoate buffer:

Step 1

Write out an equation for the dissociation of ethanoic acid and the salt dissolving in water. This is usually worth a couple of marks.

$\mathbf{CH_3COOH} \leftrightarrows CH_3COO^- + H^+$
$NaCH_3COO \Rightarrow \mathbf{CH_3COO^-} + Na^+$

In a buffer solution the weak acid does not dissociate much, and so there is a large reservoir of undissociated acid in the solution (in bold). The salt totally dissolves, so there is a large reservoir of the conjugate base (CH_3COO^-) in bold.

The buffer works because there are enough ions of the undissociated acid and the conjugate base to mop up any excess acid or base added.

For example: When acid is added (H^+). This means the top equilibrium will shift to the right. In a non-buffer solution (without the bottom equation) the ethanoate ions would soon run out. However our buffer solution has a reservoir of ethanoate ions from the salt, which allows the equilibrium to shift left.

When base is added (OH^-) this reacts with the H^+ ions in the top equation. This removes them so the equilibrium shifts right. As there is a large excess of undissociated acid in the buffer this easily replaces the H^+ ions and the pH remains the same.

Indicators

Indicators are in fact weak acids that have a unique property. The acid and the conjugate base have different colors:

$HIn \leftrightarrows H^+$ (blue) + In^- (yellow)

This means that the color shown depends on the pH. If you add acid (H^+) the equilibrium shifts left and the color is blue. If you add base, you remove the H^+ and the equilibrium shifts right and the color goes yellow.

Your data book has a list of indicators and their colors. They also give their pK_a values and their range. The range is where the change in color occurs. For a titration you have to make sure the range of your indicator is within the vertical range on a pH curve.

CHAPTER

10 Redox processes

This chapter covers material from Topics 9 and 19 of the IB Chemistry syllabus.

CORE
SPREAD 1: The three types of redox reaction

Oxidation and reduction can be considered in terms of oxygen gain/hydrogen loss, electron transfer or change in oxidation number.

Chemistry is all about chemical reactions. To date we have meet a variety, including neutralization. This topic is all about the most fundamental of reactions: oxidation and reduction, or redox for short.

The three types of redox reaction

What is redox?

Just like acid and base definitions, there is more than one definition to get your head around, depending on the circumstances.

The simplest (and historically earliest) is:

Oxidation is addition of oxygen.

$Mg + \frac{1}{2}O_2 \Rightarrow MgO$

Reduction is the removal of oxygen.

$Fe_2O_3 + 3CO \Rightarrow 2Fe + 3CO_2$

Here, the iron oxide is reduced and the carbon monoxide is oxidized.

This is always the case: something is oxidized, something is always reduced,

or

Oxidation is the removal of hydrogen.

Reduction is the addition of hydrogen.

These are less common and found more commonly in organic chemistry. Both oxidation and reduction reactions encountered there involve hydrogen

The all-encompassing one:

Oxidation is loss of electrons.

$Mg + Cu^{2+} \Rightarrow Mg^{2+} + Cu$

Reduction is gain of electrons.

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

Or OILRIG for short.

This definition is the easiest to work with, as it is always true; however, in some organic redox reactions, it is hard to follow electron transfer so the definitions above are more useful.

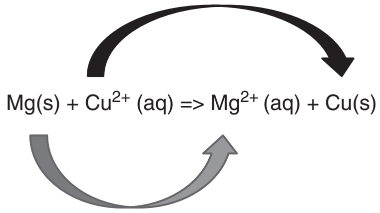
Oxidizing agents and reducing agents

It's important to have a clear idea of the terminology in this section. Things are oxidized, things are reduced, but it can never happen on its own. Something always oxidizes something and gets reduced itself. Similarly, something reduces something and gets oxidized.

The species that oxidizes something is called an oxidizing agent. The species that reduces something is called a reducing agent.

Consider the simple reaction below:

Copper ions are reduced. They are the oxidizing agent.



Magnesium is oxidized (loss of electrons).

It is the reducing agent.

CORE
SPREAD 2: Oxidation numbers

It is not easy to look at an equation and decide if it is a redox reaction. Chemists have devised a system called oxidation numbers to help work it out.

1) All elements have the oxidation number 0.
2) Group one elements in compounds always have an oxidation number of +1 (the same as their charge).
3) Group two elements in compounds always have an oxidation number of +2 (the same as their charge).
4) Aluminum is always +3.
5) Hydrogen is +1 (except in group 1 hydrides NaH, where it is −1).
6) Oxygen is −2 (except in peroxides where it is −1 H_2O_2).
7) Fluorine is −1.
8) The oxidation numbers in compounds always equal 0.
9) The oxidation numbers in ions always equal the charge on the ion.

Using these rules allows us to work out the oxidation numbers of elements where the number is not as certain. It will also help us (ultimately) work out whether a redox reaction has actually taken place.

Once these rules are learnt and applied it is easy to work out the oxidation numbers of other elements.

Stock notation is a method of naming compounds and including Roman numerals to indicate the oxidation number of the element which can vary. For example, iron (II) sulfate and iron (III) sulfate. In the first compound, Iron has an oxidation number of +2 and in the second +3. More subtle are sulfuric acid (IV) and sulfuric acid (VI). This tells us the oxidation number of sulfur each time. So sulfuric acid (IV) is H_2SO_3 and sulfuric acid (VI) is H_2SO_4.

Why are oxidation numbers used?

They are ONLY used for working out whether a reaction is redox or not.

Consider this example:

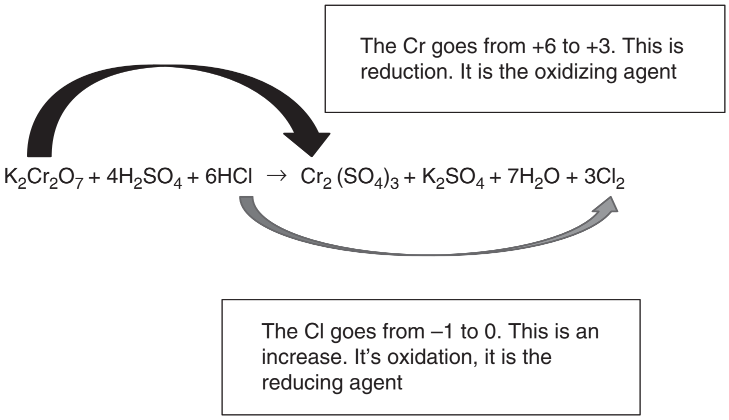
$K_2Cr_2O_7 + 4H_2SO_4 + 6HCl \rightarrow Cr_2(SO_4)_3 + K_2SO_4 + 7H_2O + 3Cl_2$

It's not easy to see immediately if this is a redox reaction or not. The trick is to assign oxidation numbers and look for change.

If oxidation goes up it's oxidation.

If oxidation goes down it's reduction.

In this example,



This is not always true.

$Cr_2O_3 + 3H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3H_2O$

In this example, there are no changes in oxidation number. Therefore, this is not a redox reaction.

CORE
SPREAD 3: Applications of redox, Winkler BOD, oxidation numbers

The Winkler method can be used to measure biochemical oxygen demand (BOD), used as a measure of the degree of pollution in a water sample.

Solution of a range of redox titration problems.

Redox titrations

Redox titrations are a variation on traditional acid/base titration. Here an oxidizing agent or a reducing agent are placed in the burette and reacted with the unknown compound.

Typical reagents used in redox titrations:

Potassium manganate (VII)

Potassium permanganate is usually found as a deep purple solution and needs to be acidified to work as an oxidizing agent. When put in a burette, its deep color makes it difficult to read the burette so permanganate titrations are read from the top of the meniscus rather than the bottom. When the permanganate is added to the unknown, it oxidizes it causing the purple color to disappear. The end point, therefore, is the first appearance of a pink color in the conical flask—the first drop of permanganate that doesn't react.

The relevant half equation is below:

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

This is combined with a species needing oxidizing; iron (II) is a typical example:

$Fe^{2+} \Rightarrow Fe^{3+} + e^-$

Then the equation is balanced for electrons:

$\mathbf{5Fe^{2+}} + MnO_4^- + 8H^+ + 5e^- \Leftrightarrow Mn^{2+} + 4H_2O + \mathbf{5Fe^{3+}} + \mathbf{5e^-}$

This then requires a 5:1 ratio in the equation.

Example:
Sodium thiosulfate

Sodium thiosulfate is a reducing agent that works well with iodine. The equation is below:

$2Na_2S_2O_3 + I_2 \Rightarrow Na_4S_4O_6 + 2I^-$

Note the 2:1 ratio of thiosulfate to iodine. This titration doesn't need an indicator as the end-point is when the yellow color of the iodine disappears. This might not be easy to judge so starch is often added. This gives a blue black color to the iodine, which disappears at the end.

On first glance this might seem a little restricting as it only works with iodine. Indeed analysis with thiosulfate does require reacting your unknown with something that will liberate iodine. This means the calculation will have a lot more steps.

Example:
0.1 g of an impure sample of potassium iodate (V) was dissolved in water and made up to 100 cm^3 in a volumetric flask. 10 cm^3 portions of this solution were taken and 10 cm^3 of 0.1 moldm^{-3} KI and 10 cm^3 of 1 moldm^{-3} sulfuric acid were added to liberate iodine. This was titrated against 0.001 moldm^{-3} sodium thiosulfate. The titration reading was 25.80 cm^3. Work out the percentage purity.

Equations:

$KIO_3 + 5KI + 3H_2SO_4 \Rightarrow 3I_2 + 3H_2O$
$2Na_2S_2O_3 + I_2 \Rightarrow 2NaI + Na_2S_4O_6$

Step 1: Work out the moles of thiosulfate

$25.80/1000 \times 0.01 = 2.58 \times 10^{-4}$ moles

Step 2: Ratio 2:1 so moles of iodine $2.58 \times 10 - 4/2 = 1.29 \times 10^{-4}$ moles

Step 3: Moles of iodate from top equation 1:3 ratio

$1.29 \times 10^{-4}/3\ 4.3 \times 10^{-5}$ moles of iodate

Step 4: Moles in original sample

You tested 10 cm portions of a 100 cm^3 solution so you need to multiply answer from 3 by 10

$4.3 \times 10^{-5} \times 10 = 4.3 \times 10^{-4}$ moles

Step 5: Work out mass of KIO_3

Mass = moles × RMM $4.3 \times 10^{-4} \times 214 = 0.092$ g

Step 6:

% $0.092/0.1 = 92\%$

CORE
SPREAD 4: The BOD of water

The BOD of water is the biochemical oxygen demand of water and represents the amount of dissolved oxygen in water that is used up by microorganisms involved with the decay process.

Decay occurs because microorganisms in the water feed on decaying vegetable matter and use up some of the oxygen dissolved in the water, leaving less for the higher marine life.

Pure water has around 1 ppm of oxygen in it. Fresh river water has about 8 ppm. If the BOD of some water is 5, then this is subtracted from 8 to produce a ppm of 3. Most fishes cannot survive in water lower than 5 ppm so the BOD is an important value to know.

There are two methods for calculating BOD. The method relevant to redox is to do a redox titration and is known as the Winkler method.

The Winkler method involves a redox titration using sodium thiosulfate.

- Add manganese dioxide and KOH to your sample of water. A brown precipitate appears.
- Adding an excess of acidified potassium iodide will liberate iodine.
- This can be titrated against sodium thiosulfate in the usual way.
- The standard way is to titrate this against 0.025 $moldm^{-3}$ sodium thiosulfate.

Using this concentration of sodium thiosulfate there is a scale-up factor of 8. So if 200 cm^3 of water sample is used, the volume of sodium thiosulfate used in the titration is equivalent to the same amount in mg of dissolved oxygen.

Other textbooks can make this very complicated, and if the IB sets a question they will give you a method to follow.

Example:
The dissolved oxygen concentration (DOC) in rivers and lakes is important for aquatic life. If the DOC falls below 5 $mgdm^{-3}$, most species of fish cannot survive.

Environmental chemists can determine the DOC in water using the procedure below.

- A sample of river water is shaken with aqueous Mn^{2+} and aqueous alkali. The dissolved oxygen oxidizes the Mn^{2+} to Mn^{3+}, forming a pale brown precipitate of $Mn(OH)_3$.

  $O_{2(aq)} + 4Mn^{2+}{}_{(aq)} + 8OH^-{}_{(aq)} + 2H_2O_{(l)} \Rightarrow 4Mn(OH)_{3(s)}$

- The $Mn(OH)_3$ precipitate is then reacted with an excess of aqueous potassium iodide, which is oxidized to iodine, I_2.

  $2Mn(OH)_{3(s)} + 2I^-{}_{(aq)} \Rightarrow I_{2(aq)} + 2Mn(OH)_{2(s)} + 2OH^-{}_{(aq)}$

- The iodine formed is then determined by titration with aqueous sodium thiosulfate.

  $Na_2S_2O_{3(aq)}$.
  $2S_2O_3{}^{2-}{}_{(aq)} + I_{2(aq)} \Rightarrow S_4O_6{}^{2-}{}_{(aq)}) + 2I^-{}_{(aq)}$

A 25.0 cm^3 sample of river water was analyzed using the procedure above.

The titration required 24.6 cm^3 of 0.00100 $moldm^{-3}$ $Na_2S_2O_{3(aq)}$.

Calculate the DOC of the sample of river water, in $mgdm^{-3}$.

Amount $S_2O_3{}^{2-}$ used $= 0.00100 \times 24.6/1000$
$= 2.46 \times 10^{-5}$ mol

Ratio (if you work through the calculations) of thiosulfate to manganese is 1:1.

Ratio of Mn^{2+} to O_2 is 1:4.

So the amount O_2 in 25 cm^3 sample:

$= 2.46 \times 10^{-5}/4$
$= 6.15 \times 10^{-6}$ mol

Concentration of O_2 in sample:

$= 6.15 \times 10^{-6} \times 1000/25$
$= 2.46 \times 10^{-4}$ ($moldm^{-3}$)

Mass concentration of O_2 in $mgdm^{-3}$.

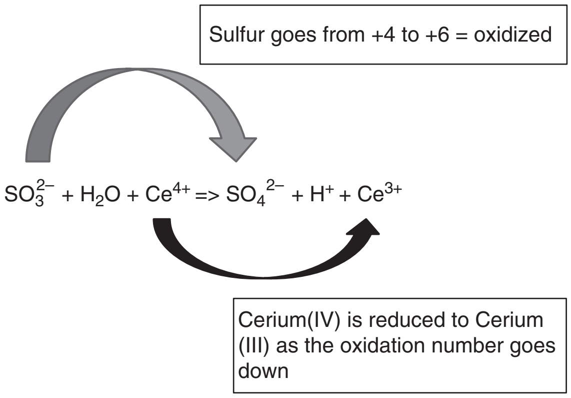
$= 2.46 \times 10^{-4} \times 32$ g $= 7.872 \times 10^{-3}$ (gdm^{-3})
$= 7.872$ ($mgdm^{-3}$)

CORE
SPREAD 5: Writing redox equations

Chemical equations involving redox must also be balanced in term of electrons. This is because an equal amount of electrons must be donated and accepted.

This means that you must balance in terms of oxidation number before you balance stoichiometrically.

Example:



Balance for oxidation numbers:

$SO_3^{2-} + H_2O + \mathbf{2}Ce^{4+} \Rightarrow SO_4^{2-} + H^+ + \mathbf{2}Ce^{3+}$

Balance as normal:

$SO_3^{2-} + H_2O + \mathbf{2}Ce^{4+} \Rightarrow SO_4^{2-} + \mathbf{2}H^+ + \mathbf{2}Ce^{3+}$

Balancing from half equations

A half equation simply shows how species change when electrons are added or taken away.
Simple example:

$Mg \Rightarrow Mg^{2+} + 2e$
$Cu^{2+} + 2e \Rightarrow Cu$

Combining:

$Mg + Cu^{2+} \Rightarrow Mg^{2+} + Cu$

This is an easy example because the electron transfer is the same. What about a tougher one? This following example is classic:

$MnO_4^- + 8H^+ + 5e^- \Rightarrow Mn^{2+} + 4H_2O$
$Fe^{2+} \Rightarrow Fe^{3+} + e^-$

Combining and balancing:

$\mathbf{5}Fe^{2+} + MnO_4^- + 8H^+ \Rightarrow Mn^{2+} + 4H_2O + 5Fe^{2+}$

CORE
SPREAD 6: The activity series

The activity series ranks metals according to the ease with which they undergo oxidation.

You've met the activity series before, if you've studied chemistry before you became an IB diploma student. We have also touched upon reactivity changes down groups in Chapter 5. Essentially, the activity series lists metals in order of their reactivity.

It is in Topic 25 of the data book and is reproduced here:

Increasing activity ↓

Li	Most reactive
Cs	
Rb	
K	
Ba	
Sr	
Ca	
Na	
Mg	
Be	
Al	
C	
Zn	
Cr	
Fe	
Cd	
Co	
Ni	
Sn	
Pb	
H	
Sb	
As	
Bi	
Cu	
Ag	
Pd	
Hg	
Pt	
Au	Least reactive

Points to note:
You may be bemused by this list, especially with Lithium at the top. There is good reason for this, as we'll see later, although chemical experiments suggest a different order.

In redox terms, the metal at the top is the best reducing agent, that is, it is the most easily oxidized element. Gold, at the bottom, is the worst reducing agent and is the least easily oxidized element.

Carbon and hydrogen are included, although they are not metals. This is because they are often involved in redox reactions with metals or their ions (and are often used to reduce metal ions in compounds to metals.

Other times (particularly in multiple choice questions) you might be given a few equations in order to work out the reactivity: For example:

$$2Cr_{(s)} + 3Fe^{2+}_{(aq)} \Rightarrow 2Cr^{3+}_{(aq)} + 3Fe_{(s)}$$
$$Fe_{(s)} + Pb^{2+}_{(aq)} \Rightarrow Fe^{2+}_{(aq)} + Pb_{(s)}$$

Here by following the equations you can see that chromium is the most reactive metal and lead must be the least reactive.

The reactivity series for the halogens

Group 17 also has a reactivity series:

↑

F	Most reactive
Cl	
Br	
I	Least reactive

Here fluorine is the most reactive halogen. It is the most easily reduced and the best oxidizing agent. Iodine is the least reactive and the worst oxidizing agent.

CORE and HL
SPREAD 7: Electrochemical cells (1): Electrolytic cells

Electrolytic cells convert electrical energy to chemical energy, by bringing about nonspontaneous processes.

Oxidation occurs at the anode (positive electrode) and reduction occurs at the cathode (negative electrode) in an electrolytic cell.

What are electrochemical cells?

These are setups that allow electrochemical conversions to take place. There are two types:

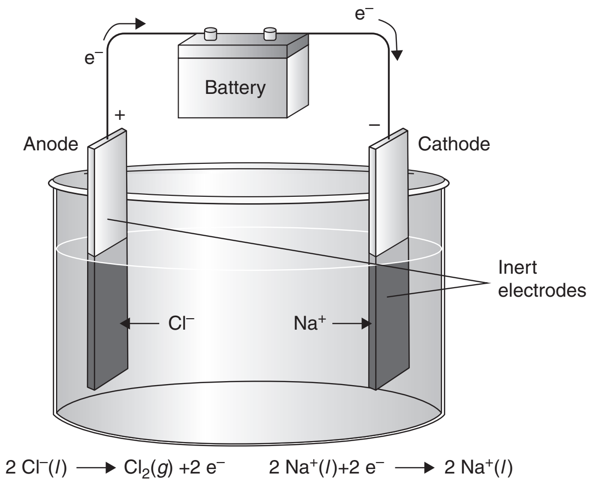
Electrolytic cells

Voltaic cells (we will consider these on the next spread)

Electrolytic cells

Electrolytic cells are involved with the process of electrolysis. This converts electrical energy into chemical energy.

In simple terms, it performs redox reactions that are NOT spontaneous.
Below is a typical setup:



Points to note:

1) There is a power source.
2) Two electrodes: the anode and the cathode. Usually made of graphite.

   In electrolysis the cathode is the negative electrode and the anode is the positive.
   The way to remember is not to PANIC: **P**ositive **A**node, **N**egative **I**s **C**athode
3) A more precise definition is that reduction always happens at the cathode.
4) The liquid is called the ELECTROLYTE. You need a molten electrolyte.

In the example above, molten sodium chloride is being electrolyzed. This will force the following nonspontaneous reactions to take place.

At the cathode:

$$Na^+ + e \Rightarrow Na_{(l)}$$

The sodium ions are forced to gain an electron and form sodium metal.

At the anode:

$$\tfrac{1}{2}Cl^- \Rightarrow Cl_2 + e$$

The chloride ions are forced to lose their electron.

What might I be examined on?

Make sure you know what the anode and cathode are and you know what will happen in terms of a half equation. Metal always goes to the cathode, the nonmetal to the anode.

Be prepared to show the flow of electrons or ions. The electrons flow from the positive anode to the negative cathode via the battery (an electron pump). In the electrolyte, the positive ions are drawn to the cathode and the negative ions to the anode. This completes the circuit.

Electrolysis of molten ionic compounds is a crucial method of extracting reactive metals from their ores where the more traditional blast furnace is incapable.

HL
SPREAD 8: Higher-level electrolytic cells

Current during electrolysis and charge on the ion affect the amount of product formed at the electrode during electrolysis.

Electroplating involves the electrolytic coating of an object with a metallic thin layer.

On the core course we looked at basic electrolysis. At HL we look at the electrolysis of solutions.

Electrolysis of solutions

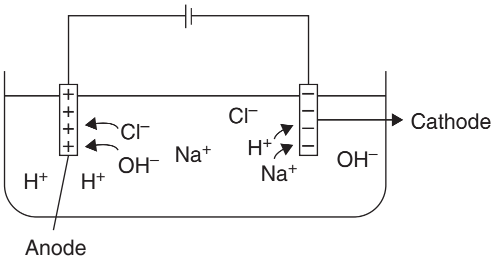
The problem with electrolyzing a metal compound dissolved in a solution is that you are not just dealing with two ions anymore.

A beaker of $NaCl_{(aq)}$ contains the following ions:

Na^+ + Cl^- of course and the water splits up too, so H^+ and OH^- ions are also present.

So what happens?

Both ions are attracted to their oppositely charged electrodes.



At the cathode:

The ion that comes off at the cathode is the one that is most easy to reduce. A quick look at the reactivity series again will show that hydrogen is far less reactive. So what you will see is the fizzing of hydrogen gas discharging at the electrode. The sodium ions remain in solution.

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

At the anode:

It is more complicated. If the concentration is high, then chloride ions come off as before. If the concentration is low, then oxygen gas is observed from the water.

---

* This is a simplification.

Copper sulfate electrolysis with inert graphite electrodes

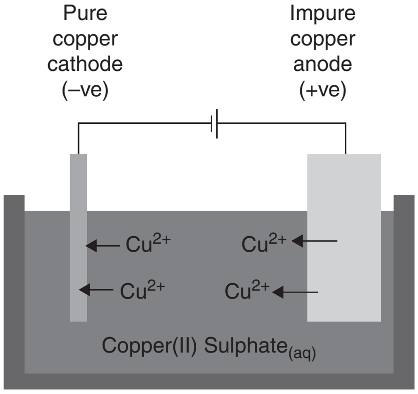
The same situation occurs although this time a quick look at the activity series will show you that copper is less reactive than hydrogen. This means that copper is discharged at the cathode.

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

At the anode the sulfate is very stable so the water breaks up.

$H_2O \Rightarrow \frac{1}{2}O_2 + 2H^{+} + e^{-}$

The situation changes again if you use copper electrodes. These are "active" electrodes and get involved.



At the cathode the copper is attracted as normal, but of course as the electrode is made of copper it means the electrode increases in mass.

At the anode the copper is turned into copper ions as the electrons are removed to move toward the cathode. This causes the anode to disintegrate:

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

This is a useful method for purifying copper. The impure copper is used as the anode and a clean piece of copper is used as the cathode. The anode disintegrates and the pure copper is deposited on the cathode. The impurities sink to the bottom of the cell.

There are many possible electrolysis experiments that can be performed. It would be too difficult to list them all. Be aware of any information given in the question, including electrode potentials, and be aware of the rules below.

Qualitative electrolysis

This refers to WHAT comes off during electrolysis. This has been discussed already.

In molten electrolytes it is the ions of the compound.

In solutions:

At the cathode it is hydrogen, unless the metal is below hydrogen in the activity series.

At the anode it depends on the concentration of the solution and the nature of the anion.

The electrodes play a part. They are usually inert but if it is an active electrode then the anode can be oxidized and fall apart.

Quantitative electrolysis

This refers to HOW MUCH comes off during electrolysis.

The following factors are important:

The time. The longer the electrolysis is performed, the more metal (or hydrogen) is deposited.

The current. Current is a flow of electrons. As electrons are added to the positive cations, the higher current the more ions can be reduced at the cathode.

Together these two factors are called charge.

The charge on the metal ion. The higher the charge, the more electrons are needed.

So for the same current more Ag^+ ions can be deposited than Cu^{2+} ions because of the charge difference.

Calculating the amount of metal that can be deposited

You need to know Faraday's constant. This is the amount of charge containing one mole of electrons.

It is 96,500 $Cmol^{-1}$.

So if charge Q = current × time, units = coulombs.

Then you can work out how many moles of a substance can be deposited.
Worked example:

Calculate the mass of silver produced at the cathode when a current of 2.3 amps is passed through a solution of silver nitrate for five hours.

Step 1

Convert hours into seconds.

$5 \times 60 \times 60 = 18{,}000$ seconds

Charge = Current × time

= $2.3 \times 18{,}000 = 41{,}400$ coulombs

Work out the number of moles.

41,400/96,500 = 0.42 moles

Mass of silver = $0.43 \times$ RMM silver = 108 = 46.44 g

Worked example with a 2+ ion

Calculate the mass of copper produced at the cathode when a current of 2.3 amps is passed through a solution of copper sulfate for five hours.

Step 1

Convert hours into seconds.

$5 \times 60 \times 60 = 18{,}000$ seconds

Charge = Current × time

= $2.3 \times 18{,}000 = 41{,}400$ coulombs

41,400/96,500 = 0.42 moles of electrons
This time the Cu^{2+} ion takes two of the electrons so the mole value per copper atom is halved.

- 0.24 moles.

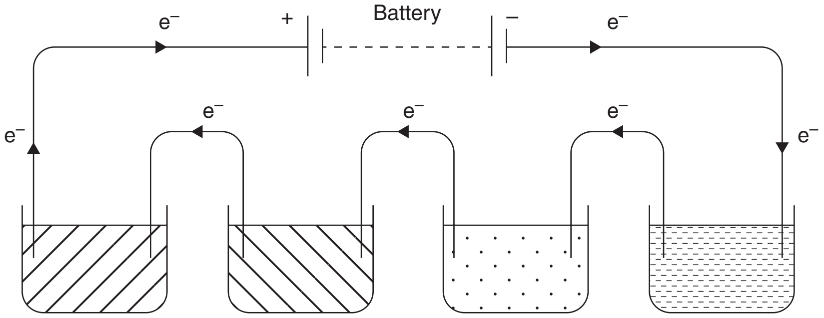
Mass deposited: $0.24 \times 63.5 = 15.24$ g

Cells in series

When two or more electrolytic cells are connected in series (see diagram below), then the same electric current and operating time apply to all the cells. That is, current and time are identical for cells connected in series and as $Q = I \times t$. This means that cells in series have the same Q (electric charge) value. The diagram below shows a setup. Essentially don't be phased by it. The current coming out of the first will move to the second, and so on.

Electroplating

Electroplating is a process by which a base metal is coated with a thin layer of a much more valuable metal. The process is simple. The item to be coated is used as the cathode. The electrolyte is a solution of the metal to be deposited (silver, gold). As the current flows, the precious metal ions are deposited on the cathode. The quantity deposited can be worked out using the calculations above.



CORE
SPREAD 9: Voltaic cells

Voltaic cells convert energy from spontaneous, exothermic chemical processes to electrical energy.

Oxidation occurs at the anode (negative electrode) and reduction occurs at the cathode (positive electrode) in a voltaic cell.

What are voltaic cells?

They are cells that allow **spontaneous** redox reactions to take place.

Consider the spontaneous test-tube reaction:

$Mg + Cu^{2+} \Rightarrow Mg^{2+} + Cu$

In chemistry terms, the magnesium dissolves and forms a colorless solution. The copper ions lose color and solid copper metal is formed.

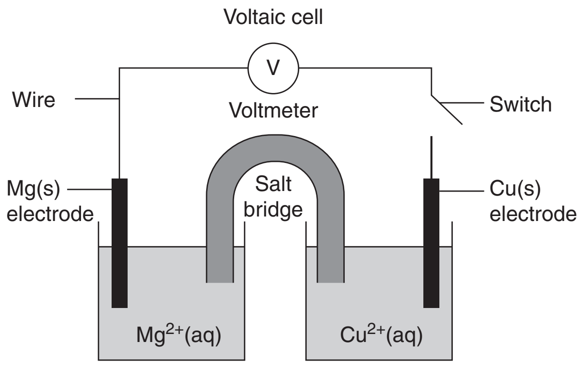
In terms of electrons, two move from the magnesium atoms to the copper ions.

In summary, the electrons do chemical "work."

In a voltaic cell, the electrons are diverted from doing chemical work by keeping the reagents apart. Instead they are channeled along a wire and do electrical work instead.

Essentially, the difference in oxidizing and reducing power of the chemicals provides a movement of electrons. Movement of electrons is called electric current. Essentially, the voltaic cell pushes electrons around. In the real world, this is known as a cell. A group of cells is called a BATTERY.

Below is a typical voltaic cell for the reaction above.

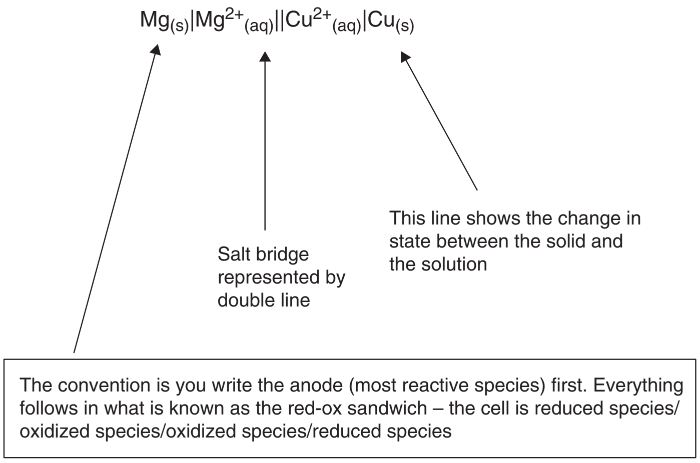


$Mg(s) + Cu^{2+}(aq) \longrightarrow Mg^{2+}(aq) + Cu(s)$

Notes:

- There are two parts to the cell. One contains one half equation's reagents. The other contains the other.
- The circuit is completed by a salt bridge. It is usually made of filter paper soaked in saturated potassium nitrate solution. Both these ions are very stable and will not interfere with the experiment.
- The anode is where oxidation takes place. In this case it is assigned to the more reactive metal. In this case it is the magnesium. It is the negative electrode (note the difference to the electrolytic cell).
- The cathode is where reduction takes place. In this case it is assigned to the less reactive metal. In this case it is the copper. It is the positive electrode.

Cell diagrams:
These are simple ways of expressing the detail of the cell. The one for the above would be:



$Mg_{(s)}|Mg^{2+}{}_{(aq)}||Cu^{2+}{}_{(aq)}|Cu_{(s)}$

Salt bridge represented by double line

This line shows the change in state between the solid and the solution

The convention is you write the anode (most reactive species) first. Everything follows in what is known as the red-ox sandwich – the cell is reduced species/oxidized species/oxidized species/reduced species

HL
SPREAD 10: HL voltaic cells

A voltaic cell generates an electromotive force (EMF) resulting in the movement of electrons from the anode (negative electrode) to the cathode (positive electrode) via the external circuit. The EMF is termed the cell potential (E^{θ}).

The standard hydrogen electrode (SHE) consists of an inert platinum electrode in contact with 1 moldm^{-3} hydrogen ion and hydrogen gas at 100 kPa and 298 K. The standard electrode potential (E^{o}) is the potential (voltage) of the reduction half-equation under standard conditions measured relative to the SHE. Solute concentration is 1 moldm^{-3} or 100 kPa for gases. E^{θ} of the SHE is 0 V.

When aqueous solutions are electrolyzed, water can be oxidized to oxygen at the anode and reduced to hydrogen at the cathode.

$\Delta G^{\theta} = -nFE^{\theta}$. When E^{o} is positive, ΔG^{θ} is negative indicative of a spontaneous process. When E^{θ} is negative, ΔG^{θ} is positive indicative of a nonspontaneous process. When E^{o} is 0, then ΔG^{o} is 0.

Current, duration of electrolysis and charge on the ion affect the amount of product formed at the electrodes during electrolysis.

The voltaic cell generates a current and a voltage dependent on the two half cells that are connected together.

This is what this topic is all about. Before we get into it we need to know what the potential is for each possible cell. And what I mean by each possible cell is anything that can be oxidized or reduced.

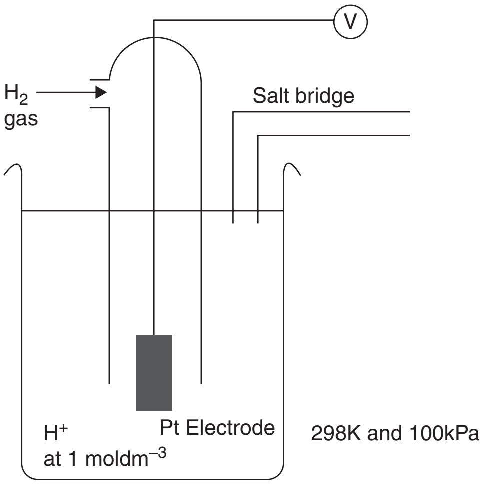
The electrode potential of a cell is E^{θ}.

Its value has to be calculated from connecting the cell to what is known as the standard hydrogen electrode. This is given the arbitrary electrode potential of 0.0 V.

The voltage of every cell is then assigned the voltage when connected to the standard hydrogen cell.

$\frac{1}{2}H_{2(g)} + \Rightarrow H^{+}_{(aq)} + e$

You need to know the details of the standard hydrogen cell. It is below:



Notes:

- The hydrogen gas is pumped into the cell at 1 atmosphere pressure and 298 K.
- The solution is 1 moldm^{-3} HCl. If you use sulfuric then it must be 0.5 moldm^{-3}.
- An inert platinum electrode is needed to complete the circuit.

The cell diagram is:

$Pt_{(s)}\,|H_{2(g)}\,|H^{+}||$ …

Calculating cell potentials

Table 24 in your data book contains a list of well-known species that can make up cells.

This can be used to work out the cell potential of any combination.

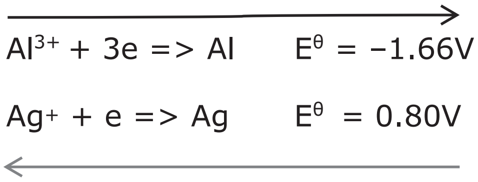
Consider two randomly chosen species from the data book.

$Al^{3+} + 3e \Rightarrow Al \quad E^{\theta} = -1.66\text{ V}$

$Ag+ + e \Rightarrow Ag \quad E^{\theta} = 0.80\text{ V}$

To work out which is the spontaneous reaction you do the following.

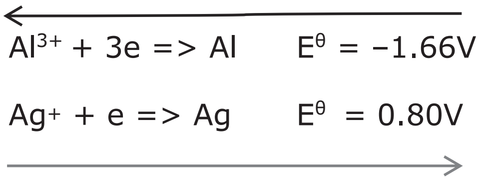
REMEMBER, one way is oxidation, the other way is reduced. You need one of each.



If the direction is this, the voltage would be −1.66 + −0.80 (because we go backwards)

The voltage is = −0.86 V.

The spontaneous direction would give a positive voltage. So this is wrong. This must be the right way:



This time the voltage would be +1.66 (because we go backwards) + 0.80 V

The voltage is +0.86 V.

This is positive and the direction is spontaneous.

The equation therefore would be:

$Al_{(s)} + 3Ag^{+}_{(aq)} \Rightarrow Al^{3+}_{(aq)} + Ag_{(s)}$

In summary, any equation can be written by using this method. The positive voltage is the spontaneous direction.

Spontaneity in voltaic cells

Spontaneity is associated with Gibbs free energy ΔG. A negative value says the reaction is spontaneous. To work it out for cells we need to use the following expression:

$\Delta G = -nFE^\theta$

Where:
n = moles
F = Faraday constant (96,500 $Cmol^{-1}$)
E = electrode potential

For the example above:

$Al_{(s)} + 3Ag^{+}_{(aq)} \Rightarrow Al^{3+}_{(aq)} + Ag_{(s)} \quad E^\theta = +0.86$ V

In this case:

$n = 3$ (3 electrons transferred)

So $\Delta G = -3 \times 96{,}500 \times +0.86 = -248{,}970$ or −249 KJ. The value is negative, so the reaction is spontaneous.

CHAPTER

11 Organic chemistry

This chapter covers the material in Topics 10 and 20 of the IB Chemistry syllabus.

CORE

SPREAD 1: Fundamentals of organic chemistry

A homologous series is a series of compounds of the same family, with the same general formula, which differ from each other by a common structural unit.

Structural formulas can be represented in full and condensed format.

Structural isomers are compounds with the same molecular formula but different arrangements of atoms.

Functional groups are the reactive parts of molecules.

Saturated compounds contain single bonds only and unsaturated compounds contain double or triple bonds.

Homologous series and other key definitions

Organic chemistry is the study of the wide variety of carbon-based molecules. Although the possible combinations of carbon and other elements are near infinite, there are patterns or families of different types of compounds. These are known as homologous series.

The alkanes are the simplest homologous series:

CH_4	Methane
C_2H_6	Ethane
C_3H_8	Propane
C_4H_{10}	Butane
C_5H_{12}	Pentane

A homologous series has the same general formula but differs by an extra CH_2 each time. They have essentially the same chemical properties and their physical properties show a trend.

Other homologous series include the alkenes, alcohols and halogenoalkanes. These will be encountered further as we go through the chapter.

Functional groups are the reactive parts of molecules; these are the parts that are not the carbon chain.
Saturated compounds contain single bonds only and unsaturated compounds contain double or triple bonds.

Naming organic compounds

Although this book is not going to teach you how to name organic compounds, the basic concepts need to be reminded. The naming of these molecules is essentially a very structured language.

The number of carbons in the chain is given the name

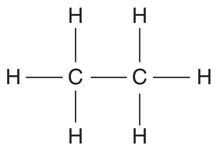
Meth-
Eth-
Prop-
But-
Pent-
Hex-

and so on.

Added to the end (usually) are the functional group names

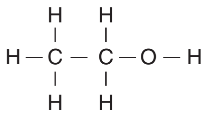
For an alkane it's -ane

So: Ethane



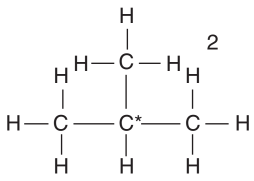
For an alcohol it's -ol

So: Ethanol



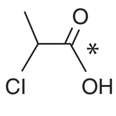
Added to the front are often other functional groups or branches. Numbers tell you where the branches or functional groups may be.

So 2-methyl propane is:



The numbering starts from the end where the number will be smallest, or if this is ambiguous, from the functional group end of the molecule.

So 2-chloropropanoic acid is:



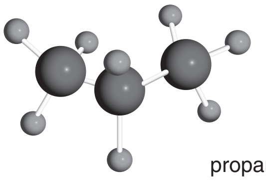
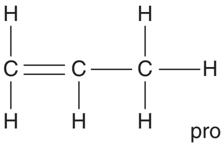
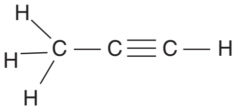
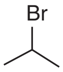
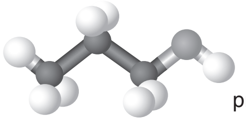
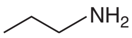
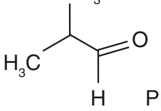
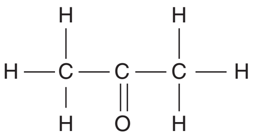
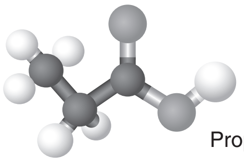
This is drawn as a skeletal formula. The carbon and hydrogen atoms are not drawn in and the bond angles are correct (in this case 120°).

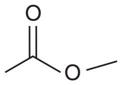
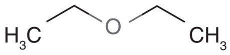
Because the first carbon is the one with the asterisk

There are other rules of naming beyond the scope of this book. There are plenty of web-based activities to help you practice this important skill.

CORE
SPREAD 2: More on the homologous series

The list below is not an exhaustive list of organic molecules but it gives a list of the homologous series most often found in IB chemistry courses. The examples include molecules shown in displayed formula, skeletal formula and 3-D computer images. You should be comfortable with all of them.

Name	**Functional group**	**General formula where applicable**	**Example with three or four carbons**
Alkanes	None	C_nH_{2n+2}	 propane
Alkenes	Double bond =	C_nH_{2n}	 propene
Alkynes	Triple bond	C_nH_{2n-2}	propyne 
Halogenoalkanes	R–X*		2 bromo propane 
Alcohols	R–OH		 propan-1 –ol
Amines	R-NH_2		 Propyl amine
Aldehyde	R-CHO	$C_nH_{2n}O$	 Propanal
Ketone	R-CO-R'	$C_nH_{2n}O$	 Propanone
Carboxylic acid	R-COOH	$C_nH_{2n}O_2$	 Propanoic acid

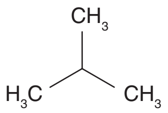
Name	**Functional group**	**General formula where applicable**	**Example with three or four carbons**
Esters	RCOOR'		Methyl ethanoate 
Amide	$RCONH_2$		
Nitrile	RCN		
Ether	R–O–R'		 ethoxyethane
Benzene	C_6H_6		

Isomers

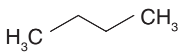
The nature of the carbon compounds discussed here means that there is **almost infinite** variety. There is also confusion.

Consider the molecule with the formula $C_4H_{10.}$

There are two ways of arranging these atoms:



2-Methyl propane (C_4H_{10})



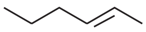
n-Butane (C_4H_{10})

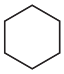
These molecules have similar reactions but their physical properties would vary, as would their names. The longer chain molecule would have a higher boiling point. The London forces have more points of contact across the molecules.

Such molecules are said to be structural isomers of each other.

This is defined as the same molecular formula but a different structure.

This can be taken to extremes with molecules like hexane and cyclohexane which have the same molecular formula C_6H_{12} but very different structures:





More on isomers in the HL course.

CORE
SPREAD 3: The alkanes

Alkanes have low reactivity and undergo free-radical substitution reactions.

Writing equations for the complete and incomplete combustion of hydrocarbons.

Explanation of the reaction of methane and ethane with halogens in terms of a free-radical substitution mechanism involving photochemical homolytic fission.

Alkanes

General formula: C_nH_{2n+2}
Functional group: None
Reactivity comment: Alkanes are essentially inert because the C–H is strong; however, they do burn easily.

$CH_4 + 2O_2 \Rightarrow CO_2 + 2H_2O$

You would be expected to write combustion equations up to six carbons.

Balance the RHS to carbon, and then do the same for hydrogen, then total the RHS oxygens to work out the LHS oxygens.

Example: propane

$C_3H_8 + O_2 \Rightarrow CO_2 + H_2O$

Three carbons on LHS, so do the same to RHS

$C_3H_8 + O_2 \Rightarrow \mathbf{3}CO_2 + H_2O$

Eight hydrogens on LHS

$C_3H_8 + O_2 \Rightarrow 3CO_2 + \mathbf{4}H_2O$

Count the oxygens on RHS = 10

So:

$C_3H_8 + 2½O_2 \Rightarrow 3CO_2 + 4H_2O$

Or

$2C_3H_8 + 5O_2 \Rightarrow 6CO_2 + 8H_2O$

Incomplete combustion

This is where there is insufficient oxygen for the reaction to take place. In this case the product is CARBON MONOXIDE, not CARBON DIOXIDE.

You balance the same way, so,

$CH_4 + 1½O_2 \Rightarrow CO + 2H_2O$

The only other reaction that alkanes do is the reaction with halogens to form halogenoalkanes:

$CH_4 + Cl_2 \Rightarrow CH_3Cl + HCl$

This reaction only happens in the presence of UV light, so it will not work in the dark.

The mechanism for this reaction is as follows:

The UV light has sufficient energy to break up the chlorine–chlorine bond to form free radicals:

$Cl_2 \Rightarrow 2Cl\cdot$ (INITIATION)

Radicals are atoms with an unpaired electron and are very reactive. These radicals then collide with the alkane (or any organic molecule) to form more radicals:

$Cl\cdot + CH_4 \Rightarrow CH_3\cdot + HCl$ (PROPAGATION)

Then a chain reaction starts:

$CH_3\cdot + Cl_2 \Rightarrow CH_3Cl + Cl\cdot$ (PROPAGATION)

Sometimes radicals collide and don't form new radicals. These are TERMINATION STEPS:

$Cl\cdot + Cl\cdot \Rightarrow Cl_2$
$CH_3\cdot + Cl\cdot \Rightarrow CH_3Cl$
$CH_3\cdot + CH_3\cdot \Rightarrow C_2H_6$

These termination steps stop the reaction.

The propagation steps continue to react causing all sorts of different chlorine compounds. The reaction is therefore difficult to control and not much use in synthesis.

CORE
SPREAD 4: The alkenes

Alkenes are more reactive than alkanes and undergo addition reactions. Bromine water can be used to distinguish between alkenes and alkanes.

Writing equations for the reactions of alkenes with hydrogen and halogens and of symmetrical alkenes with hydrogen halides and water.

Outline of the addition polymerization of alkenes.

Relationship between the structure of the monomer to the polymer and the repeating unit.

Alkenes

General formula: C_nH_{2n}
Functional group: = (double bond)

Reactivity comment

Alkenes are much more reactive than alkanes because the pi bond is comparatively weaker than the sigma bond. As it is made of electrons, it is susceptible to attack from species with positive charges, or species lacking in electrons. We call these species ELECTROPHILES. The proper definition is "lone pair acceptor."

Alkenes burn of course:

$C_3H_6 + 4\frac{1}{2}O_2 \Rightarrow 3CO_2 + 3H_2O$

You would be expected to write combustion equations up to six carbons.

The reactions of the alkenes are as follows:

- They can react with halogens under ANY CONDITIONS to form dihalogenoalkanes:

  $C_2H_4 + Cl_2 \Rightarrow C_2H_4Cl_2$

Note that the double bond breaks and the chlorines add on to the molecules. This therefore is an electrophilic addition reaction.

Reacting alkenes with bromine gives dibromoalkenes. These are colorless. This is the basis of the chemical test for alkenes. As bromine is brown and the product has no color, an alkene can be identified if it decolorizes bromine water.

- They can react with hydrogen halides to form halogenoalkanes:

  $C_2H_4 + HCl \Rightarrow C_2H_4Cl$

- With hydrogen:

  $C_2H_4 + H_2 \Rightarrow C_2H_6$

Conditions: Nickel catalyst, heat, pressure

This might seem a pointless reaction as alkenes come from alkanes and you'd be right. It is often used on unsaturated oils to turn them into saturated fats and harden them. It is an essential part of manufacturing margarine.

- With water to make alcohols:

  $C_2H_4 + H_2O \Rightarrow C_2H_5OH$

Conditions: Steam, catalyst: concentrated sulfuric acid

This reaction is an electrophilic addition like the others but requires a catalyst. The reaction is a way of making alcohol for industrial uses.

Polymerization

Alkenes can be forced to break their double bonds and react with themselves. When they do this they form polymers.

Example:
The starting molecule is the monomer; the end product is the polymer:

Ethene ⇒ Polyethene

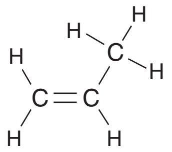
Conditions: High pressure and a catalyst (Ziegler Natter) are required.

Writing polymers from Monomers.

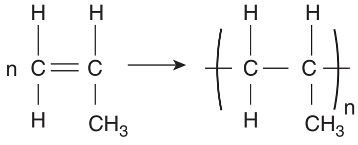
The trick is to draw the monomer in the shape of a letter H.

H

Example:
Propene



Drawn like this is easy to draw the carbon chain wrong. Writing the alkene as an H with everything above and below the double bond allows you to structure the polymer correctly.



Propene Polypropene

CORE
SPREAD 5: The alcohols

Alcohols undergo nucleophilic substitution reactions with acids (also called esterification or condensation) and some undergo oxidation reactions.

Writing equations for the complete combustion of alcohols.

Writing equations for the oxidation reactions of primary and secondary alcohols

(Using acidified potassium dichromate(VI) or potassium manganate (VII) as oxidizing agents). Explanation of distillation and reflux in the isolation of the aldehyde and carboxylic acid products.

Writing the equation for the condensation reaction of an alcohol with a carboxylic acid, in the presence of a catalyst (e.g., concentrated sulfuric acid) to form an ester.

Alcohols

General formula: $C_nH_{2n+2} + O$
Functional group: –OH (known as hydroxyl)
Naming: as noted earlier, the alcohol is usually signified by -ol added as a suffix to the root of the name,
For example, ethanol.
However, if there is more than one functional group it can also go by another name.
For example, 2-hydroxy propanoic acid.
Here the OH is considered a branch off the acid so it is called -hydroxy.

Reactivity comment

Alcohols burn easily too and the combustion equation is as you'd expect:

$$C_2H_5OH + 3O_2 \Rightarrow 2CO_2 + 3H_2O$$

The balancing must take into account that there is an oxygen in the alcohol already, which must be accounted for. You would be expected to write combustion equations up to six carbons.

Oxidation reactions

The most common reaction of the alcohols is the oxidation reaction. These are unlike other reactions.

Essentially, you can turn an alcohol into a carbonyl (aldehyde or ketone) and/or a carboxylic acid by oxidation.

$$\underset{\text{Ethanol}}{C_2H_5OH} + [O] \Rightarrow \underset{\text{Ethanal}}{C_2H_4O} + H_2O$$

Or, going all the way:

$$C_2H_5OH + 2[O] \Rightarrow CH_3COOH + H_2O$$

What is the [O]?

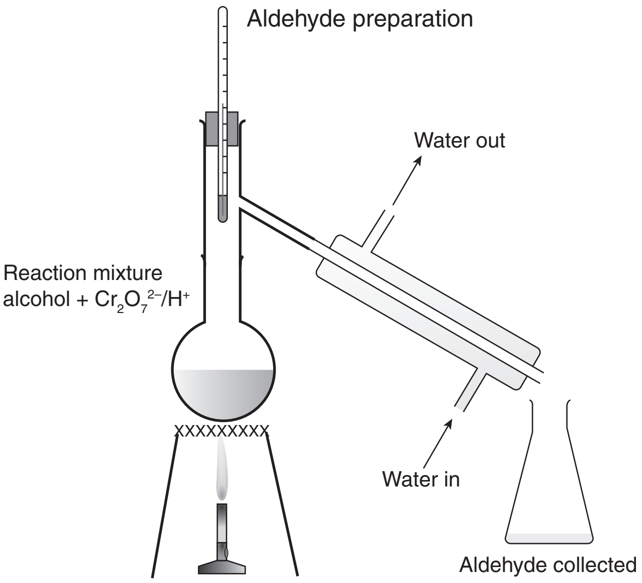
This is shorthand for the oxidizing agent. In this case it is a mixture of acidified potassium or sodium chromate (VII). This is a bright orange compound. The mixture needs to be heated to make it work. You can also use potassium manganite (VII)

Problems?

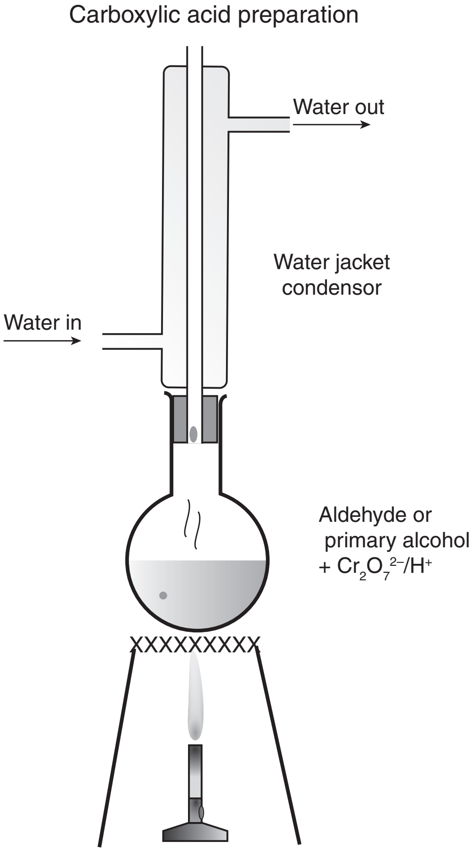
What are you going to make?

The first problem is that there are two possible products: the carbonyl or the carboxylic acid. Which one have you made? Essentially, in the first instance you will make the carbonyl but if you further heat the reaction then you can make the carboxylic acid.

But if you heat an organic mixture it evaporates!
Correct. Therefore, if you want to make the carbonyl, you heat and distil the product immediately.



If you want to make the carboxylic acid, you need to heat the mixture without allowing it to evaporate. The process is called "heating under reflux" and you should have done a lab on it.



To get the acid you then change the apparatus to distill.

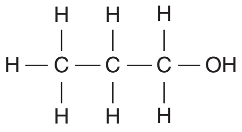
Primary, secondary and tertiary alcohols

One of the differences about organic chemistry is that reactions will be different depending on the shape of the molecule. This is no better illustrated than in this set of reactions.

Because the functional group can be anywhere on the carbon chain, the consequences are significant. There are three possible types of alcohol.

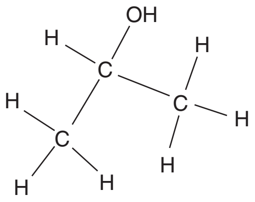
Primary

Where the OH is attached to a carbon attached to one other carbon (propan-1-ol).



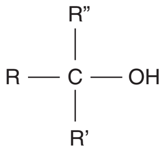
Secondary

Where the OH is attached to a carbon attached to two other carbons (propan-2-ol).



Tertiary

Where the OH is attached to three other carbons (2 methyl propan-2-ol).



When these alcohols are oxidized, three different reactions occur:

In primary alcohols, the OH is at the end of a chain. Therefore, the carbonyl group is on the end of the chain. We call that an aldehyde. Aldehydes can be converted to carboxylic acids, which MUST be on the end of a chain.

In secondary alcohols, the OH is in the middle of a chain. Therefore, the carbonyl group is in the middle of the chain. This is known as a ketone. There are not enough bonds for a carboxylic acid to form so FURTHER OXIDATION IS NOT POSSIBLE.

In tertiary alcohols, the OH is in the middle of a chain and the opposite hydrogen is a methyl group. This means a double bond cannot form and no oxidation is possible.

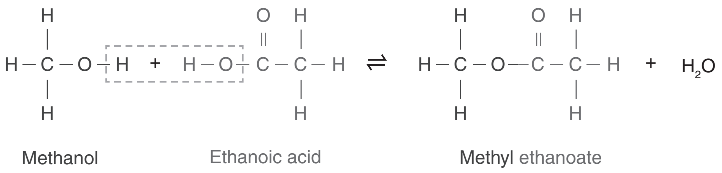
Summary

Type of alcohol	**Product on distilling**	**Product upon refluxing then distilling**
Primary	Aldehyde	Carboxylic acid
Secondary	Ketone	No further oxidation possible
Tertiary	Oxidation not possible	Oxidation not possible

Esterification

Alcohols can also react with carboxylic acids to form esters.

Example:
With concentrated sulfuric acid catalyst and warmed:



These are known as condensation reactions because water is eliminated. They can also be known as elimination reactions for similar reasons.

CORE
SPREAD 6: The halogenoalkanes

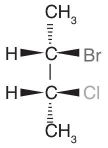
Halogenoalkanes are more reactive than alkanes. They can undergo (nucleophilic) substitution reactions. A nucleophile is an electron-rich species containing a lone pair that it donates to an electron-deficient carbon.

Writing the equation for the substitution reactions of halogenoalkanes with aqueous sodium hydroxide.

Halogenoalkanes

Functional Group: F, Cl, Br or I
Naming: usually by adding fluoro-, chloro-, bromo- or iodo- to the root of the carbon chain. This is often prefixed by a number indicating where the halogen is. If there is more than one halogen they are named alphabetically. See below.

So 2 bromo, 3 chloro butane is:



Reactions of the halogens

The reactivity of the halogenoalkanes is because of the halogen. As we have seen halogens are more electronegative than carbon; this creates a dipole in the molecule. This dipole means that the carbon has a δ+ charge. It will be susceptible to attack from species with negative charges or lone pairs. These are called nucleophiles.

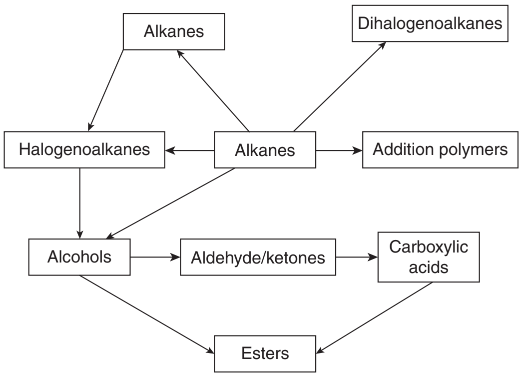
Halogenoalkanes exchange their halogen for something else (usually). Therefore, halogenoalkanes perform nucleophilic substitution reactions.

Nucleophilic substitution with the nucleophile sodium hydroxide:

$CH_3CH_2Cl + NaOH \Rightarrow CH_3CH_2OH + NaCl$

SL ORGANIC SUMMARY

Fill in the reagents and other information.



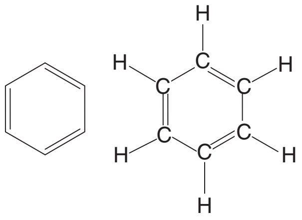
CORE and HL
SPREAD 7: Benzene reactions and its mechanism

Benzene is an aromatic, unsaturated hydrocarbon.

Discussion of the structure of benzene using physical and chemical evidence.

Introduction

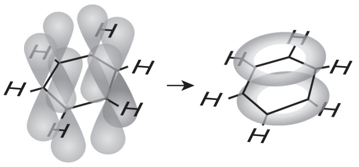
Benzene is the root functional group in a series of organic molecules called aromatic hydrocarbons. Its formula is C_6H_6 and its structure can be written as:



On paper this appears to be a structure made up of a ring of six carbon atoms with double bonds on alternative carbons. This would make it an unsaturated hydrocarbon like an alkene.

The problem is that benzene does not react like an alkene.

If you're an HL student, you will have met benzene before in the Bonding section. As we noted there, structures with alternating double and single bonds delocalize. Their π electrons merge to form two continuous rings of π electrons above and below the ring. This stabilizes the whole structure.



6 p-orbitals Delocalized

Benzene, therefore, is often written as:

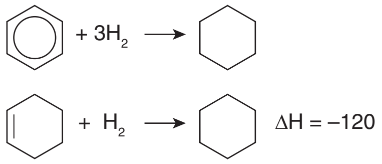
Evidence for the delocalized model

Physical

Bond lengths

The data book confirms the typical C–C bond length is 0.154 nm and C=C bonds are 0.134 nm. However, benzene does not have ANY bonds of this length. All are the same length (0.140 nm).

Enthalpy of hydration value
If you do the reaction:



If benzene did have the cyclohexa 1, 3, 5 triene structure, the value should be three times this, that is, -360 kJmol^{-1}. The extra stability of the "real benzene" is due to its delocalized ring.

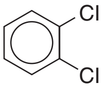
Chemical

Addition reactions

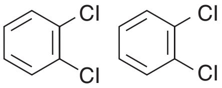
Benzene does not do the simple addition reactions associated with alkenes and does not decolorize bromine water.

Isomers

The molecule 1, 2 di chlorobenzene has no isomers:



If it had the double bond structure, it would have two isomers, shown below.



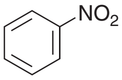
To this end benzene carries out only electrophilic substitution reactions.

HL
SPREAD 8: Benzene reactions and its mechanism

Benzene is the simplest aromatic hydrocarbon compound (or arene) and has a delocalized structure of π bonds around its ring. Each carbon to carbon bond has a bond order of 1.5. Benzene is susceptible to attack by electrophiles.

The reactions of benzene

Benzene can be converted to nitrobenzene:



Uses

Nitrobenzene is an important reagent for making drugs and explosives.

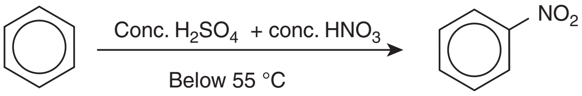
Reagents and conditions

Concentrated sulfuric acid (catalyst), concentrated nitric acid

Temperature around 50°C

Type of reaction

Electrophilic substitution



Points to learn:
Generating the electrophile

As we have seen, an electrophile is a lone pair acceptor. In this reaction it is NO_2^+.

This is how it's made:

$$H_2SO_4 + HNO_3 \leftrightarrows HSO_4^- + H_2NO_3^+$$

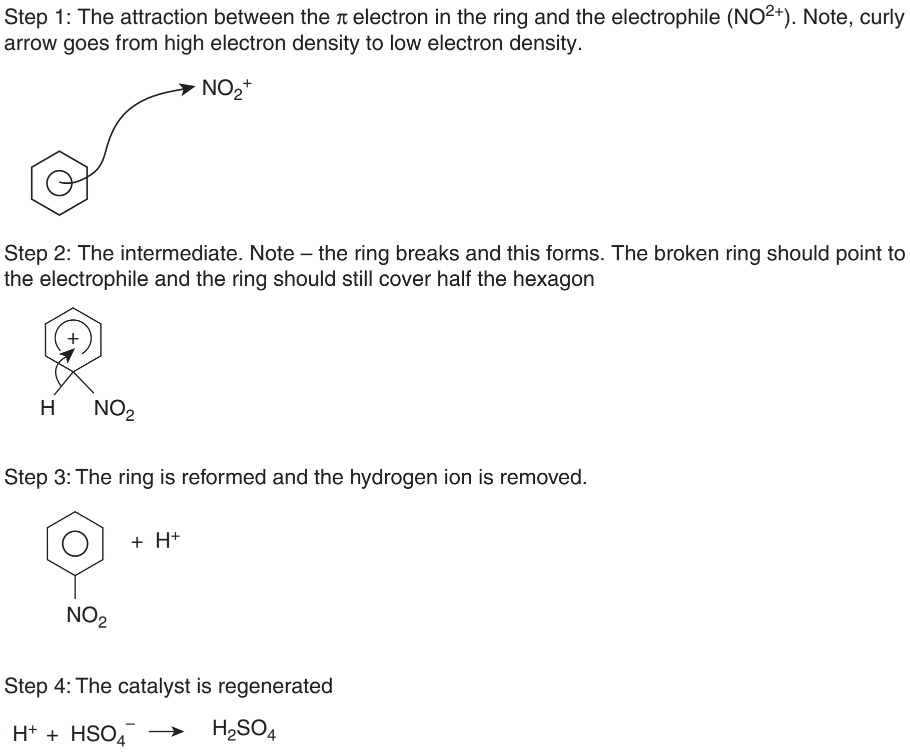
(This is an acid–base reaction! The sulfuric acid donates a proton to the nitric acid.)

The $H_2NO_3^+$ is unstable and falls apart to H_2O and NO_2^+.

Mechanisms

Mechanisms are explanations as to how reactions go. They utilize "curly arrows"; these show the movement of electron pairs from high electron density to low electron density.

The mechanism for nitration of benzene



Step 1: The attraction between the π electron in the ring and the electrophile (NO^{2+}). Note, curly arrow goes from high electron density to low electron density.

Step 2: The intermediate. Note – the ring breaks and this forms. The broken ring should point to the electrophile and the ring should still cover half the hexagon

Step 3: The ring is reformed and the hydrogen ion is removed.

Step 4: The catalyst is regenerated

$$H^+ + HSO_4^- \longrightarrow H_2SO_4$$

HL
SPREAD 9: Further electrophilic substitution

An electrophile is an electron-deficient species that can accept electron pairs from a nucleophile. Electrophiles are Lewis acids.

Markovnikov's rule can be applied to predict the major product in electrophilic addition reactions of unsymmetrical alkenes with hydrogen halides and interhalogens. The formation of the major product can be explained in terms of the relative stability of possible carbocations in the reaction mechanism.

Lewis acids

The Bronsted Lowry model of acids and bases does not cover all acid behavior. An alternative is the Lewis model.

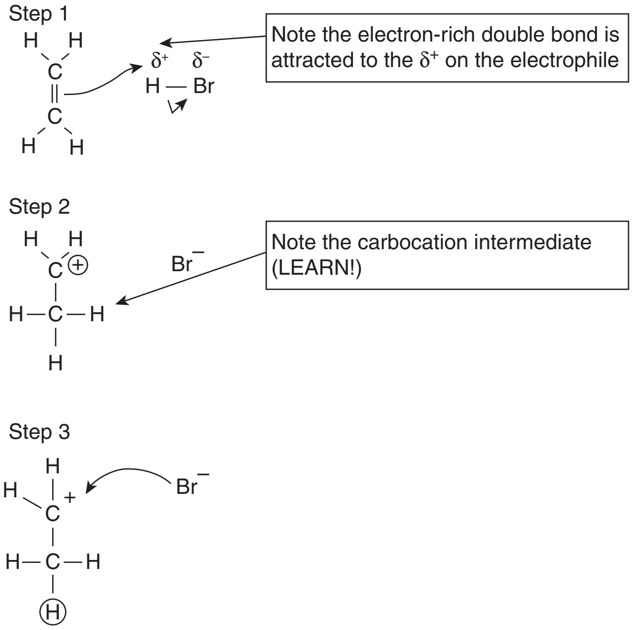
Lewis acids are lone pair acceptors.

Lewis bases are lone pair donors.

An example of a Lewis acid is something that is lacking a pair of electrons. BF$_3$ is a good example. Lewis bases are substances with lone pairs. Ammonia is a good example.

We mention them here because electrophiles are Lewis acids.

The mechanism for electrophilic addition



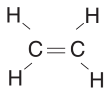
Note the electron-rich double bond is attracted to the δ+ on the electrophile

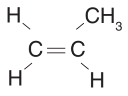
Note the carbocation intermediate (LEARN!)

The mechanism also works for halogens (Cl$_2$, etc.) but the dipole is induced by electron clouds rather than a permanent.

The problem with asymmetric alkenes

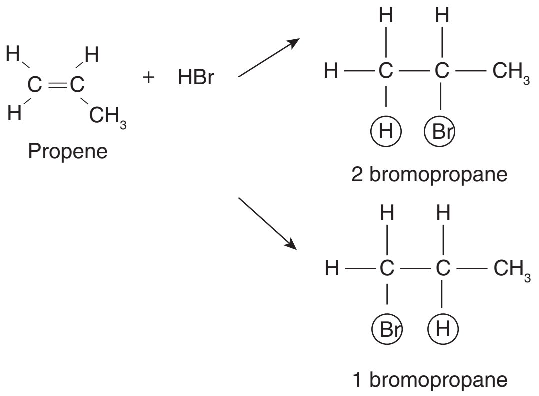
Consider propene and ethane:


Ethene


Propene

Ethene is symmetrical around the double bond, propene is asymmetrical.

This means addition reactions of asymmetric alkenes have two possible products:



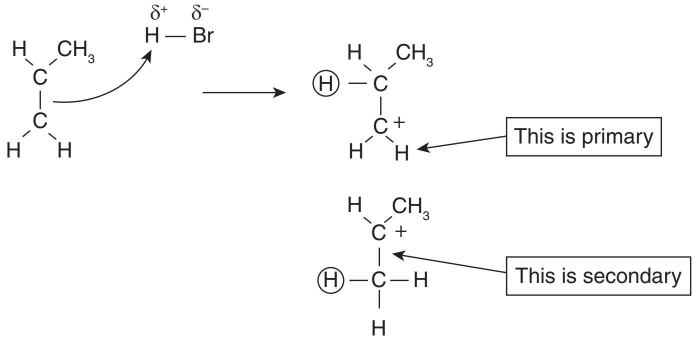
So which one forms?

Well both do! The 2-bromopropane forms faster so it predominates. The rule for knowing this is known as Markovnikov's rule. Essentially, The hydrogen attaches to the carbon that already has the most hydrogens attached to it.

Why?

Some difficult chemistry here. The secret is in the carbocation.

For propene there are two carbocations possible:



Now the more stable carbocation will form fastest and predominate. Stability is down to the number of CH_3 groups attached to the carbon with the C⊕. With primary there are none. With the secondary there are two. The CH_3 groups are said to have a positive inductive effect and push electrons onto the carbocation. This stabilizes it.

HL
SPREAD 10: Further nucleophilic substitution

S_N1 represents a nucleophilic unimolecular substitution reaction and S_N2 represents a nucleophilic bimolecular substitution reaction. S_N1 involves a carbocation intermediate. S_N2 involves a concerted reaction with a transition state.

For tertiary halogenoalkanes the predominant mechanism is S_N1 and for primary halogenoalkanes it is S_N2. Both mechanisms occur for secondary halogenoalkanes.

The rate-determining step (slow step) in an S_N1 reaction depends only on the concentration of the halogenoalkane, rate = k[halogenoalkane]. For S_N2, rate = k[halogenoalkane][nucleophile].

S_N2 reactions are best conducted using aprotic, nonpolar solvents and S_N1 reactions are best conducted using protic, polar solvents.

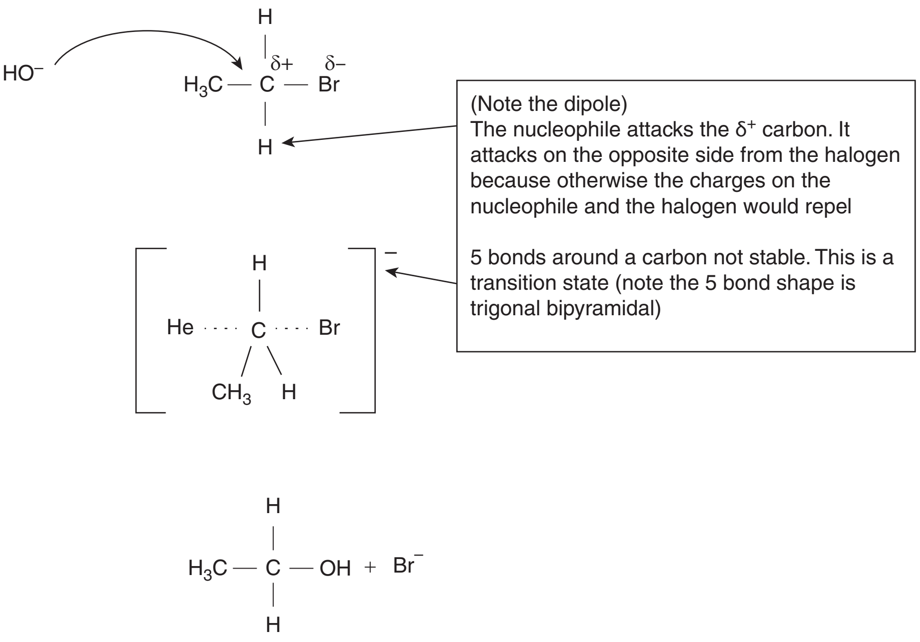
We saw that halogenoalkanes react by nucleophilic substitution. At HL we investigate the mechanisms in more details.

Mechanisms

Yes, plural! There are two mechanisms for nucleophilic substitution, depending on the nature of the halogenoalkane.

Primary halogenoalkanes.

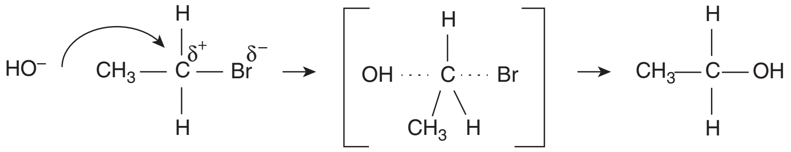
These go by a mechanism known as S_N2:



(Note the dipole)
The nucleophile attacks the δ^+ carbon. It attacks on the opposite side from the halogen because otherwise the charges on the nucleophile and the halogen would repel

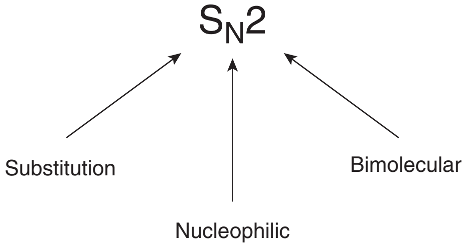
5 bonds around a carbon not stable. This is a transition state (note the 5 bond shape is trigonal bipyramidal)

So, as a whole:



This is a single-step mechanism but it has two reagents in the step (bimolecular). The molecularity is 2.

This is why it is:



Kinetics

Experiments confirm the reaction is first order with respect to the halogenoalkane and OH$^-$.

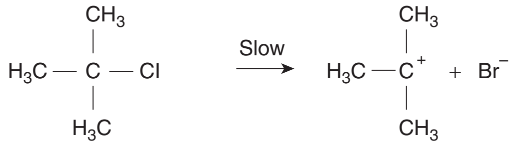
Rate = k [halogenoalkane] [OH$^-$]

As the contents of the rate expression confirm the molecules in the rate-determining step, this shows the mechanism is correct.

Tertiary halogenoalkanes

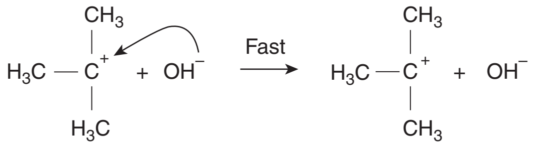
These go by the S_N1 mechanism:

Step 1



Note: The C – Cl bond breaks Heterontically to form two ions

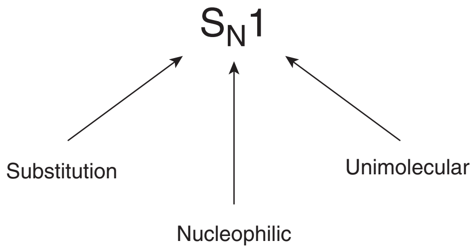
Step 2



This is unimolecular because the slow step contains only one species.

Kinetics

The rate expression is rate = *k* [halogenoalkane]^1. This confirms one species in the rate-determining step, so the mechanism is:



What about secondary halogenoalkanes?

The good news is that you can't be assessed on these because they could do either, or both!

Further factors affecting the rate of nucleophilic substitution

Solvent

Protic solvents are solvents containing hydrogen bound to oxygen (or nitrogen). Essentially water or ethanol. They are polar and this favors the S_N1 mechanism as they make heterolytic fission more likely to happen.

Aprotic solvents do not contain such a hydrogen and are less polar. They support S_N2. Ethoxyethane (an ether) is a good example.

Nature of the nucleophile

Although water and NaOH both contain the required OH group, NaOH is a much better nucleophile and the reaction is much faster. This is because the electron density of the nucleophile is much higher with a negative charge than a mere dipole.

Type of halogenoalkane

Tertiary reacts faster than secondary, which reacts faster than primary.

The reason is the high activation energy of the transition state in the primary SN2 mechanism.

Nature of the halogen

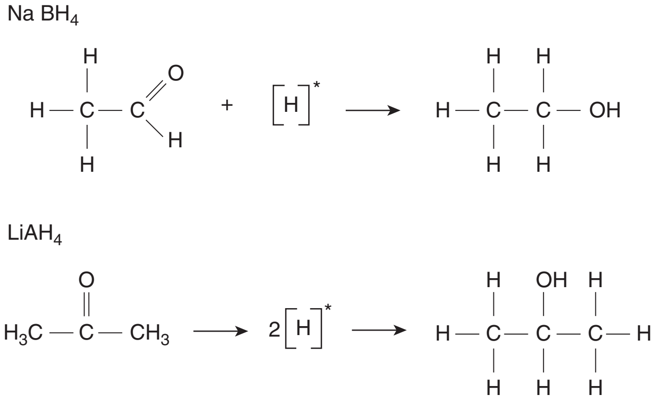
Iodoalkanes react faster than chloroalkanes. The reason for this is to do with the strength of the carbon–halogen bond. The C–I bond is weaker than the C–Cl bond. It's weaker because it is longer. It is longer because the iodine atom is bigger than the chlorine atom. A weaker bond requires less energy to break so the chances of a successful collision increase. The activation energy is more likely to be met.

HL
SPREAD 11: Reduction reactions

Carboxylic acids can be reduced to primary alcohols (via the aldehyde). Ketones can be reduced to secondary alcohols. Typical reducing agents are lithium aluminum hydride (used to reduce carboxylic acids) and sodium borohydride.

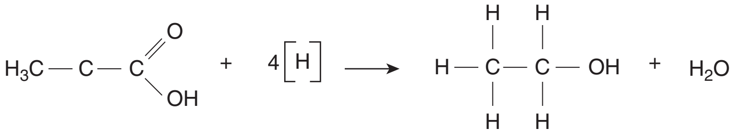
As we have seen before, reduction reactions remove oxygen or add hydrogen. We have also met organic oxidation reaction when alcohols are oxidized to carbonyl and carboxylic acids. These reactions can be "reversed" so the aldehyde or ketone can be converted to an alcohol. They need a reducing agent to carry out this reaction.

There are two well-known reducing agents for organic reactions (although you are unlikely to have used either). They are lithium aluminum hydride ($LiAlH_4$) and sodium tetrahydridoborate ($NaBH_4$). Both have hydrogen in the rare −1 oxidation state, which is necessary for the conversion. Both can be used to reduce aldehydes or ketones to their respective primary or secondary alcohol.



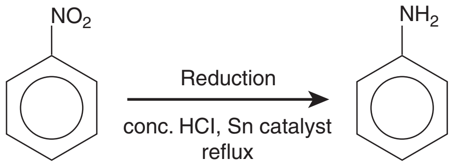
* **Short for** $LiAlH_4$ in dry ether (it reacts with water so you need an aprotic solvent)

$LiAlH_4$ can also be used to reduce carboxylic acid to primary alcohols and aldehydes.



Reduction in aromatic chemistry

This is a little counterintuitive but nitrobenzene can be converted to phenyl amine by reduction:



The reducing mixture with balancing is 6[H].

Firstly, note the naming of the product. It is called phenyl amine. Benzene rings can sometimes be named with phenyl, usually when the benzene is considered the branch. Casting the name aside the reaction is simple.

Tin and conc. HCl followed by NaOH refluxed are not the most obvious reagents. The tin does the reducing, providing the electrons.

HL
SPREAD 12: Synthetic routes

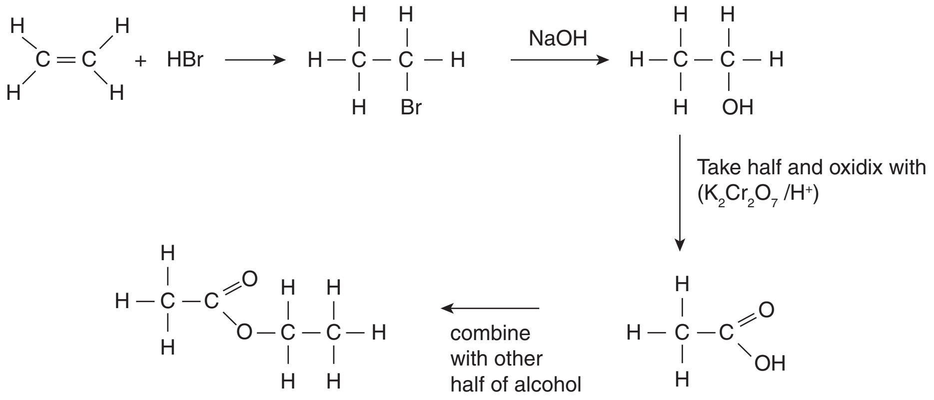
The synthesis of an organic compound stems from a readily available starting material via a series of discrete steps. Functional group interconversions are the basis of such synthetic routes.

Retro-synthesis of organic compounds.

Practicalities

The IB guide states that you should be able to make any compound on the reaction scheme from any other molecule on the reaction scheme, up to four steps. This means you have to know by heart all the connections between each one (including reagents and conditions).

For example: making ethyl ethanoate from ethane:



You should also know the link from benzene through to phenyl amine and be aware the functional groups on the aliphatic scheme can appear on benzene rings and react normally.

What a synthetic chemist does

In simple terms, synthetic chemists try to find a cheap starting material and make the target molecule with as few steps as possible (each step causes a loss of product) so the percentage yield drops.

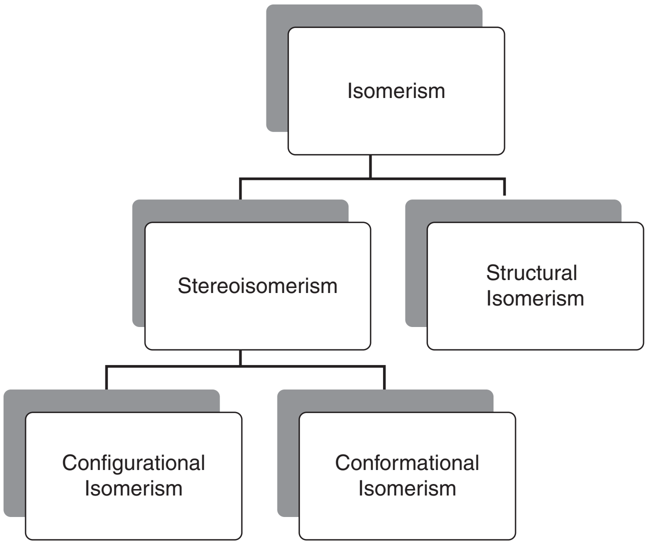
Sometimes this can seem daunting so it is important to focus on the functional group only.

Retro-synthesis can help. Sometimes it is easier to look at the product first, the target molecule, and work backwards. In any question of this sort it is often best to work backwards, especially if you are stuck.

HL
SPREAD 13: Isomerism

Cis-trans isomers can occur in alkenes or cycloalkanes (or heteroanalogues) and differ in the positions of atoms (or groups) relative to a reference plane. According to IUPAC, E/Z isomers refer to alkenes of the form R1 R2 C=C R3 R4 (R1 ≠ R2, R3 ≠ R4) where neither R1 nor R2 need be different from R3 or R4.

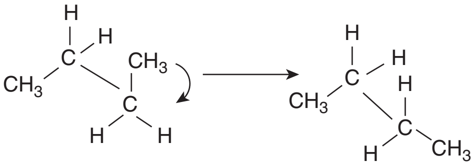
Structural isomerism has been discussed in the core course. There is more to it than that. The IB Guide shows you how it works in a flow chart, reproduced below:



There is a second form of isomerism called stereoisomerism. This is defined as molecules having the same structural formula but having a different arrangement in space.
There are two divisions of this:

Conformational

Here the σ bond allows rotation and groups CAN rotate around it. It is not permanent.



Configurational

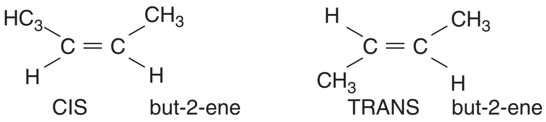
These are permanent changes where reverting to the original required breaking bonds.

These are more important, so let's look at them:

Type 1

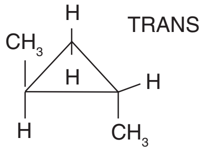
Cis-trans isomers

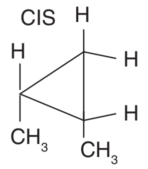
The "different arrangement in space" here is due to the double bond. The π bond restricts rotation so the two versions are not interchangeable:



(Trans, as in transatlantic flight. Cis, because you are close to your sister!)

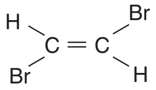
Cycloalkanes also display cis-trans isomerism. The ring system is the cause of the restriction here:





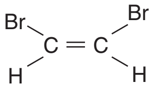
E/Z isomerism

Cis-trans is the simplified form of E/Z isomerism. Cis-trans ONLY works when the nonhydrogen groups are the same:



Trans 1, 2 dibromoethene

E 1, 2 dibromoethene



CIS 1, 2 dibromoethene

Z 1, 2 dibromoethene

These are also E/Z

E = entgegen (apart)

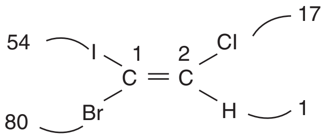
Z = zusammen (together)

E/Z is more useful because it can work out the isomer type even if all the groups are different.

To do that you need to understand the Cahn-Ingold-Prelog (CIP) rules.

You need to:

Know the atomic number of each atom attached to the carbon. The highest number gets the highest priority:



So on carbon 1, iodine has the higher priority.

And on carbon 2, chlorine has the higher priority.

The high priority atoms are on the same side, so this is Z 1 bromo, 2 chloro 1 iodoethene.

HL

SPREAD 14: Optical isomerism

A chiral carbon is a carbon joined to four different atoms or groups.

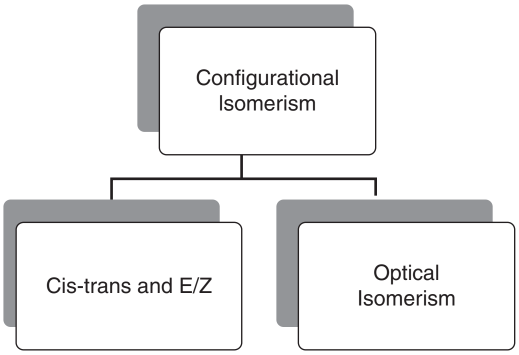
An optically active compound can rotate the plane of polarized light as it passes through a solution of the compound. Optical isomers are enantiomers. Enantiomers are nonsuperimposeable mirror images of each other.

Diastereomers are not mirror images of each other.

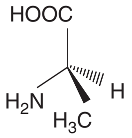
A racemic mixture (or racemate) is a mixture of two enantiomers in equal amounts and is optically inactive.

S_N2 is stereospecific with an inversion of configuration at the carbon.

The guide continues its isomerism flow chart with optical isomerism:



This is another form of stereoisomerism and it arises from molecules containing at least one carbon which has four different atoms or groups attached to it:



The carbon here is an example and is known as a chiral carbon, or a chiral center. Such a carbon allows two versions of the molecule to exist. They are, if you like, left or right handed and are mirror images. The two different versions are known as enantiomers.

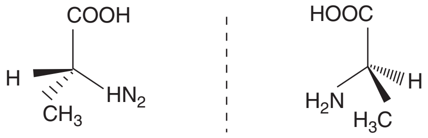
When representing these optical isomers, it is important to use 3-D diagrams, with wedges.

Best advice:

Draw the molecule in 3D.

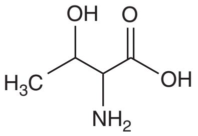
Draw a line next to it to represent the mirror.

Copy the molecule as a mirror image.

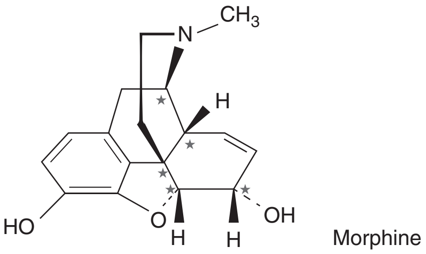


(*S*)-alanine Mirror plane (*R*)-alanine

Complicated molecules can have many chiral centers. You may be asked to spot them all. On skeletal formula be careful as hydrogens are not shown. For example, threonine has two centers.



And morphine has five!



There are five chiralitv centers in morphine.
It has 2^5 stereoisomers in principle.

How can we identify optical isomers?

Optical isomers have an effect on polarized light. Plane polarized light vibrates only on one plane. When such light is shone through one isomer, that plane of the polarized light is rotated in one direction. The other enantiomer rotates in the opposite direction.

What happens if you have a mixture of enantiomers? There will be no effect on the polarized light.

Such a mixture is called a racemic mixture.

Stereospecificity in S_N2 mechanisms

A fancy word for a technical occurrence. Remember the S_N2 mechanism the nucleophile attacks from behind? If the halogenoalkane was an enantiomer and the carbon was chiral, something interesting happens.

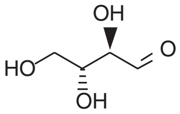
Imagine this. The attack to the tetrahedral molecule means that three of the bonds are pointing toward the nucleophile. As it attacks it sends them flying in the opposite direction. A bit like an umbrella caught by the wind. One minute everything is pointing toward your head (the nucleophile), the next it is pointing away from you.

This has the effect of fixing the position of the bonds and allows the molecule to form only one enantiomer: the same as the starting reagent. A racemic mixture is not formed.

Diastereoisomers

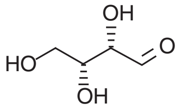
These are molecules with two or more chiral centers. The arrangement is such that they do not form mirror images of each other but are superimposable. Also in contrast to enantiomers they have different physical and chemical properties from each other.

Below are a couple of examples:



D-Threose

D-Threose
D-Ethryose



D-Ethryose

CHAPTER

12

Measurement and data processing: Part 2

This chapter covers material in the second part of Topics 11 and 21 of the IB syllabus.

SPREAD 1: Index of hydrogen deficiency

The degree of unsaturation or index of hydrogen deficiency (IHD) can be used to determine from a molecular formula the number of rings or multiple bonds in a molecule.

One of the most important concepts in chemistry is, rather predictably, trying to work out what chemical you actually have in front of you. Chemical substances cannot communicate with us so we have to use a variety of techniques and analyses to work it out. This IB Chemistry Diploma Program course doesn't cover everything in this enormous field, so the following sections are just a summary of a few useful concepts.

The degree of unsaturation of IHD is a simple calculation to help you decide on possible structures of an organic molecule. It only works if you know the molecular formula of the compound in question and it only really works for compounds containing mainly carbon and hydrogen.

You also need to remember unsaturation in this context means either a multiple bond or a ring. A saturated carbon has four single bonds around it.

The formula is:

$$\mathrm{IHD} = \frac{2x + 2 - y}{2}$$

where x is the number of carbons and y is the number of hydrogens.

So, for C_2H_4

The IHD is 2.2 + 2 − 4/2 = 1.

This molecule must contain either a double bond or a ring, but as it only has two carbons it must have a double bond.

Double bonds and rings on their own always give an IHD of 1. Triple bonds give an IHD of 2. IHD values can add up over a complicated molecule, but this simple technique can help rule out possibilities.

Example:

C_4H_6 gives an IHD of 2. So it either has a triple bond or a double bond within a ring.

Don't forget that when double bonds and rings are involved, stereoisomers are also possible.

Compounds containing elements other than carbon and hydrogen

Oxygen and sulfur atoms do not affect the IHD, so can be ignored. The same can be said for halogens (F, Cl, Br, I), which are treated like H atoms.

Nitrogen is more complicated, for each nitrogen add one to the value for the number of carbons and one to the number hydrogens.

CORE

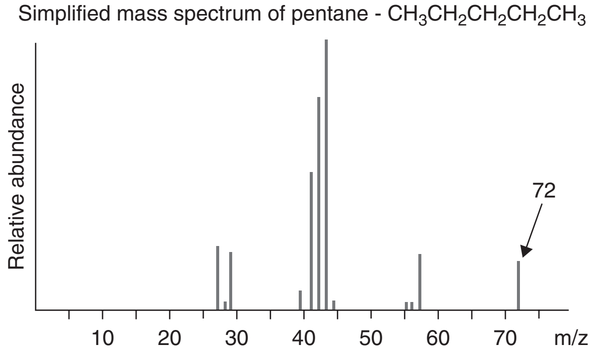
SPREAD 2: Mass spectrometry

Mass spectrometry (MS), proton nuclear magnetic resonance spectroscopy (^1H NMR) and infrared spectroscopy (IR) are techniques that can be used to help identify compounds and to determine their structure.

MS was briefly discussed in the Atomic Structure topic, but we will go into more detail here.

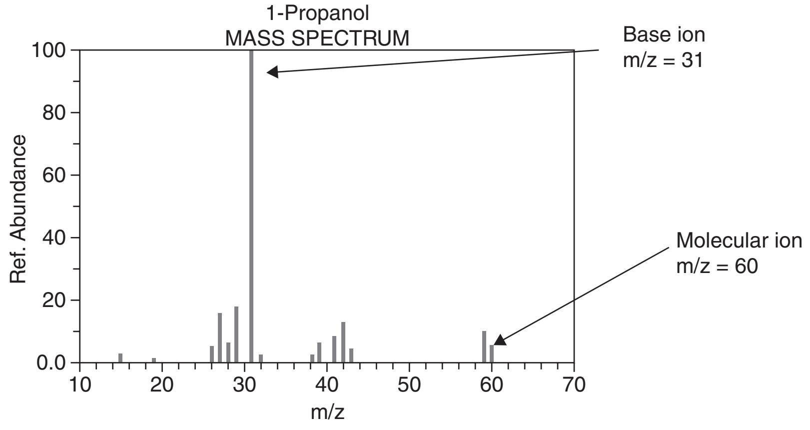
Essentially, MS is a destructive technique for working out the molecular formula of a compound. It does this by subjecting the compound in question to a bombardment of electrons, which breaks it up and knocks electrons off giving them a charge. These charged fragments all have a different mass (and charge) and are therefore susceptible to different deflections when accelerated through a magnetic field. These different deflections can be measured and can ultimately be used to work out the mass of fragments.

For example, here is the mass spectrum of propane below:



The peak farthest to the right is the most useful on first inspection. This is known as molecular ion peak. It will give you the relative molecular mass of the compound. From this you could use IHD to narrow down the number of possibilities for your molecule.

The other peaks can also be useful. The peak at 29 is $CH_3CH_2^+$, for example. Analysis of these peaks can help narrow down the possibilities.



Virtual labs, Leeds

Here, note the molecular ion again, and the peak at 15 CH_3^+. The base ion in the above example is simply the name given to the peak which is most abundant.

Points to note:

Any discussion about peaks or species detected by a mass spectrometer must be carefully thought through. Anything detected by a mass spectrometer has a positive ion so any answer to a question about what species is responsible for a certain peak must have a + somewhere. For example, the fragment at 60 in the propan-1-ol spectrum is the $C_3H_6O^+$ species.

MS has its uses for working out the relative molecular mass of a compound, but as far as we are concerned it is less useful for making an absolute judgment about the exact structure and the nature of the functional groups in a particular molecule. For that we need a couple of other techniques.

CORE
SPREAD 3: Infrared spectroscopy

The electromagnetic spectrum is very helpful in the analysis of chemical substances. We've mentioned the spectrum before:

It is in your data book, so it is always available.

This energy can be absorbed or emitted depending on what is being done to the compound. Here we will focus on what happens when infrared radiation is absorbed by a chemical compound.

Bond stretching and vibrating

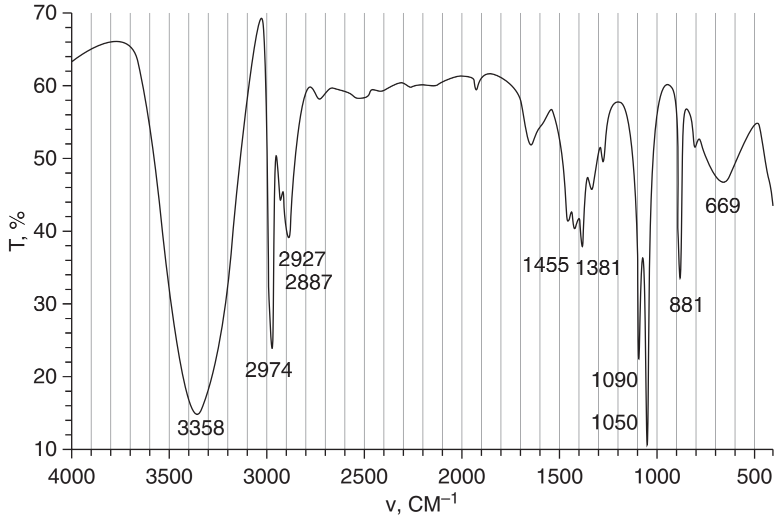
When infrared radiation is absorbed by a covalently bonded substance, the covalent bonds absorb the energy, which causes them to stretch and vibrate, a bit like a spring. The nature of these stretches and bends will depend on the nature of the bond itself and this gives us the clues we need to identify functional groups in covalent molecules.

In summary, each type of covalent bond gives a unique peak (although they are displayed downwards so they really ought to be troughs) on an infrared spectrum. The frequency of these peaks are well known and are in your data book.

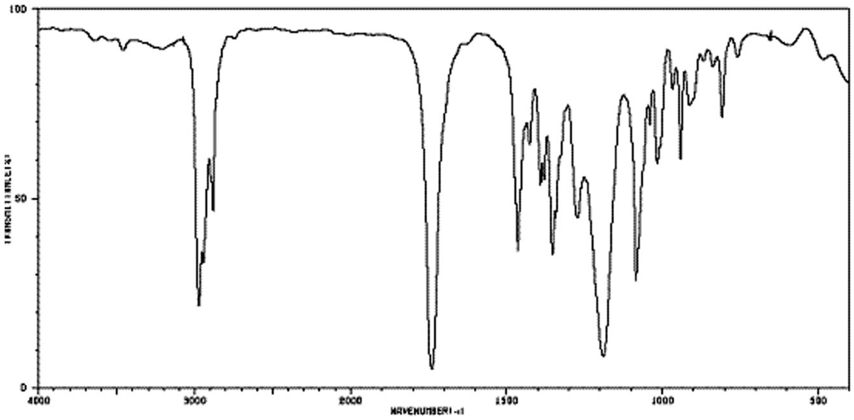
The most common ones are summarized here:

C=C 1610–1680 cm^{-1}
C=O 1680–1750 cm^{-1}
C–H 2840–3100 cm^{-1}
O–H alcohols (broad) 3230–3500 cm^{-1}
O–H carboxylic acids (very broad) 2500–3500 cm^{-1}

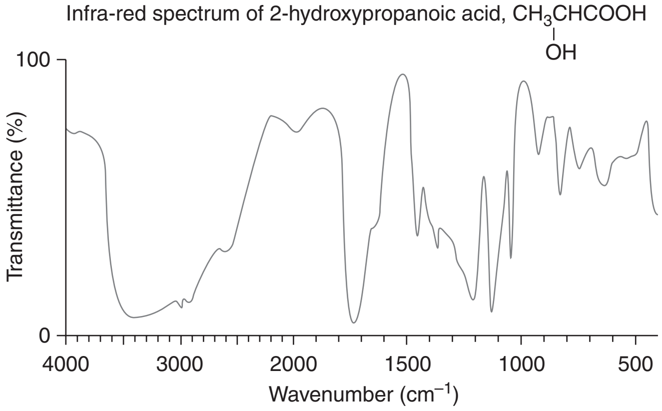
Studying infrared spectra



Ethanol



Ethanal


Infra-red spectrum of 2-hydroxypropanoic acid, $\underset{\displaystyle OH}{CH_3CHCOOH}$

These three IR-spectra illustrate nicely the differences in different compounds and the ease with which IR can be used.

In the ethanol spectrum, you can see the C–H peak and the O–H peak at 3500 cm^{-1}, like a big thumb print.

In ethanal, another compound containing one oxygen, you can see the spectrum looks completely different; the C–H peak is still there but the C=O peak appears around 1750 cm^{-1}.

For the final carboxylic acid you can see the C=O peak and the O–H peak, but note how the O–H peak in a carboxylic acid is so much broader and completely covers the C–H peak.

Points to note

Infrared spectroscopy is a very useful device used to work out what SORT of compound you have got but it cannot tell you anything about the relative number of each type of bond or the relative molecular mass. It must therefore be used in tandem with another technique like MS or NMR.

CORE
SPREAD 4: Nuclear magnetic resonance spectroscopy

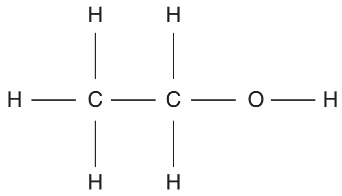
Basics

Nuclear magnetic resonance is a very powerful analytical technique. You do not need to know too much about how it works, but essentially, in a powerful magnetic field nuclei with odd number, mass numbers interact with the magnet and can exist in two different “spin” states of equal energy. When transferring between the two, a nucleus can absorb a photon of energy. This energy is very small and occurs in the radio region of the electromagnetic spectrum. This can produce a characteristic spectrum of tremendous use to chemists.

What does it detect?

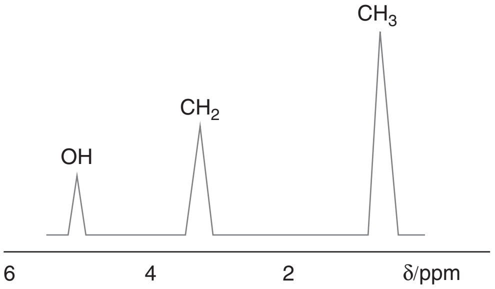
Focusing on H^1, regular hydrogen atoms, NMR can identify each unique environment for a hydrogen atom in a molecule.

Let's consider a molecule of ethanol:


$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-O-H$

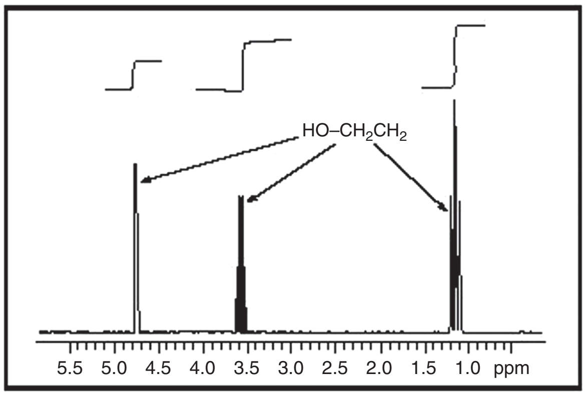
You can see there are three different environments. The CH_3 hydrogens, the CH_2 hydrogens and the OH hydrogen all "live" in different parts of the molecule. This would produce three distinct peaks on an NMR spectrum.

A very simplified version of spectrum is below. As you can see, there are three peaks and the size of the peaks corresponds to the number of hydrogens in the environment.



Check list for NMR spectra:

1) Number of peaks
   It really is that simple. The number of peaks lists the number of unique hydrogen/proton environments in the molecule.
2) Relative size of the peaks
   This is perhaps slightly trickier. How do you know which peak is larger? NMR peaks can be quite broad as well as tall. The NMR machine is aware of this and produces an integration trace which gives you the relative proportions. You can see it on the more complicated spectrum below



In an exam you will be given the relative sizes of the peaks or an easy-to-decipher integration trace.

3) Chemical shift

How far the peak has shifted from the 0.0 line on the far right also gives us some useful information. In your data book on page 27 is a table detailing the shifts commonly associated with the most common type of proton/hydrogen environments. Again a quick glance shows that all the peaks associated with ethanol are in the right place.

CH_3 is between 1 and 2 ppm.
CH_2 is also between 1 and 2 ppm.
OH is between 1 and 5.5 ppm.

NMR is a really powerful tool for telling you the exact shape and nature of the carbon chain in conjunction with MS to get the RMM and IR to confirm functional groups and you can be almost certain as to what an unknown compound will be.

HL
SPREAD 5: Further NMR

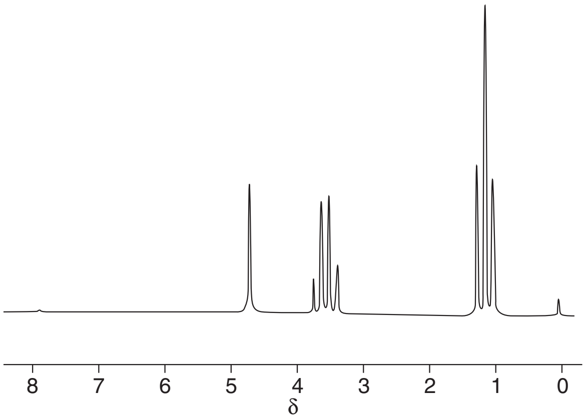
In a high resolution ^{1}H NMR spectrum, single peaks present in low resolution can split into further clusters of peaks.

NMR is an excellent technique but not necessarily used on its own. The IB Diploma Program course will expect you to analyze a lot of information from a variety of sources, not just one.

Tetramethylsilane
Tetramethylsilane (TMS) is the reference standard for all NMR spectra. The compound Si $(CH_3)_4$ produces a peak of 0.0 ppm to which all other peaks are measured. You should be aware of this and watch out for it in any spectra you are given to analyze.

Splitting patterns

Low resolution NMR is useful, but to really see the power of NMR you need to use high resolution. Below is the high resolution spectra for ethanol again.



The peak far right is the CH_3 peak, the peak in the middle is the CH_2 and the far left is the OH.

Look carefully. The CH_3 peak is split into three; the CH_2 into four and the OH is not split at all.

NMR also detects how many hydrogens are next to the hydrogens in each environment, but confusingly it shows it by adding an extra split to the peak. It is known as the N + 1 rule. So the CH_3 is split into three because it is next to two hydrogens in the CH_2 environment (N + 1). The CH_2 is split into four because it is next to CH_3 (3 + 1). The OH has no splitting because it is next to an oxygen with no hydrogens (0 + 1 = 1 peak).

A double split is known as a doublet, a triple a triplet, four = quartet and anything more is often covered by the word “mulitplet.”

NMR in summary:

1) Number of peaks
2) Relative height of peaks
3) Chemical shift
4) Splitting patterns

Any analysis of an NMR spectra must include all of these. Avoiding one will make it hard to work out what compound you have.

Combining techniques

It is not unreasonable to be given a series of spectra: mass spec, IR, NMR and be asked to work out the compound, plus other relevant information.

In summary:

Mass Spectrometry

Gives you the RMM from the molecular ion.

Can give information about branching.

IR

Used to determine the functional group.

NMR

Allows the exact structure to be determined.

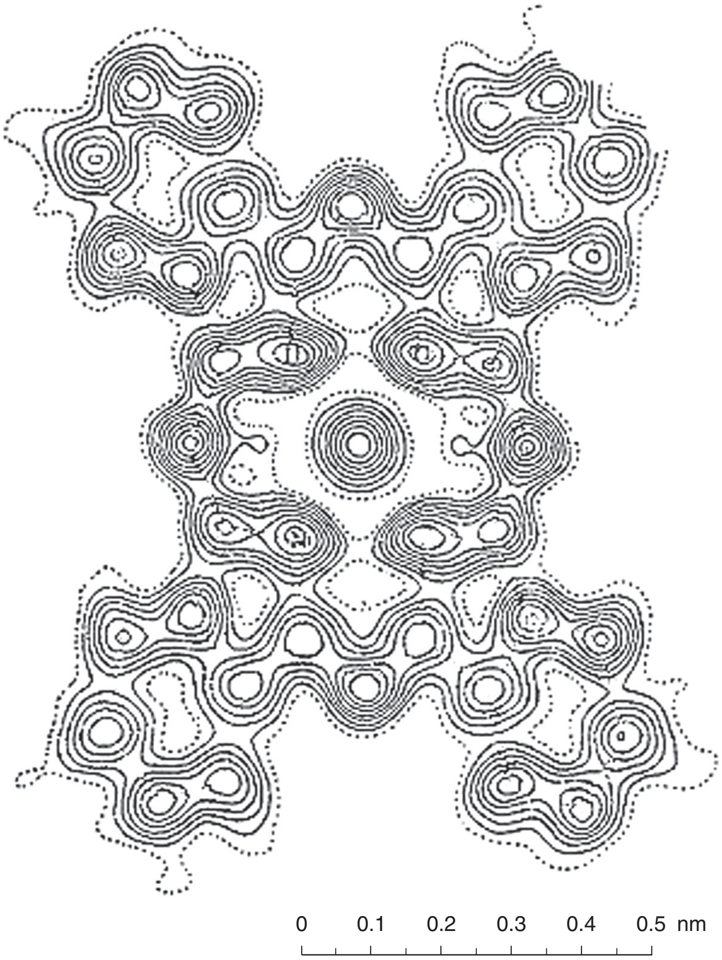
HL
SPREAD 6: X-ray crystallography

The structural technique of single crystal X-ray crystallography can be used to identify the bond lengths and bond angles of crystalline compounds.

The electron clouds in atoms diffract X-rays. When crystals (and the substance must be crystalline to work) are subjected to X-rays, the diffraction patterns can be analyzed and a pattern will emerge which will correspond to the 3-D structure of the crystal lattice.

Point to note, the bigger the atom/ion, the bigger the dots/splodges on the pattern, so hydrogens are rarely seen.

Complicated mathematical analysis will allow you to get an electron density map like the one below. This is a haem-based structure, the Fe is in the center and the rings are clearly seen around the outside. You will not need to be able to analyze this in great detail but …



From this you can work out bond lengths and bond angles of the atoms in a particular model. This is the way many of the data were originally calculated.

CHAPTER

13 Option A: Materials

This chapter covers material from Option A of the syllabus.

CORE
SPREAD 1: An introduction to material science

Materials are classified based on their uses, properties or bonding and structure.

The properties of a material based on the degree of covalent, ionic or metallic character in a compound can be deduced from its position on a bonding triangle.

Composites are mixtures in which materials are composed of two distinct phases, a reinforcing phase that is embedded in a matrix phase.

What is a material?

A material is a substance that is intended to be used for certain applications. This doesn't get us very far, so let's subdivide further. Materials can generally be divided into two classes: crystalline and noncrystalline and the traditional types of materials encountered are metals, ceramics and polymers. New materials that are being developed include semiconductors and nano-materials.

It is important for a material scientist to understand the structure of materials, and relate them to their properties. This can lead to a better understanding of the relative performance of the material and its suitability for the task required. As with all chemical substance the structure of a material and its properties will be determined by its constituent chemical elements, the bonding in the material and the way in which it has been processed.

Classification of materials

There are many types of materials. This course covers the following:

Metals
Liquid crystals
Polymers
Nanotechnology

A quick glance over this list, adding other common materials such as ceramic or glass and you can see there is a wide variety shown in the properties of these materials. In fact, one of the most important skills is classifying the materials so that the right material can be found for the right job.

All chemical substances are made of atoms, and all chemical compounds are made of two different types of atom bonding together. The *Bonding* chapter of the core covers this ground, but in summary the different type of bonding gives rise to a huge amount of difference in properties. Simply think about carbon dioxide, a gas and the oxide of the element below it, silicon to realize how structure and bonding have an effect. Silicon dioxide is a giant covalent solid with a very high melting point. It can also be made into glass, a transparent amorphous solid, of tremendous use to us.

The general properties of structures are found in the bonding chapter.

Materials can also be classified in terms of their uses, properties or bonding and structure. Let's look at bonding first. It is possible to classify substances in terms of bonding a Van Arkel/Ketelaar diagram of bonding. It is in your data book.

You need to know the electronegativity values of each element in the compound. The *y* axis is simply the difference between the two numbers, expressed as a positive number. The *x* axis is the mean of the same data. The value is plotted and the structure of the substance can be worked out.

Example: Beryllium Oxide, BeO

Using this diagram

y axis:

Electronegativity of Be = 1.6

Electronegativity of O = 3.4

3.4 – 1.6 =1.8

x axis = mean of 3.4 + 1.6 = 5/2 = 2.5

This puts BeO into the polar covalent category and will have properties associated with other compounds of its type.

Knowing the structure and the bonding type is useful but isn't necessarily the best way of classifying materials.

CORE
SPREAD 2: More on classifying materials

Here are some other ways of classifying materials:

Performance,
Physical and chemical properties,
Composition and structure,
Processing and synthesis.

Performance

The performance of a material is discussed in the context of an application. For example, many materials are used for building houses and often teachers remind students of the story of the three little pigs and the big bad wolf. As we're sure you remember the houses were made of straw, sticks or bricks. When the wolf huffed and puffed, the straw and stick houses fell down. Brick had the best performance. What should a good house material do? Protect the things inside from weather—wind, cold, heat, rain, snow, hail—and from fire and choosing the right material is crucial.

Physical properties

Some physical properties describe how an object responds to mechanical forces. Hardness is one example of a mechanical property. If you drag a steel knife blade across a hard object, such as a plate, the hard surface is unchanged; if you drag the blade across a soft object, such as a piece of chalk, the soft surface will be scratched. An object is tough if force is unable to break or tear it. The response to force depends on the material's structure, and also on its shape and size. A piece of paper can be torn easily, but a telephone book requires a much greater force.

We can easily bend a flexible object such as a nylon jacket, but more force is required to bend a stiff object like a metal fork. If an object returns to its original shape and size when the force is removed, we call it elastic. If the deformation remains, it is plastic. An object that breaks rather than bending then is brittle.

An object is strong if an applied force is unable to deform or break it. Canvas is strong, since pulling on it does not change its length. Sometimes the manner of applying a force makes a difference to the strength of an object. Ceramics can bear a lot of weight, but will break if stretched or bent. Nylon survives compression, pulling and twisting.

Color, texture and reflectivity can be observed by shining light on a sample. Mirrors are colorless, smooth and shiny. Electrical conductivity is detected by applying a voltage across an object. Applying heat to a sample reveals its ability to conduct heat, its melting point (temperature at which a solid changes to liquid) and its boiling point (temperature at which a liquid changes to gas). Some properties are independent of the amount of sample. Melting point does not change if a sample is divided in half. Other properties, including mass and volume, increase with the amount of sample being studied.

Composition and structure

This tells what chemicals are in a sample. The most specific description will reveal the chemical elements that are present in the sample. Structure is the three dimensional arrangement of atoms in a sample. When sand changes into glass, its silicon and oxygen atoms shift positions to make a continuous sheet. Even though the chemical composition is the same, some of the properties have changed. The bonding chapter will help with structure.

Processing and synthesis

Processing a material could be as simple as hammering a piece of copper. When sand is melted and formed into glass, the primary change *is how the atoms are arranged.* The different processes used to produce cast and wrought iron result in different ratios of iron and carbon which create different properties in the final objects and make them suitable for different applications.

Synthesis implies a major change in chemical composition, the manufacture of polymers is a good example of subtle changes to a basic hydrocarbon structure.

Composite materials

A composite material is a mixture in which materials are composed of two distinct phases, a reinforcing phase is embedded in a matrix phase. Such examples can include reinforced concrete, fiber strengthened polymers and fiberglass.

Permeability

The process of permeation involves the diffusion of molecules, called the permeant, through a membrane or interface. Permeation works through diffusion; the permeant will move from high concentration to low concentration across the interface. A material can be semipermeable, with the presence of a semipermeable membrane. Only molecules or ions with certain properties will be able to diffuse across such a membrane. This is a very important mechanism in biology where fluids inside a blood vessel need to be regulated and controlled. Permeation can occur through most materials, including metals, ceramics and polymers. However, the permeability of metals is much lower than that of ceramics and polymers due to their crystal structure and porosity. Porosity is the interlinkedness of crystals or grains within a material. The more gaps, the more porous. Breathability in textiles has been made possible by a better understanding of this part of materials science.

CORE
SPREAD 3: Metal extraction 1 (reduction with carbon)

Reduction by coke (carbon), a more reactive metal, and electrolysis are means of obtaining some metals from their ores.

Metals are very important materials. There are 73 metallic elements and most are reactive enough to only be found in compounds in the Earth's crust. These compounds are often oxides and therefore a reduction reaction of some sort will be required to extract them. The position in the reactivity series will decide the method used.

Using your data book you can use the reactivity series in Table 25. Any metal below carbon can be extracted by reducing it using carbon (coke) or carbon dioxide.

The procedure for iron is below, but it would be similar for other metals.

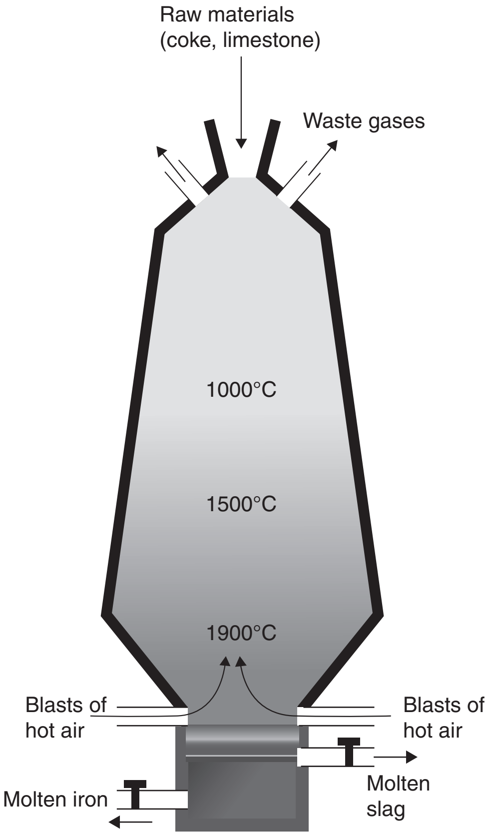
The main sources of iron are the ores below:

- **Hematite, Fe_2O_3**
- **Magnetite, Fe_3O_4**
- Goethite, FeOH.OH

- Limonite, $Fe_2O_3.H_2O$
- Scrap (recycled) iron
- Pyrites (Fool's gold)

It is not important to learn all of them. The top two should be known though.

Iron can be extracted from its ore in a blast furnace. The iron oxide is reduced by carbon (and its compounds) to form iron, as iron is below carbon in the reactivity series. Three raw materials are fed into the blast furnace. These are the iron ore, coke and limestone. Coke is a form of carbon which is made by heating coal in the absence of air. The limestone, $CaCO_3$, is used to remove impurities. Hot air is blown into the bottom of the furnace.



Firstly, the coke reacts with oxygen in the hot air blasts to form carbon monoxide (***Reaction 1***). The hydrocarbons such as methane will undergo incomplete combustion to form more carbon monoxide (***Reaction 2***). Carbon monoxide is the main reducing agent in the reduction of iron oxide.

There are an awful lot of reactions in the blast furnace. The IB syllabus is not specific in precisely which ones you need. We have included all relevant equations. Those in bold are the ones that are the most important and the ones you should ensure are memorized.

***Reaction 1*:** $\mathbf{2C_{(s)} + O_{2(g)} \rightarrow 2CO_{(g)}}$

The reducing gases reduce the iron oxides as shown in ***Reactions 2–5***. If the temperature is high enough, the coke itself can also act as a reducing agent as in ***Reaction 5***. The resulting liquid iron falls to the bottom of the tower where it is tapped off. At this point, it is called "pig iron" and contains 4–5% carbon.

***Reaction 2*:** $\mathbf{Fe_2O_{3(s)} + 3CO_{(g)} \rightarrow 2Fe_{(l)} + 3CO_{2(g)}}$

Reaction 3: $Fe_3O_{4(s)} + 4H_{2(g)} \rightarrow 3Fe_{(l)} + 4H_2O_{(g)}$

Reaction 4: $FeO_{(s)} + CO_{(g)} \rightarrow Fe_{(l)} + CO_{2(g)}$

***Reaction 5*:** $\mathbf{Fe_2O_{3(s)} + 3C_{(s)} \rightarrow 2Fe_{(l)} + 3CO_{(g)}}$

You probably do not need to learn ALL the reactions above. You are probably better served memorizing the most common one (Reaction 2) and being able to work out the other reduction reaction should you be given one. Similarly, be prepared to do this for any metal below carbon in the reactivity series.

Concurrently, the limestone decomposes to give calcium oxide and carbon dioxide (***Reaction 6***). The carbon dioxide can then react with more carbon to form carbon monoxide and any remaining coke reacts with water to form more CO and hydrogen (***Reactions 7*** and ***8***).

***Reaction 6*:** $\mathbf{CaCO_{3(s)} \Rightarrow CaO_{(s)} + CO_{2(g)}}$

***Reaction 7*:** $CO_{2(g)} + C_{(s)} \Rightarrow 2CO_{(g)}$

***Reaction 8*:** $H_2O_{(g)} + C_{(s)} \Rightarrow H_{2(g)} + CO_{(g)}$

The gases that emerge from the top of the furnace are recirculated and used to heat the air which is blasted into the bottom.

The calcium oxide formed from the decomposition of the limestone reacts with high melting point impurities such as silicon dioxide, forming a calcium silicate compound which is tapped off as "slag" (***Reaction 9***). The slag falls to the bottom of the tower and floats on top of the molten iron. From here, it is tapped off and has many uses, particularly in road-making and cement manufacture.

***Reaction 9*:** $\mathbf{CaO_{(s)} + SiO_{2(s)} \Rightarrow CaSiO_{3(l)}}$

CORE

SPREAD 4: Metal extraction: The production of aluminum by electrolysis

Aluminum is extracted from its ore using electrolysis, as it is too reactive a metal for the ore to undergo reduction using carbon. First the ore, bauxite, is purified to alumina (aluminum oxide).

Alumina has a very high melting point (2045°C) and so it is dissolved in cryolite, Na_3AlF_6, thus lowering the operating temperature of the electrolysis to about 950°C.

The electrolysis cell is made of steel-lined heat resistant brick and the cathode, made of carbon, lines the bottom of the cell. Anodes (again of carbon) dip into the cell (see diagram below).

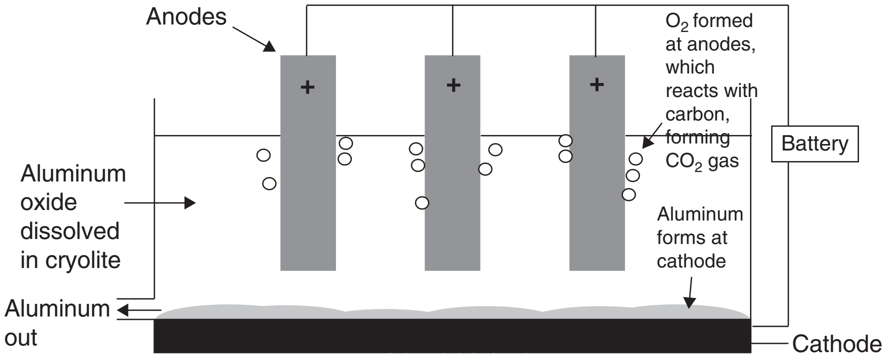
Aluminum ions travel to the cathode, where they are reduced, gaining electrons to form aluminum, which can be tapped off out of the bottom of the cell.

$Al^{3+}_{(l)} + 3e^- \rightarrow Al_{(l)}$

Oxide ions are attracted to the anode, where they lose electrons and are oxidized, forming oxygen gas. The oxygen reacts with the carbon anodes, producing carbon dioxide and so the anodes gradually wear away and need replacing frequently.

$2O^{2-}_{(l)} \rightarrow O_{2(g)} + 4e^-$

$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$



Aluminum, like all metals, has good electrical and heat conductivity and can be drawn into a wire. It is therefore used for household items such as cookware and also as a packaging material and food takeaway containers. Its more unique advantages are that it is also resistant to corrosion due to a thin oxide layer that naturally forms on it. It also has a low density. This means it can also be used for lightweight window frames and step ladders. Alloys of aluminum are favored for their use in airplane bodies. Aluminum is also used as the reflective surface in car headlights and for overhead power cables.

CORE
SPREAD 5: Stoichiometric problems using electrolysis

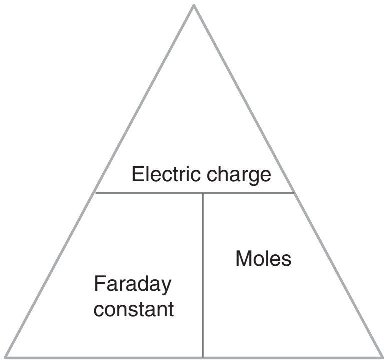
The relationship between charge and the number of moles of electrons is given by Faraday's constant, F.

Given that current is a flow of electrons it is possible to find out how much of a substance can be deposited using electrolysis.

We need the following information:

The current, in amps.
The amount of time the electrolysis will take place for in seconds.
Together this is known as electric charge and is measured in coulombs (*Q*).
You also need to know the quantity of electricity required to deposit one mole electrons. This is 96,500 *Q* and is known as the Faraday constant.
From this you can work out the number of moles of a substance deposited.

The relationship is:



Example 1:
Calculate the mass of silver deposited in an experiment where the current was 0.5 amps and the experiment was left for two hours.

Time 60 × 60 × 2= 7200 seconds

Current = 0.5 amps

7200 × 0.5 = 3600 coulombs

3600/96,500 = 0.0373 moles

Mass 0.0373 × 108 (RMM of silver) = 4.02 g.

Complications include: if the ion is not a 1+ ion, for example, Cu^{2+}. In this case, twice the amount of charge is required to discharge it, or in the example above, half the amount in moles would be deposited for the same charge and time.

Example 2:
Find out how long it would take to deposit one gram of iron when a current of 0.3 amps flows through a solution of iron (III) chloride

Method:

Since $Fe^{3+} + 3e^{-} \Rightarrow Fe_{(s)}$

Then three moles of electrons are required to deposit one mole of iron (55.8 g). To find how many moles of electrons for 1 g divide 3 by RMM,

3/55.8 = 0.0538 moles

Number of coulombs = 96,500 × 0.0538 = 5188 coulombs

Coulombs = current × seconds

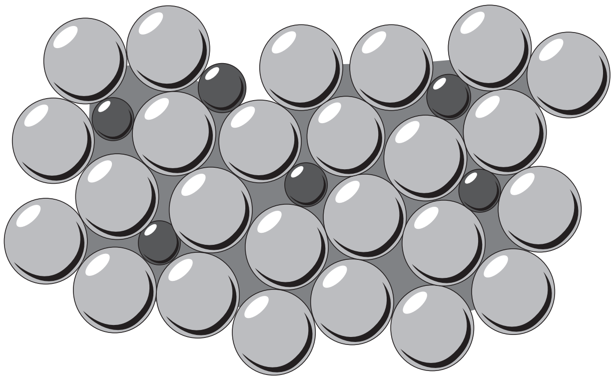
So seconds = coulombs/current 5188/.3 = 17,293 seconds = 4.8 hours.

The trick is to think in moles of electrons and balance your calculations in terms of those.

CORE
SPREAD 6: Alloys

Alloys are homogeneous mixtures of metals with other metals or nonmetals.

Alloys are mixtures of metals or metals and nonmetals that are created due to their specific properties. Although there are 73 metals on the periodic table, they don't necessarily satisfy all our needs for metallic materials. By combining the elements with other metallic elements (or carbon), we can create new metals that have different properties. Using iron as an example, it is far too soft to be used for any of the uses associated with steel. Adding carbon in various proportions can harden the steel and make it more useful. Other metals such as molybdenum can also be added to produce tougher steel for drill bits. Adding chromium and nickel to steel creates stainless steel, which doesn't corrode as quickly as regular steel.



Alloying works because by adding another type of atom to the metallic lattice it disrupts the regular array causing the metal ions to slide less easily over them. In this case this might make the metal stronger.

Heat treatment of steel results in a change in the structure of the individual crystals of steel, whilst retaining the overall shape of the metal.

Tempering involves heating the steel to 400–600°C before allowing it to slowly cool. This process makes the steel less brittle.

Annealing involves heating the steel to about 1040°C before allowing it to cool slowly. This makes the steel more ductile (able to be pulled into a wire).

Quenching usually follows a very high temperature treatment, but instead of allowing the steel to cool slowly, it is cooled extremely rapidly. This makes the steel very hard.

Other examples of alloys include bronze brass, solder (a table?), and so on.

CORE
SPREAD 7: Magnetism in metals

Diamagnetic and paramagnetic compounds differ in electron spin pairing and their behavior in magnetic fields.

Everybody knows that some metals are magnetic. But what causes magnetism?

Magnetic forces originate in the movement of electrons in atoms. As we have seen before, electrons can have a spin state and can have two possible spin states in each orbital. This "spin" is in reality a magnetic dipole moment, that is, it behaves like a tiny magnet. Electrons can also move within the orbital they have been assigned. Both of these movements can cause tiny electric currents to exist. If you have studied physics you will be aware that a current in an electrical coil can also generate a magnetic field.

Materials (mainly metals) can be classified into three different categories of magnetic behavior:

Diamagnetic
Paramagnetic
Ferromagnetic

Diamagnetism

Diamagnetism is essentially a property of all materials that contain only paired electrons. It is a very weak force, essentially unnoticeable; this is often because the paired electrons are held in very tight orbitals and hence they cannot respond easily to an applied magnetic field. Even though the force is very weak, if they do respond, they will be REPELLED by a magnetic field.

Paramagnetism

Paramagnetism is when materials respond to an applied magnetic field by being attracted to it. Paramagnetic metals have free, unpaired electrons, which allow them to create a magnetic moment associated with the free spinning electron. When looking at d block metals, it is important to look for unpaired electrons.

So, for example, Cr^{3+} is paramagnetic because it has three unpaired electrons, whereas Zn^{2+} is only diamagnetic because it has no unpaired electrons.

Any question requiring you to work out whether a metal is paramagnetic or not will require you to draw out the electrons orbitals to confirm whether the ion has unpaired electrons or not.

Ferromagnetism

Ferromagnetism is a special form of paramagnetism where there is a favorable alignment of the spins of the electrons. In reality this is only found in iron, cobalt and nickel, which are next to each other on the periodic table. Ferromagnetism can be felt and such materials are easily magnetized.

CORE
SPREAD 8: Inductively coupled plasma spectroscopy and optical emission spectroscopy

Trace amounts of metals can be identified and quantified by ionizing them with argon gas plasma in Inductively Coupled Plasma (ICP) Spectroscopy using Mass Spectroscopy ICP-MS and Optical Emission Spectroscopy ICP-OES.

What is the plasma state?

Plasma is sometimes known as the fourth state of matter. Essentially, plasma is the gaseous state where sufficient energy has been provided to free electrons from the substance causing them to exist in an ionized state. The electrons have been freed but haven't necessarily left the influence of the nucleus. So it is an electrically neutral medium of positive and negative particles. Plasma is believed to be the most common phase of matter in the universe, and is commonly encountered on earth in the form of lightning strikes and in neon lights, which should more correctly be called plasma lights. The sun is a big ball of plasma.

Inductively coupled plasma spectroscopy

This is a very sensitive analytical technique for separating trace amounts of metals in a sample. It is widely used in forensic analysis and toxicology.

Essentially, a flow of argon gas interacts with a spark and an induction coil supplied with a radio frequency electric current. These conditions produce an argon plasma state. This allows any vaporized sample containing trace metals to break down into atoms and become ionized.

Mass spectrometry and optical emission spectroscopy

On its own an ICP machine isn't much use. It can separate these trace amounts of metals but cannot necessarily detect them. There are two ways to do this, and they need to be added to the ICP machine.

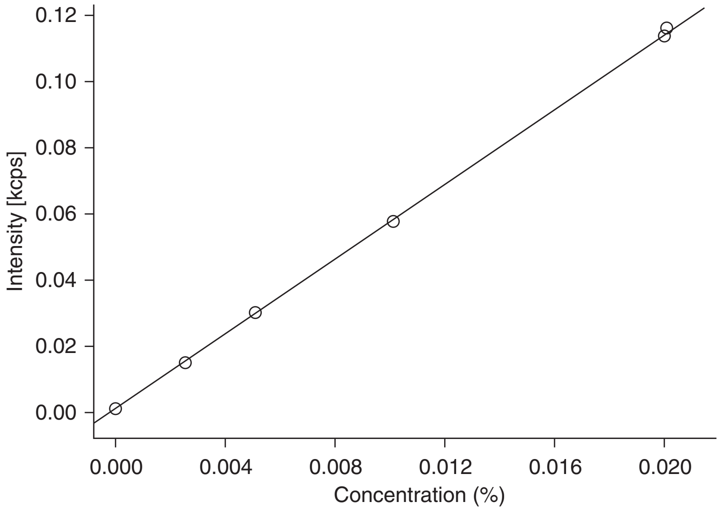
Qualitative: Mass spectrometry

As we have seen before, mass spectrometry is a device that can detect charged particles in a magnetic field and produce a reading of the mass of the particles in the sample. In this case, the ions produced from the trace metal can be fed into a MS and then be used to identify these charge particles in the usual way. See previous chapter.

Quantitative: Optical emission spectroscopy

This works in a slightly different way: the elements of the sample to be analyzed lose and gain electrons repeatedly in the plasma giving off radiation of characteristic wavelengths for the elements involved.

When dealing with a sample of tiny mass (as is often the case in forensic science), the sample would be too small to weigh accurately; therefore, the sample is diluted successively to make a series of solutions that can be used to make a calibration curve. This makes a sample that can be introduced to the ICP OES as a mist. This would then produce a curve like the one for cadmium below.



The intensity (*y*) axis units are kilocycles per second and are the same as kilohertz. It refers to the frequency of the emission.

You would be expected to work out the mass of an element from the graph given and other questions related to basic graph techniques. For example, a reading above 0.12 Kcps may not be as reliable as it lies outside the range of the experiments carried out.

The importance of calibration:

ICP is a comparative technique, which means that the sample is compared to a perfect example for comparison at similar concentrations.

CORE
SPREAD 9: Catalysts

Reactants adsorb onto heterogeneous catalysts at active sites and the products desorb.

Homogeneous catalysts chemically combine with the reactants to form a temporary activated complex or a reaction intermediate.

What is a catalyst?

Catalysts increase the rate of a chemical reaction by providing an alternative pathway for the reaction to follow, which has a lower activation energy.

There are two types of catalysts—*homogeneous* and *heterogeneous.*

Homogeneous catalysts are in the same state as the reactants and products of the reaction. Here, the two reactants behave in a normal chemical way, produce an intermediate (transitionary state) and then produce a product. An example from the course would include esterification reactions, where concentrated acid is the catalyst. The same catalyst is used in the hydration of alkenes to alcohols.

Heterogeneous catalysts are in a different phase (state) to the reactants and/or products. This process involves a change of the oxidation number of the central atom in the catalyst. Transition metal compounds, with variable oxidation states, make good catalysts. For example, vanadium (V) oxide is used as the catalyst in the contact process or iron in the Haber process. The reactant molecules *adsorb* (a fancy chemical word for "join") onto the catalyst surface and react from there.

The process is:

Reactant gases pass over the catalyst surface.
Adsorption takes place.
Temporary bonds form between the catalyst and the reactants allowing a reaction to occur.
Desorption takes place.

Homogeneous catalysts are often reaction specific, so you must make sure that you choose the right one. They are also difficult to remove from the products as they are in the same phase. However, they are very efficient, as the whole surface of the catalyst is exposed to the reactants.

Heterogeneous catalysts are very easily removed from the products, for example, by filtration. They are also broader in their usage, so you do not have to choose a specific catalyst. However, only one surface of the catalyst is used and so they are not very efficient.

In choosing a catalyst, the following considerations must be made:

- How selective must the catalyst be? Is there only one desired product and does the catalyst produce this?
- How efficient is it?
- Can it work under the temperature and pressure required for the reaction?
- Are there any environmental impacts?
- Does it poison easily? Some substances, such as sulfur, block the active sites in any catalysts, rendering them "poisoned" or unusable. Will it become unusable in this reaction?

CORE
SPREAD 10: Transition metal catalysts and zeolites

Transition metal catalytic properties depend on the adsorption/absorption properties of the metal and the variable oxidation states.

Zeolites act as selective catalysts because of their cage structure.

Catalytic particles are nearly always nanoparticles that have large surface areas per unit mass.

How do transition metal catalysts work?

As we have seen transition metals have a variety of oxidation states. This is one reason why they are good catalysts. They can change oxidation state and return back once the reaction is complete. The reaction between iron (II) and peroxydisulfate ions is a good example. Here the peroxydisulfate will oxidase iodide ions to iodine in the presence of iron (II):

$S_2O_8^{2-} + 2Fe^{2+} \Rightarrow 2SO_4^{2-} + 2Fe^{3+}$

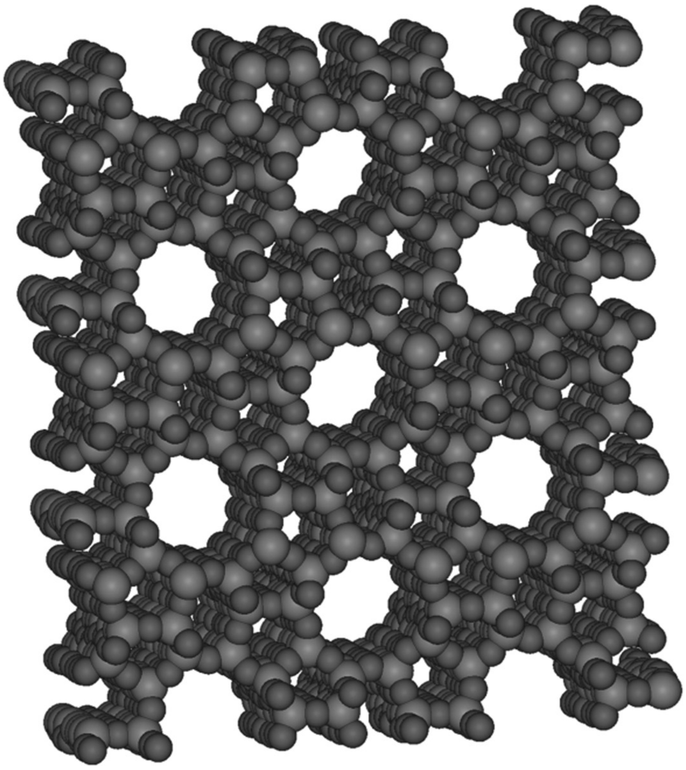
The iron (II) is oxidized, which generates the Fe (III) to oxidase the iodide:

$2I^- + 2Fe^{3+} \Rightarrow 2Fe^{2+} + I_2$

The second factor is that transition metals provide an excellent surface for adsorption to take place. The can physically adsorb large quantities of reactant gases as they pass over them.

Zeolites

Zeolites are a family of aluminosilicate compounds and will contain aluminum, silicon and oxygen, along with other elements. Typically, there must be at least one aluminum atom per silicon atom. The structure of these naturally occurring minerals is very porous and contains many cavities. They are also described as cage-like. This allows other cations and water molecules to occupy them and have considerable freedom movement. This cage structure allows a strong electrostatic field to occur within the cavities, which allows strong adsorptions to take place. This makes them very useful as catalysts. The hole size in the zeolite cage also allows the catalyst to be very selective.



A typical zeolite structure

Carbon nano catalysts

As we will see, nanotechnology involves particles on the nano scale. Most effective heterogeneous catalysts have nano particles, which give them an enormous surface area per unit mass, which allows them to have a high activity. Owing to degradation of the particles they should be used in mild conditions, which is good green chemistry.

Carbon nano tubes can be used instead of the more traditional zeolite support. They have larger surface areas and excellent electrical conductivity and are stable in oxygen. Although research is still in the early stages, there is some evidence that their use is throwing new light on many advanced technologies.

CORE
SPREAD 11: Liquid crystals

Liquid crystals are fluids that have physical properties (electrical, optical and elasticity) that are dependent on molecular orientation to some fixed axis in the material.

Thermotropic liquid-crystal materials are pure substances that show liquid-crystal behavior over a temperature range.

Lyotropic liquid crystals are solutions that show the liquid-crystal state over a (certain) range of concentrations.

Nematic liquid crystal phase is characterized by rod-shaped molecules which are randomly distributed but on average align in the same direction.

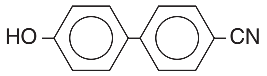
What are liquid crystals?

At first glance the phrase "liquid crystal" seems to not make sense. "Crystal" implies an ordered arrangement of a solid. "Liquid" implies particles of matter in a random arrangement. It's actually referring to certain rod-shaped molecules that, when taken to their theoretical melting point, can still arrange themselves in an ordered way because of their shape. The typical analogy is to imagine some pencils. When in a small box with little room to maneuver they are analogous to a solid. When they are in a large box they can arrange themselves in any direction (liquid). However, if the box is big enough to allow the pencils to move around but NOT face other directions, the pencils will retain some of the properties of the other two boxes (phases). This, simply, is the liquid crystal phase: its more technical term is *mesophase*.

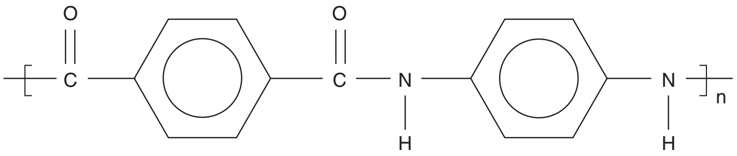
All very exciting but what do you need to be able to write? You need to define a "liquid crystal." The IB defines it thus, and you need to memories it: "Liquid crystals are fluids that have physical properties (electrical, optical and elasticity) that are dependent on molecular orientation relative to some fixed axis in the material."

An exam question might also ask you to list some examples of common substances displaying liquid crystal properties (AND IT IS IMPORTANT TO REMEMBER THAT THESE PROPERTIES WILL ONLY BE DISPLAYED UNDER CERTAIN CONDITIONS). The most common are:

Soap solutions (soaps and detergents are long molecules, a bit like tadpoles; the slimy residue in the soap dish is the soap in the liquid-crystal phase, more later).
Spider web solution (the "silk" molecule in spiders is called fibroin. It is a molecule that is wrapped up like a ball of wool. When dissolved in water they uncoil forming a liquid-crystal solution that is tremendously resilient.)
DNA
Graphite
Cellulose
Biphenyl nitriles (two benzene rings connected by nitrogens)



Kevlar®



Thermotropic and *lyotropic* liquid crystals

Thermotropic liquid-crystal materials are pure substances that show liquid-crystal behavior over a temperature range between the solid and the liquid states. The biphenyl nitriles are common examples and are most commonly used in "liquid crystal" displays on calculators.

Lyotropic liquid crystals are solutions that show the liquid-crystal state at certain concentrations. The most obvious example is soap and water. One end of a soap molecule loves water, the other "hates" it and is more attracted to the dirt. When the concentration is right the molecules arrange themselves so that all the water loving ends are all next to water molecules and vice versa. This allows the dirt to be surrounded by the other ends of the molecules (known as micelles).

How do liquid crystals work?

It is easiest to describe this in an exam in a "before and after way." This will show the examiner that you understand liquid-crystal behavior. So solids are arranged in the typical solid formation. Then, as the temperature increases, the molecules free from their neighbors and start to become disordered. Yet, because of their shape they point in the same direction. This is the liquid-crystal or nematic phase. Over certain temperatures this is lost and typical liquid phase properties occur. See the pencil analogy above if it helps.

The principles of the liquid crystal display device

Liquid crystal molecules will allow light of a certain orientation through if they too are facing in the correct direction. If they are not, then no light will pass. If you look at a simple LCD display on a calculator or wrist watch you will see that the numbers and letters are formed in black (the absence of light). The liquid crystal molecules used in such displays are polar and the direction they lie in can be changed by the application of a small electric field and can therefore be switched on and off depending on which button has been pressed. A more detailed explanation is given in the HL section of this book.

Liquid crystal displays require very little current and are therefore very useful in such devices as battery usage is much less. As discussed earlier, liquid crystals are affected by heat and, as you may have noticed, they can give strange displays when the temperature is changed.

Properties needed for a substance to be used in liquid crystal displays

A little thought after reading the above will help you see what a molecule to be used in a liquid crystal screen would need:

- They need to be polar to allow the molecules to be "switched" by current.
- They need to change orientation very quickly.
- Given the temperature changes around the world, the liquid-crystal phase needs to be stable under all normal human living conditions.
- In addition they need to be chemically stable over the reasonable working life of the device.

CORE
SPREAD 12: Polymers

Thermoplastics soften when heated and harden when cooled.

A thermosetting polymer is a prepolymer in a soft solid or viscous state that changes irreversibly into a hardened thermoset by curing.

High density polyethene (HDPE) has no branching allowing chains to be packed together.

Low density polyethene (LDPE) has some branching and is more flexible.

Plasticizers added to a polymer increase the flexibility by weakening the inter-molecular forces between the polymer chains.

Atom economy is a measure of efficiency applied in green chemistry.

Isotactic addition polymers have substituents on the same side.

Atactic addition polymers have the substituents randomly placed.

Classifying polymers

Essentially from a materials science perspective, we can classify polymers as either thermoplastics or thermosetting plastics.

Thermoplastics soften on heating and harden on cooling, so they are used to make moldable materials.

In thermoplastics this process can be repeated many times; the plastic can be remolded into new shapes as many times as you like.

Thermosetting plastics are soft on initial manufacture and can be molded but once cooled and hardened the plastic retains its shape permanently and cannot be reshaped. This is because polymers consisting of long chains form permanent new covalent bonds between the chains, like rungs in a ladder.

Elastomers are flexible and can be deformed under force but will return to nearly their original shape once the stress is released.

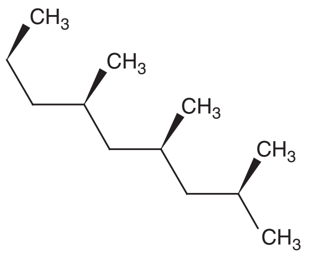
Different types of polymer

In the main course addition, polymerization is assumed to be a simple process of producing simple long chain molecules. In fact, the chains produced by the polymerization process can be branched, due to the mechanism used. Such branching will give the polymer specific properties.

In polyethene, for example, the production of a long chain with very little branching allows the chains to fit together very closely. This has the effect of making the polymer strong, dense and stiff. Such polyethene is known as high density polyethene (HDPE).

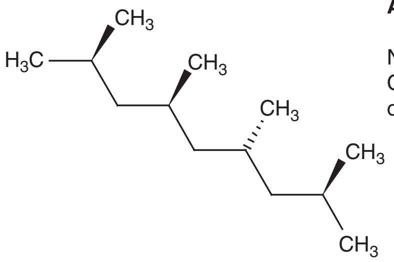
Low density polyethene (LDPE) has more branching, which prevents the chains from getting close together. This makes it less strong and less dense than HDPE. It has the advantage of making the polymer flexible and is often used in food packaging.

Polypropene is another addition polymer. Its formula gives it a CH_3 group every other carbon (see diagram). If these methyl groups are all lined up the same way, the polymer becomes tough and crystalline. It is known as isotactic. If the methyl groups are arranged in a random manner, it is known as atactic. This makes the polymer much more flexible.



Isotactic polypropene chain

Note all CH_3 groups are facing in the same direction.



Atactic polypropene chain

Note that the occasional CH_3 groups are facing in opposite directions.

Modifying the properties of addition polymers

Plasticizers make the plastic more flexible. These are small molecules that work by inserting themselves between the polymer chains, weakening the attraction between them. Plasticizers are often added to polyvinylchloride (PVC)—this can be done in varying amounts and means the rigidity or flexibility of the polymer can be altered to suit its use.

Volatile hydrocarbons can be used to change the structure of a plastic. For example, pentane, a volatile hydrocarbon, is added to styrene during the formation of polystyrene. At high temperatures the pentane vaporizes, causing expanded polystyrene to be produced. Expanded polystyrene is used in lots of packaging and is a good thermal insulator (coffee cups).

Atom economy

Atom economy is a measure of efficiency in green chemistry.

It is in the data book and defined as:

$$\%\ \text{Atom economy} = \frac{\text{Molar mass of desired product}}{\text{Molar mass of all reactants}} \times 100$$

A green chemistry goal is to focus on reactions with near 100% atom economy. This means reactions that only produce one product, the desired one. Addition reactions in organic chemistry are good examples of 100% atom economy reactions and are keenly sought after in green circles. As addition polymerization gives 100% atom economy they are considered desirable in such terms, especially if the monomer can be sourced from something other than crude oil.

The advantages and disadvantages of polymer use.

Advantages: Polymers can do almost anything these days. As discussed above, they can be strong, flexible and inert, all good things.

Disadvantages: At the moment the only realistic way of manufacturing polymers is by using crude oil as a raw material. As this is a fossil fuel our supplies are dwindling. Although polymer inertness is a good thing in some applications it can also cause disposal problems. Landfill is increasing and most polymers are nonbiodegradable. Some can be recycled but others cannot. Polymers cannot be burned either as the products of incineration can be very poisonous compounds.

CORE
SPREAD 13: Nanotechnology

Molecular self-assembly is the bottom-up assembly of nanoparticles and can occur by selectively attaching molecules to specific surfaces. Self-assembly can also occur spontaneously in solution.

Possible methods of producing nanotubes are arc discharge, chemical vapor deposition (CVD) and high pressure carbon monoxide (HIPCO).

Arc discharge involves either vaporizing the surface of one of the carbon electrodes or discharging an arc through metal electrodes submersed in a hydrocarbon solvent, which forms a small rod-shaped deposit on the anode.

What is nanotechnology?

Nanotechnology is “the research and technology development at the 1 nm to 100 nm range,” so learning their definition is probably a good place to start. It is used to create structures that have novel properties due to their small size and relies and builds upon the ability to manipulate atoms (see below).

Carbon nanotubes are made from carbon atoms which are covalently bonded to each other in hexagons, like in graphite, which join together to form cylinders. Single- or multi-walled tubes can be formed. Bundles of these tubes have very high tensile strength, much more than graphite, which is soft and malleable in comparison. Some nanotubes can conduct electricity and some have been found to be semi-conductors. This behavior depends on the length of the tube. The reason nanotubes conduct electricity is for the same reason graphite conducts electricity: each carbon has one free delocalized electron to carry electric charge.

Molecular self-assembly

This is the bottom-up assembly of nanoparticles and can occur by selectively attaching molecules to specific surfaces. Self-assembly can also occur spontaneously in solution.

Physical techniques used in nanotechnology include atomic force microscopy and dip pen nanolithography. These techniques allow atoms to be picked up, one by one, on a very thin, sharp tip, and deposited in specific places, as required.

Arc discharge

Arc discharge is another technique. Here a direct current arc voltage is applied across two carbon electrodes immersed in an inert gas or a hydrocarbon solvent. This vaporizes the surfaces of the electrodes. If the rods are pure graphite then fullerenes are deposited as soot and carbon nanotubes form on the cathode. They can also form on the anode if doped with a metal catalyst. This allows the vaporized carbon to be reduced to carbide particles (C2), which allows rod-like carbon tubes to form.

Chemical vapor deposition

Here metal catalysts (Nickel, cobalt) are heated to a high temperature. Then a process gas (like ammonia, or nitrogen or hydrogen) and a carbon-containing gas like ethane are passed over the catalyst. Essentially it's a bit like cracking. Carbon nanotubes grow on sites on the catalyst surface. Oxygen cannot be used because the carbon would react with the oxygen forming CO_2.

High pressure carbon monoxide

Here a continuous flow of carbon monoxide at high pressure and temperature with an $Fe(CO)_5$ iron pentacarbonyl catalyst:

$Fe(CO)_5 \Rightarrow Fe + 5CO$

The iron produced here produces a nice surface for nanotubes to grow:

$x\text{CO (iron cat)} \Rightarrow \text{Carbon nanotubes} + x/2CO_2$

In contrast, chemical techniques such as in DNA nanotechnology involve using chemical reactions to position atoms in particular places. In this particular example, the base pair hydrogen bonds are exploited and used to create new molecules.

Nanotechnology is a good thing, although it has to be understood properly. When Prince Charles mentioned that nanotechnology was all about "grey goo" in one of his speeches, he created widespread hysteria. It is vital that the public are properly educated about nanotechnology so as not to be unnecessarily scared of it and its beneficial applications.

Nanotechnology may be used in the future to solve food shortages, to prevent, cure and monitor diseases and to improve communication technology. There are, however, potential problems. Worries include the unknown problems of having nanoparticles in the air and the effects of these particles on humans and animal life. Toxicity regulations are nonexistent at present and would have to be calculated. Also, if nanotechnology does really take off, the divide between countries will increase and focus on those that have the money and power to conduct such research. Michael Crichton's hysterical (in all senses) novel "Swarm" is probably not a good place to start.

CORE
SPREAD 14: Environmental impact—plastics

Plastics do not degrade easily because of their strong covalent bonds.

Plastics require more processing to be recycled than other materials.

Plastics are recycled based on different resin types.

Plastics are of tremendous importance to us as material for the twenty-first century. Unfortunately, due to the strong covalent bonds in the carbon chains traditional polymers do not degrade easily when put in land fill and will remain in the same form almost indefinitely. If you add in the use of crude oil used to manufacture many plastics and other factors based on the carbon footprint and it is clear plastics are bad news for the environment. Plastics need a lot more processing than other materials in order to be used again.

With land fill space at a premium, other methods of dealing with plastics need to be found. They are summarized below:

- Recycling: plastics are collected and sorted into their different types, chopped up into small pieces, melted and remolded into new materials. Apart from the labor intensity of the sorting process, this is a very good way to deal with plastic waste. It only works for thermoplastics. Thermosetting plastics cannot be reused.

- Incineration: plastics can be burned to release energy in the same way that any hydrocarbon can be burned. The problems occur if the polymer in question being burned contains other elements other than hydrogen and carbon. PVC contains chlorine and if it is burned it produces incomplete combustion products (CO, C, etc.) as well as HCl and dioxins.
- Cracking—polymers can also be cracked back to original monomers, in the same way as discussed in earlier chapters. This process is expensive and unviable at the moment.

All the processes above are highly energy intensive.

Resin identification codes

You are probably familiar with the resin identification codes below seen on plastic bottles.

Pet = polyethene terephthalate

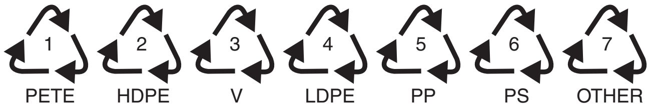
HDPE = high density polyethene

V = PVC

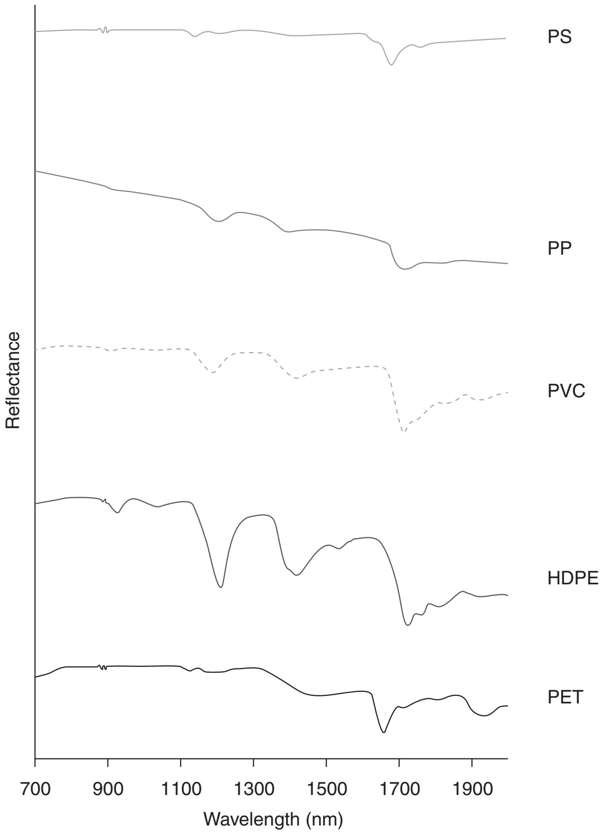
LDPE = low density polyethene

PP = polypropene

PS = polystyrene



There are other methods of identifying plastics. They also reflect infrared radiation and provided the plastic is transparent they can be easily identified. See the plot below to see how easily they can be separated.



World Academy of Science, Engineering and Technology, Vol. 6, May 22, 2012.

CORE
SPREAD 15: Dioxins and plasticizers

Burning of polyvinyl chloride releases dioxins, HCl gas and incomplete hydrocarbon combustion products.

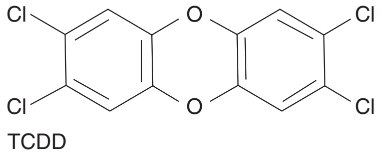
Dioxins contain unsaturated six-member heterocyclic rings with two oxygen atoms, usually in positions 1 and 4.

Chlorinated dioxins are hormone disrupting, leading to cellular and genetic damage.

Dioxins

Dioxins are the by-product of burning chlorinated plastics like PVC.

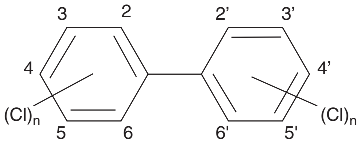
As you can see from the general formula below (in your data book), they contain oxygen in the 1.4 position



TCDD

They are very persistent in the environment and highly toxic. They are hormone disrupting and can cause cellular and genetic damage. They do not decompose and can be passed on through the food chain.

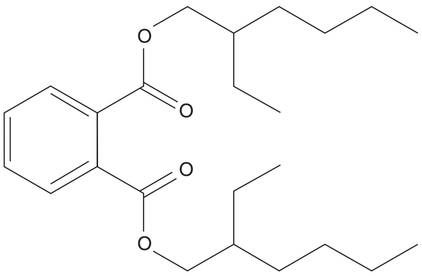
Polychlorinated biphenyls are similar molecules but without the oxygen atoms at one and four. They are very good chemical resistors and were used in electrical equipment like transformers and capacitors. They are similarly long lasting in the environment to dioxins and similarly toxic. Their use is now banned in many countries.



House fires were often a big provider of toxins such as dioxins into the environment. Plastics in soft furnishings, shower curtains and cabling often produced such waste products. Low halogen cabling is often used in homes now to prevent such damage.

Plasticizers

Plasticizers were discussed earlier; they make plastics more flexible. Phthalate esters are the most common plasticizers. Bis (2-ethylhexyl) phthalate (below) is a common example of a plasticizer. They are often used to soften PVC and were used in toys and other products because they were not chemically bound to the PVC they can leech out. There are health issues surrounding their use. They are said to affect the endocrine system (hormone) and can have an effect on children's behavior, although the effects are not proven. They are also a possible carcinogen. Many are now banned.



HL
SPREAD 16: Superconducting metals

Superconductors are materials that offer no resistance to electric currents below a critical temperature.

The Meissner effect is the ability of a superconductor to create a mirror image magnetic field of an external field, thus expelling it.

Resistance in metallic conductors is caused by collisions between electrons and positive ions of the lattice.

The Bardeen–Cooper–Schrieffer (BCS) theory explains that below the critical temperature, electrons in superconductors form Cooper pairs, which move freely through the superconductor.

Type 1 superconductors have sharp transitions to superconductivity whereas Type 2 superconductors have more gradual transitions

What is superconductivity?

In electrical conduction the resistance is the major factor in energy loss. It is a fundamental part of physics. However, superconductors have exactly zero resistance at certain critical temperature. Electrical resistivity decreases with temperature, but even at near absolute zero good conductors still show some resistance. Superconductors, however, when they reach their critical temperature, the resistance drops completely to zero. At the moment, these temperatures are still very low, way below zero.

What is resistance?

In a normal metal the electrons are packed together moving freely (as we saw in Chapter 4). But there are many of them and they will bump into each other and into the positive ion, like people in a busy railway station. Heat increases the movement and so increases the chances of collisions, so resistance increases. This is why, in general, resistance is lower at lower temperatures.

So what happens in superconductors?

At the critical temperature all resistance disappears. So what happens? At this temperature an electron moving through the lattice of the metal cations will attract the metal cations. This deforms the lattice a little and causes an electron with opposite spin to move into this region. The electrons pair up. (They are called Cooper pairs.) These pairs condense together and can resist the "bumps" from the oscillating atoms and can pass through the lattice with no resistance. This is known as the Bardeen–Cooper–Schrieffer (BCS) theory.

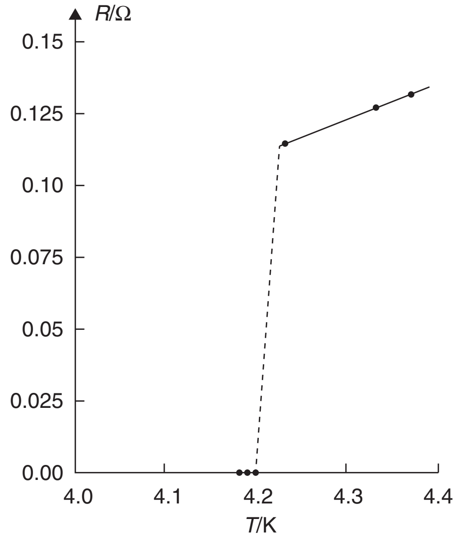
How can we classify superconductors?

In this course we will classify them thus:

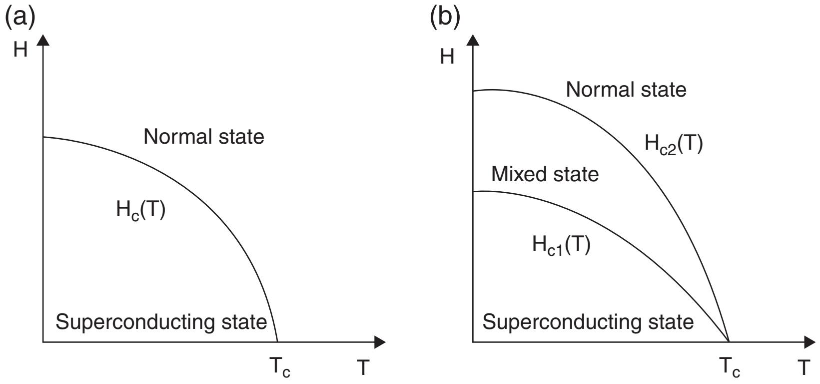
Type 1 Superconductors: these are usually pure metals, and at the critical temperature they have no resistance and are diamagnetic. Their resistance changes abruptly at the critical temperature.

Type 2 Superconductors: they are usually alloys and their resistance changes gradually until it reaches zero resistance. You might be expected to analyze graphs to identify a type 1 or a type 2.

Type 1



In type two there is a gradual push to a mixed state before reaching the full super conducting state. This makes them more useful for modern applications.



The Meissner effect is seen when superconductors reach their critical temperatures. At normal temperatures superconductors allow magnetic fields to go through them, but as they approach their critical temperature the electrons in the material set up eddy currents that create a mirror image magnetic field of an external field. It is observed that the superconductor seems to expel the same magnetic field that was applied to it. The effect was first observed by Walther Meissner in 1932 when he cooled some time to 3.72 K and found the Earth's magnetic field was expelled from the sample at the critical temperature.

HL
SPREAD 17: X-ray crystallography

X-ray diffraction can be used to analyze structures of metallic and ionic compounds.

Crystal lattices contain simple repeating unit cells.

Atoms on faces and edges of unit cells are shared.

The number of nearest neighbors of an atom/ion is its coordination number.

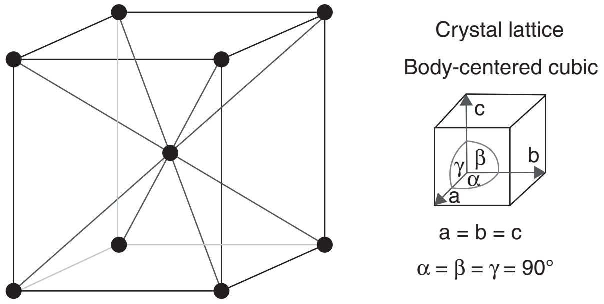
As discussed before, X-ray diffraction can be used to analyze structures of metallic and ionic compounds. It produces a pattern that can give an accurate idea of the positioning of the atoms in the crystal.

This crystal structure is traditionally represented in terms of a unit cell. This is a three-dimensional cube showing the atoms within the cube. This cell repeats itself through the whole crystal. Atoms on faces and edges of unit cells are shared with the next cell.

The study of such structures could be an entire course as the ability of atoms to pack can be dependent on many things and produces huge variety.

Type 1—Body Centered Cubic (BCC)

BCC has one atom in each corner of the unit cell and one in the center.

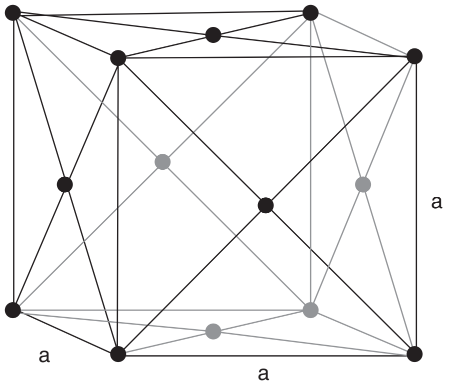


The coordination number is the number of atoms each atom is joined to. Here the number is eight.

The number of atoms to which the unit cell is equivalent is two. The center atom is unique to the cell; the outside atoms each share eight other cells. This means 8/8ths = 1.

1+1 = 2

Face centered cubic (FCC) is the other type to be studied.



Here there are atoms in each corner and in the middle of each face, but not one in the middle.

The unit cell contains the equivalent of four atoms this time. The 8/8th pattern round the edge plus ½ from each of the centers = 3.

The coordination number is 12.

Bragg's law

This is the mathematics behind the scattering that occurs during X-ray diffraction in a lattice. The equation is below:

$$n\lambda = 2d\sin\theta$$

Where:

n = integer
λ = wavelength of incident wave
d = spacing of the planes in the lattice
θ = angle between the ray and the planes

Working out the density of a pure metal

The calculation is possible if you know the crystal packing structure and the atomic radius of the metal in question.

$$\text{Density} = \frac{\text{Number of atoms} \times \text{RAM}}{\text{Volume of the cell} \times \text{Avogadro's number}}$$

The volume is essentially the cube of the length of the cell.

Example

Chromium is a BCC structure and the length of the cell is 2.956×10^{-8} meters (29 nano meters). What is the density?

Top of equation:

RAM chromium = 52

Number of atoms in BCC = 2

So 52 × 2 = 104

Bottom of the equation:

Volume is the cube of $(2.956 \times 10^{-8})^3 = 2.583 \times 10^{-23}$

Avogadro = 6.02×10^{23}.
$6.02 \times 10^{23} \times 2.583 \times 10^{-23} = 15.54$

So density = 104/15.54 = 6.692 g/m^3

Watch out for the units required in questions like this and remember the atom number is different for FCC.

HL
SPREAD 18: Condensation polymers

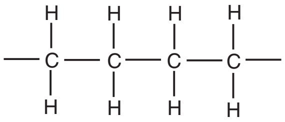
Condensation polymers require two functional groups on each monomer.

NH_3, HCl and H_2O are possible products of condensation reactions.

Kevlar® is a polyamide with a strong and ordered structure. The hydrogen bonds between O and N can be broken with the use of concentrated sulfuric acid.

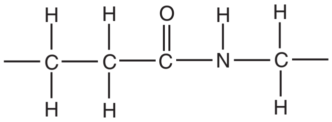
Monomers with a carbon–carbon double bond form addition polymers, such as polyethene. The polymer chain is made of carbon only. Condensation polymers are formed when two reactive functional groups on neighboring monomers react together eliminating a small molecule like water or HCl. The polymer chain will include noncarbon atoms like nitrogen and oxygen.

Polyamides and polyesters are examples of condensation polymers (see the core course Organic Chemistry section for more).



Addition polymer.

Note only carbons in the chain.



Condensation polymer.

Note the nitrogen in the chain.

Condensation polymers are formed when monomers, each with two functional groups, come together and react, with the elimination of a small molecule which is usually water or hydrogen chloride.

Phenol–methanal plastics

When an acid or an alkali is added to phenol and methanal, a phenol–methanal plastic is formed. Firstly, the methanal takes the place of a hydrogen in the 2 or 4 position on the phenol ring. Then, this undergoes a condensation reaction with another phenol molecule. This process then continues until a long chain has built up. The chains form cross links between each other so that the structure is maintained.

Polyurethanes

Polyurethanes are formed when diols or triols react with compounds containing one or more isocyanate group. A peptide link is formed. No actual condensation takes place (there is no elimination of a small molecule).

Polyethylene terephthalate (PET)

PET is a polyester, formed when benzene-1,4-dicarboxylic acid is reacted with ethane-1,2-diol in a typical condensation reaction where a molecule of water is lost. This results in an ester linkage.

Properties of condensation polymers

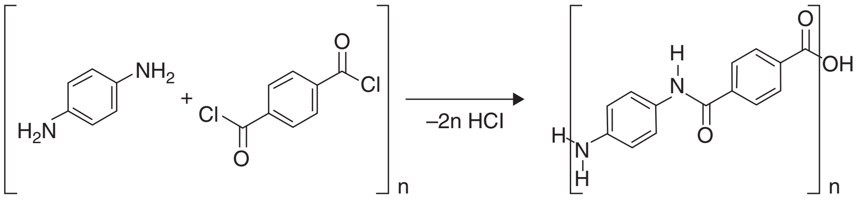
The properties of polymers depend largely on their structure. Polymers that can form cross-links between chains tend to be stronger, more insoluble and unreactive than those that cannot.

Phenol–methanal plastics are extremely strong due to the covalent cross-linking between the polymer chains, which forms a rigid three-dimensional structure.

Another example of cross-linking is Kevlar. Kevlar is used to make bullet-proof vests and motorcycle helmets. It is strong because the polyamide chains are able to form hydrogen bonds between each other, keeping the structure tight and solid.

Kevlar®

Kevlar is formed from the condensation reaction between the two monomers below, eliminating HCl. The polymer chain is strong and ordered. Its strength to weight ratio makes it useful in body armor and tyres.



Its strength comes from the ability it has to form hydrogen bonds between chains rather than the usual van der Waals forces. Concentrated sulfuric acid can break down these hydrogen bonds and cause it to dissolve.

HL
SPREAD 19: Environmental impact—heavy metals

Toxic doses of transition metals can disturb the normal oxidation/reduction balance in cells through various mechanisms.

Some methods of removing heavy metals are precipitation, adsorption and chelation.

Polydentate ligands form more stable complexes than similar monodentate ligands due to the chelate effect, which can be explained by considering entropy changes.

The toxicity of heavy metals

Heavy metals such as lead and cadmium are known to have a toxic effect on life forms. They can disturb the normal redox processes in cells producing dangerous free radicals.

The Haber-Weiss reaction is a typical reaction in a cell:

$Fe^{2+} + H_2O_2 \Rightarrow Fe^{3+} + OH\cdot + OH\cdot$

The Fenton reaction is another possibility that can follow ion from this:

$Fe^{3+} + H_2O_2 \Rightarrow Fe^{2+} + HOO\cdot + H^+$

Note, the different radicals produced and the different catalysts used.

This reaction, as you can see, is catalyzed by iron and produces free radicals in cells. Other heavy metals can also catalyze this reaction causing excessive free radical production causing severe cell damage.

Removing heavy metals from water

There are three ways:

Precipitation

Most heavy metal hydroxides are all insoluble. Therefore, adding hydroxide ions to the contaminated water will precipitate out the metal ions, which can then be filtered. An example using nickel:

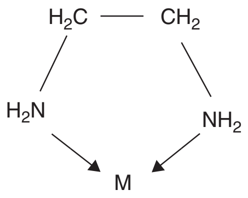
$Ni^{2+}_{(aq)} + 2OH^{-}_{(aq)} \Rightarrow Ni(OH)_{2(s)}$

Adsorption

We've seen before that adsorption is a process where atoms in the gas or aqueous phase bind to a suitable surface with temporary bonds. A high surface area is advisable for the adsorbent. Heavy metals in solution are easily removed this way. The adsorbents can be zeolite, or even some forms of clay, or a variety of agricultural waste products like maze husk.

Chelation

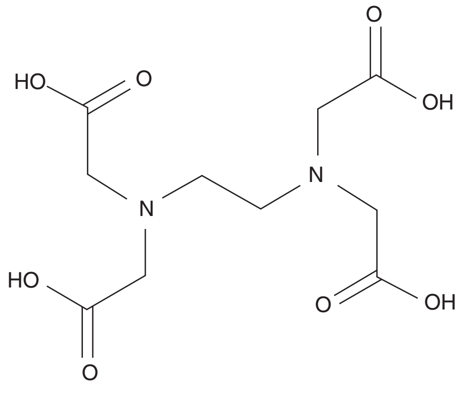
Chelation is a fancy word for complex ion formation. Chelation applies to ligands that bond in more than one place around the metal ion.



En, formula $NH_2CH_2C_2NH_{2,}$ has two lone pairs and can form two coordinate bonds with a metal. This will form a bidentate ligand (bi meaning two).

As we have seen in the periodicity section, metal cations can form complex ion with ligands, species with negative charges or lone pairs. In this case, heavy metal ions can form stable, chemically inert chelates which can be easily removed, whether from a source of water or from an organism which has been subject to poisoning.

For example, lead can be removed by using the ligand EDTA (below):



As the molecule has six lone pairs, four oxygens (in OH groups) and the two N atoms, it can bond to the metal ion in all six places in the octahedral shape. Such a ligand is known as a hexadentate ligand.

EDTA can dissolve deposits of metal ions very well:

$Pb^{2+}(H_2O)_6 + EDTA \Rightarrow Pb(EDTA)^{2+} + 6H_2O$

The chelate effect

This describes the enhanced ability of chelating ligands (ligands bonding in more than one place) for metal ions. This can be explained by considering the entropy of the reaction.

For example,

$Cu(H_2O)_6^{2+} + en \Rightarrow [Cu(H_2O)_4(en)_2]^{2+} + 2H_2O$

This reaction produces an increase in disorder because there are more species on the right hand side than on the left.

With EDTA the entropy change will be much more significant. Look at the equation above for yourself.

HL
SPREAD 20: Solubility product and removal methods with heavy metals

The solubility product is the equilibrium expression used for substances that are not particularly soluble.

For example, barium sulfate is not particularly soluble in water. When you add some to water this equilibrium is formed:

$BaSO_{4(s)} \leftrightarrows Ba^{2+}_{(aq)} + SO_4{}^{2-}{}_{(aq)}$

The equilibrium lies to the left and the K_c expression would be:

$K_c = [Ba^{2+}][SO_4{}^{2-}]$.

The solid is not written as only solutions can appear in a K_c expression.

This is known as the solubility product and is written Ksp:

$K_{sp} = [Ba^{2+}][SO_4{}^{2-}]$

Knowledge of solubility products can help us work out the efficiency of a removal method.

Example:
Water contaminated with lead ions was treated with carbonate ions to form a precipitate of lead carbonate $PbCO_3$. Work out how much lead was left in the water:

$K_{sp}\ PbCO_3 = 7.40 \times 10^{-14}$

Step 1
Write the K_{sp} expression, watch out for the multiples of the anions:

$K_{sp} = [Pb^{2+}{}_{(aq)}][CO_3{}^{2-}{}_{(aq)}]$

In this example, $[Pb^{2+}] = [CO_3{}^{2-}]$ according to the formula:

So $Ksp = [Pb^{2+}]^2$
Or $7.40 \times 10^{-14} = [Pb^{2+}]^2$

Therefore, $[Pb^{2+}] = \sqrt{7.4 \times 10^{-14}} = 2.72 \times 10^{-7}$.

Multiplying this by the RMM of lead 207.19 gives us 5.636×10^{-5} g of lead left in the water. This assumes the water is at 298 K, which is quite a large assumption to make.

You might be expected to work out the remaining ion content of any substance given in the solubility product table in your data book.

CHAPTER

14 Option B: Biochemistry

This covers the material in Option B: Biochemistry.

CORE
SPREAD 1: Introduction to biochemistry

The diverse functions of biological molecules depend on their structures and shapes.

Metabolic reactions take place in highly controlled aqueous environments.

Reactions of breakdown are called catabolism, and reactions of synthesis are called anabolism.

Biopolymers form by condensation reactions and are broken down by hydrolysis reactions.

Photosynthesis is the synthesis of energy-rich molecules from carbon dioxide and water using light energy.

Respiration is a complex set of metabolic processes providing energy for cells.

What is biochemistry?

It's the branch of science concerned with the chemical and physico-chemical processes and substances that occur within living organisms, in other words, the chemistry of the body.

This mainly involves organic reactions, but there are inorganic aspects to some reactions. Given that molecules involved in biological function are inevitably organic and organic molecules have functional groups at specific locations on the chain, it is no surprise that a lot of the functions of these biological molecules depend on their structure and their shape. The intermolecular forces, in particular hydrogen bonds, are also of great importance.

The other significant factor to understand is that the solvent in which the reactions are carried out is also crucial. It's water of course, water that is under a very tight set of conditions. Water is a solvent, a reagent, a coolant, a temperature control and a transport medium.

A few significant terms:

Metabolism—these are the name given to the set of chemical reactions that happen in cells that are crucial for sustaining reactions. They are also known as metabolic reactions.

These metabolic reactions can be further broken down into:

Catabolism: reactions where organic matter is broken down to use for in respiration and other energy-based needs.

Anabolism: reactions where new molecules are made from the energy provided by catabolic reactions, such as proteins or nucleic acids.

Biopolymers—these are, as the name suggests, polymers found in organisms: there are three sorts—polysaccharides, poly peptides (proteins) and polynucleotides (DNA, RNA). As with all condensation polymers they can be broken down by hydrolysis reactions (reaction with water) and can be created by the elimination of a small molecule from between the polymers: more later.

Photosynthesis—the synthesis of energy-rich molecules (like sugars) from carbon dioxide and water using light energy.

$6CO_2 + 6H_2O \Rightarrow C_6H_{12}O_6$ (glucose) $+ O_2$

Respiration—a complex set of metabolic process that provides energy for cells.

$C_6H_{12}O_6 + O_2 \Rightarrow 6CO_2 + 6H_2O$

Note how the equations balance themselves out; the CO_2 and the oxygen are regenerated by use of both processes.

CORE
SPREAD 2: Amino acids

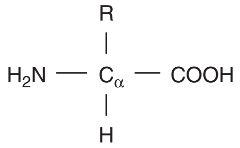
Proteins are polymers of 2-amino acids, joined by amide links (also known as peptide bonds).

Amino acids are amphoteric and can exist as zwitterions, cations and anions.

What are amino acids?

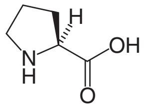
They are a crucial building block for the biopolymers known as proteins. Proteins have a special sub-section called enzymes, which are biological catalysts. To understand proteins and enzymes you need to understand amino acids first.

Amino acids are not just acids. They contain both carboxylic acid functional group as well as the amine functional group. So one end of the molecule can act as an acid, and one end can act as a base. There are only 20 amino acids known in nature, and they all have the same general formula (below).



$$\mathrm{H_2N - \overset{\displaystyle R}{\underset{\displaystyle H}{C_\alpha}} - COOH}$$

The structure is tetrahedral, and the R group is the part that makes each amino acid different. All amino acids except one (proline, a cyclic amino acid below) have this structure.



Amino acids, as stated, have an acidic end and a basic end. This means they are amphoteric (they can react with either an acid or a base depending on the conditions). Amino acids are usually soluble in water because of their ability to form hydrogen bonds and have comparatively high melting points for the same reason.

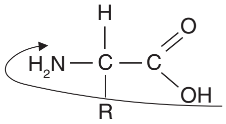
In acid the amine group reacts accepting the proton:

(Amino acid) + HCl ⇒ $NH_3^+CHRCOOH + Cl^-$ (cation)

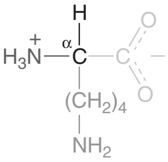
In basic conditions the proton is donated from the carbocyclic acid group:

(Amino acid) + NaOH ⇒ Na^+ amino acid salt + H_2O (anion)

Perhaps more important is that the amino acid can react with itself, donating a proton to itself.



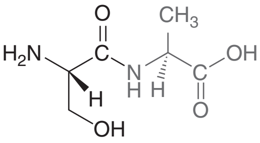
The compound formed is a zwitterion. For each amino acid there is a unique pH where it will exist in the zwitterion state. This often depends on the nature of the R group.



Zwitterions have very high melting points compared to their amino acids. This is because the molecule has a positive and negative end and can form extremely strong attractions to neighboring molecules. Effectively they are ionic bonds.

Amino acids as building blocks

You may also have noticed that amino acids are perfectly set up to work as reagents in condensation reactions.

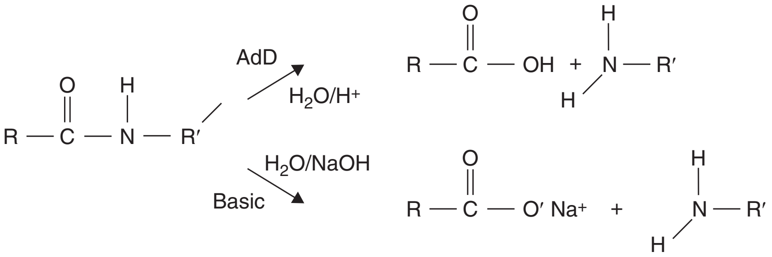


Note the amide link (known as a peptide link in biochemistry). The molecule above is a dipeptide.

Proteins are polymers of amino acids known as polypeptides. The combination of all the possible amino acids in any number of different combinations gives an infinite amount of different protein types to exist.

The side groups play a crucial part in the final structure of the resulting protein. Depending on their nature and polarity it can affect the properties of the protein including how it folds (more later).

Peptides can also be hydrolyzed to break up into their constituent amino acids. This can be done using either acid or basic conditions.



CORE
SPREAD 3: Proteins

Protein structures are diverse and are described at the primary, secondary, tertiary and quaternary levels.

A protein's three-dimensional shape determines its role in structural components or in metabolic processes.

What do proteins do?

Proteins are the cell's "worker" molecules. There are many thousands of different proteins in a body. Some are used as building blocks: hair and nails contain the protein keratin, while muscles contain actin and myosin. Other kinds of proteins carry oxygen around the body, fight infections and detect the light entering your eyes. A vital group of proteins—enzymes—controls the rate of the chemical reactions in your body that make all the other molecules you need.

As we have seen outlined simply on the previous page proteins are condensation polymers made from combinations of amino acids. The combination of the available amino acid building blocks and their particular shape gives rise to the unique structure of each protein. Crucially the way the amino acids combine and their side chain can make a huge difference to the SHAPE of the protein, and shape plays a big part in the functionality.

Protein shapes can be subdivided into four sub-sections: primary, secondary, tertiary and quaternary.

Primary structure

The primary structure is the simple sequence of amino acids along the chain,

gly—ala-leu-gly-gly

The shorthand used here are the three-letter shorthand for amino acids.

The primary structure is crucial in determining the next levels of protein structure.

Secondary structure

The secondary structure is related to the hydrogen bonding that is possible between the protein chains, and this can give rise to folds where the intermolecular forces are. This usually gives rise to either helix-like structures (Alpha helix) or sheet-like (beta pleated) structures.

Tertiary structure

The tertiary structure is crucial to protein function. This is another layer of folding but brought about by the nature of the R-groups and their position. The R-groups form further non-covalent bonds to other parts of the protein. These can be:

- instantaneous dipole-induced dipole) forces between non-polar side-chains,
- hydrogen bonding between polar R-groups,
- ionic bonds (salt bridges) between ionized R-groups,
- covalent disulfide bridges between amino acid sections in cysteine that contain sulfur although they are beyond the scope of this course.

The tertiary structure is crucial in the function of proteins because it gives them the shapes that are crucial to their function.

Quaternary structure

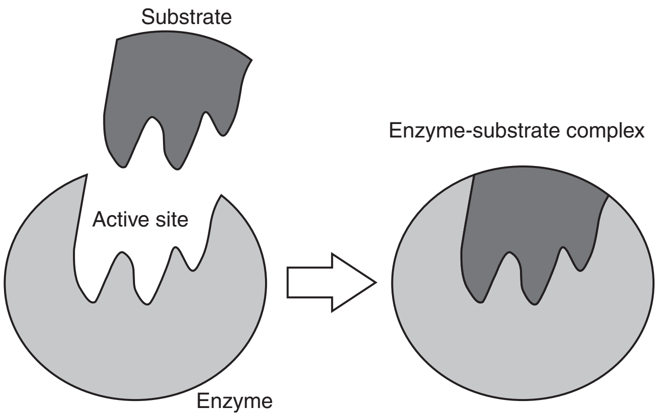
Quaternary structure is usually associated with hemoglobin. This is where separate polypeptide chain interacts to form a more complicated structure. Hemoglobin contains four polypeptides grouped around four heme molecules.

CORE
SPREAD 4: Enzymes

Most enzymes are proteins that act as catalysts by binding specifically to a substrate at the active site.

As enzyme activity depends on the conformation, it is sensitive to changes in temperature and pH and the presence of heavy metal ions.

Enzymes are often simply known as biological catalysts, but this could be a little simplistic. Yes, they provide an alternate pathway with a lower activation energy, but there is much more to them than that. They are usually specific only to one reaction within an organism. The substrate is the name given to the molecule on which the enzyme acts. The enzyme has an active site, a small “port” where the substrate molecule can bind and a chemical reaction occurs. This is often described in terms of a lock and key mechanism.



What affects enzyme activity?

Four factors affect an enzyme's activity: conformation, temperature, pH and presence of heavy metal ions.

Conformation

Essentially this means the shape of the enzyme. As we have discussed before enzymes are complex proteins with tertiary shapes held together by the folds and forces of attraction between them. This creates a very specific molecule that works because it has a particular shape. Any slight changes to this conformation will stop the enzyme working effectively.

Temperature

Enzymes (certainly those found in humans) work at around 37°C. Above this they become denatured. This is because the complicated sequence of hydrogen bonds that hold the enzyme in its shape get broken and the shape changes. This means the active site will no longer be effective.

pH

Similar issues here, the pH can have an effect on the charged parts of the enzyme that will also alter the shape of the enzyme. It will have a similar denaturing effect on the active site.

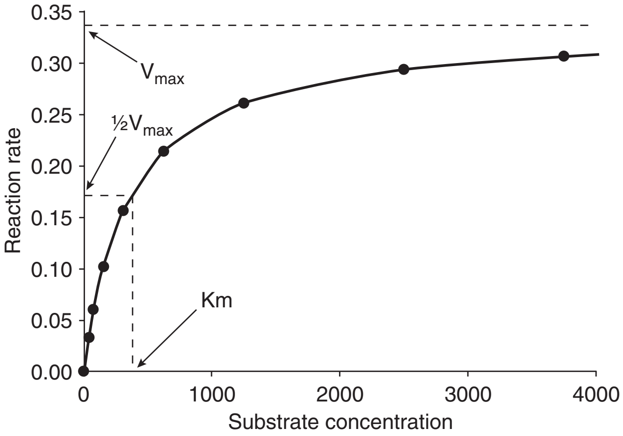
Heavy metals

Heavy metals can replace the hydrogen in an S–H group in cysteine. This disrupts the shape of the enzyme rendering it unable to work properly.

Enzyme activity in graph form

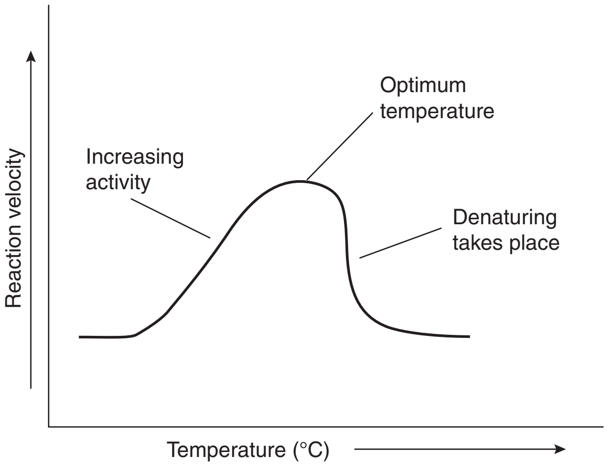
Concentration

At low concentrations of substrate the rate is proportional to the concentration. At high concentrations there is a limiting factor called $V_{\max}$, where all the active site on the enzyme are occupied and no further increases in rate are possible.



Temperature

The rate increases up to around 40°C, where there is a rapid drop off as denaturing occurs.



pH

Similar shape graph here although the peak is more specific to the optimum pH for the enzyme to work. There is a rapid drop-off on both sides in this case.

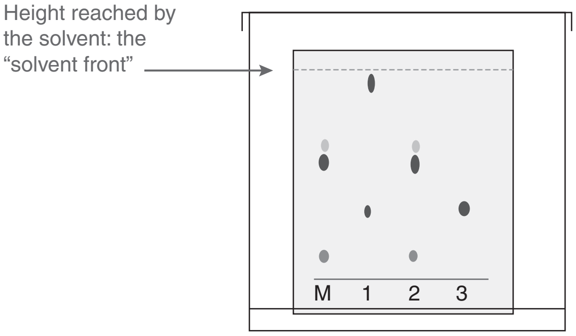
CORE
SPREAD 5: Separating and identifying amino acids and proteins

Chromatography separation is based on different physical and chemical principles.

There are two techniques to learn about here: chromatography and gel electrophoresis. Both will separate amino acids, so if you wish to use them to identify a protein you need to HYDROLYZE the protein to break down the peptide structure and release the individual amino acids.

Chromatography

Chromatography works because depending on their structure samples have a different attraction to the solvent (mobile phase) and the paper (stationary phase). This means they travel up the paper at different rates.



Once the solvent has reached the top, the paper is sprayed with ninhydrin to make the spots appear. Each spot can be identified using the Rf value.

This is:

$$\frac{\text{Distance travelled by the sample}}{\text{Distance travelled by the solvent}}$$

Rf values are published and can be used to identify the individual amino acids.

The Rf values are different in different solvents. It is possible for some amino acids to have the same Rf value in some solvents. In this case the paper can be turned in 90° and run again to do a second separation.

Gel electrophoresis

As we have seen amino acids have different structures at different pHs. At high pH the carboxylic acid donates its proton. At low pHs the amino group accepts a proton. At a certain pH the amino acid will be in the zwitterion form. In gel electrophoresis the sample is placed on the gel surface and a voltage is applied across it. This causes the amino acids to move in one direction or another. At their isoelectric point they will not move any more. This point can be sprayed with ninhydrin and identified using their isoelectric point table or other comparative tools.

CORE
SPREAD 6: Lipids

Fats are more reduced than carbohydrates and so yield more energy when oxidized.

Triglycerides are produced by condensation of glycerol with three fatty acids and contain ester links. Fatty acids can be saturated, monounsaturated or polyunsaturated.

Hydrolysis of triglycerides and phospholipids can occur using enzymes or in alkaline or acidic conditions.

Lipids act as structural components of cell membranes, in energy storage, thermal and electrical insulation, as transporters of lipid soluble vitamins and as hormones.

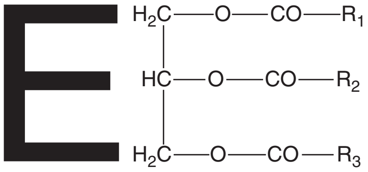
What are lipids?

Lipids are molecules with long carbon chains that are insoluble in water but are soluble in non-polar solvents. They are primarily used as energy storers and protecting vital organs. Lipids act as structural components of cell membranes, in energy storage, thermal and electrical insulation, as transporters of lipid soluble vitamins and as hormones.

There are four types of lipids, and we will look at them all.

Fats and oils

These are triesters (or triglycerides), esters formed between propane 1,2,3 triol (glycerol) and long chain carboxylic acids (known as fatty acids in biochemistry). The general structure is below. The glycerol is like the shape of a capital letter E with OH groups on each "prong." The ester forms there.



The difference between fats and oils is simply to do with the state at room temperature. A fat is a solid at room temperature, an oil is a liquid.

Oils and fats contain more energy than carbohydrates. This is because they are more reduced.

You might be expected to construct the formula of a triglyceride given the formula of the fatty acids joining to the glycerol. This is not difficult and involves a normal esterification reaction. Just make sure the O is in the right place (see above).

Fats and oils can be saturated, monounsaturated or polyunsaturated. This refers to the number of double bonds in the fatty acid chain. A saturated fat contains no double bonds, monounsaturated contains one and polyunsaturated contains many.

The degree of unsaturation of a fat is important because there are health factors associated with unsaturation. The IODINE number is a measure of unsaturation. As iodine, like all halogens will react electrophilically with double bonds. The more double bonds the more iodine will react with it. The iodine number of a fat is the amount in gram of iodine that a particular fat can absorb. The greater the number the greater the degree of unsaturation. The more double bonds, the lower the melting point. This is because double bonds allow a molecule to have a flatter structure around the planar 120° shape. This allows closer packing and greater intermolecular forces.

CORE
SPREAD 7: Lipids and health issues

- Health-wise fats are an essential part of any diet. Unsaturated fats are saturated fat. This is a type of fat that comes mainly from animal sources of food, such as red meat, poultry and full-fat dairy products. Saturated fat raises total blood cholesterol levels and low-density lipoprotein (LDL) cholesterol levels, which can increase your risk of cardiovascular disease. Saturated fat may also increase your risk of type 2 diabetes.
- Trans fat. This is a type of fat that occurs naturally in some foods in small amounts. But most trans fats are made from oils through a food processing method called partial hydrogenation. By partially hydrogenating oils, they become easier to cook with and less likely to spoil than do naturally occurring oils. Research studies show that these partially hydrogenated trans fats can increase unhealthy LDL cholesterol and lower healthy high-density lipoprotein (HDL) cholesterol. This can increase your risk of cardiovascular disease.
- Most fats that have a high percentage of saturated fat or that contain trans fat are solid at room temperature. Because of this, they're typically referred to as solid fats. They include beef fat, pork fat, butter, shortening and stick margarine.

Healthier dietary fat

The types of potentially helpful dietary fat are mostly unsaturated:

- Monounsaturated fat. This is a type of fat found in a variety of foods and oils. Studies show that eating foods rich in monounsaturated fats (MUFAs) improves blood cholesterol levels, which can decrease your risk of heart disease. Research also shows that MUFAs may benefit insulin levels and blood sugar control, which can be especially helpful if you have type 2 diabetes.
- Polyunsaturated fat. This is a type of fat found mostly in plant-based foods and oils. Evidence shows that eating foods rich in polyunsaturated fats (PUFAs) improves blood cholesterol levels, which can decrease your risk of heart disease. PUFAs may also help decrease the risk of type 2 diabetes.

Rancidity

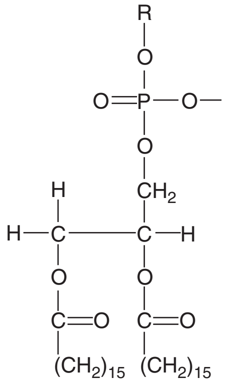
Oxidative rancidity is associated with the degradation by oxygen in the air. Via a free radical process, the double bonds of an unsaturated fatty acid can undergo cleavage, releasing volatile aldehydes and ketones. The more double bonds the more this process can occur. Saturated fatty acids cannot undergo this process as they do not contain double bonds. Hydrolytic rancidity refers to the odor that develops when triglycerides are hydrolyzed and free fatty acids are released. This reaction of lipid with water sometimes requires a catalyst, but results in the formation of free fatty acids and salts of free fatty acids. In particular, short-chain fatty acids, such as common butter fats, are odorous.

CORE
SPREAD 8: Phospholipids and steroids

Phospholipids are derivatives of triglycerides.

Steroids have a characteristic fused ring structure, known as a steroidal backbone.

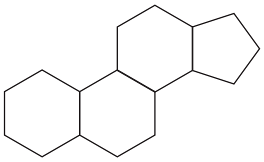
Phospholipids are found in cell membranes. Structurally they are very similar to triglycerides. They have the glycerol backbone, and two of the "prongs" contain a fatty acid joined by an ester group. The third prong contains a phosphate group and an alcohol containing a nitrogen. The general formula is below:



Steroids

Steroids have unique four-ring structure known as the steroid backbone below:

Steroid backbone



Cholesterol is an important steroid because it is an essential structural component of animal cell membranes that is required to maintain both membrane structural integrity and fluidity.

Cholesterol enables animal cells to (a) not need a cell wall (like plants and bacteria) to protect membrane integrity/cell-viability and thus be able to (b) change shape and (c) move about (unlike bacteria and plant cells that are restricted by their cell walls).

Steroids are signaling molecules; other examples include testosterone and estrogen. Anabolic steroid are subject to abuse by athletes—because they mimic the actions of testosterone. Steroids have wide spread use as medicines. Cortisol steroids mimic messenger hormones to relive symptoms of auto immune diseases like lupus. Steroids can also be used to rebuild muscle after injury or cancer treatments.

Low density lipoproteins and high density lipoproteins (LDL and HDL)

These are lipids that transport cholesterol around the body. LDL transports it to parts of the body where excess cholesterol can line artery walls leading to heart problems. LDL is often known as "bad cholesterol." HDL removes cholesterol from arteries and takes it to process in the liver.

Energy density relates the mass of the fuel to the volume it takes up. The higher the energy density the greater energy may be transported or stored for the same volume. It is an important consideration in fuel choice. The formula is below.

CORE
SPREAD 9: Carbohydrates

Carbohydrates have the general formula $C_x(H_2O)_y$*.*

Haworth projections represent the cyclic structures of monosaccharides.

Monosaccharides contain either an aldehyde group (aldose) or a ketone group (ketose) and several –OH groups.

Straight chain forms of sugars cyclize in solution to form ring structures containing an ether linkage.

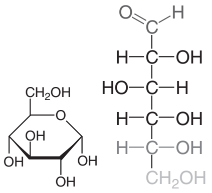
Glycosidic bonds form between monosaccharides forming disaccharides and polysaccharides.

Carbohydrates are used as energy sources and energy reserves.

What are carbohydrates?

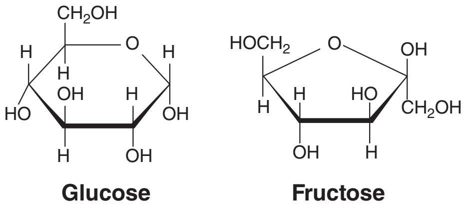
A carbohydrate is a large biological molecule containing carbon, hydrogen and oxygen. In most cases they exist with the general empirical formula $C_x(H_2O)_y$, with x and y being different.

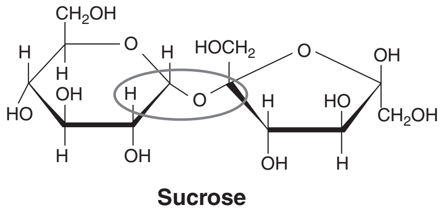
Structurally they are more technically poly hydroxy aldehydes or ketones. If the carbohydrate contains an aldehyde it is an aldose, and if it contains a ketone it is a ketose. D-glucose is an example of an aldose. Such structures are called monosaccharides. Saccharide and carbohydrate mean essentially the same thing. In solution the chain recombines and then forms the ring structure with the ether linkage.



Monosaccharides can combine together to form disaccharides. These form links between two monosaccharides by forming a new covalent bond by a condensation reaction. An example is given below:

D-glucose and D-fructose ⇒ sucrose





You might be expected to work out the structures of disaccharides from given monosaccharides, or do the reverse to work out the original monosaccharides.

The bond form is called a glyosidic bond. Many monosaccharides can combine together to form polysaccharides. The most common polysaccharide is called starch. Carbohydrates provide energy (short terms), but starch can store energy for longer.

CORE
SPREAD 10: Vitamins

Vitamins are organic micronutrients that (mostly) cannot be synthesized by the body but must be obtained from suitable food sources.

The solubility (water or fat) of a vitamin can be predicted from its structure.

Most vitamins are sensitive to heat.

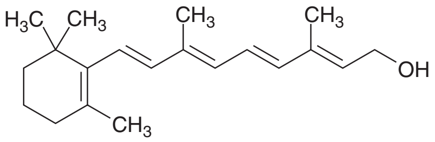
Vitamin deficiencies in the diet cause particular diseases and affect millions of people worldwide.

What are vitamins?

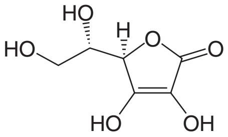
Vitamins were known to be important long before their structures were isolated and were given arbitrary names, Vitamin A, B and so on. Nowadays vitamins are more likely to have correct names. Vitamins are classified by their solubility in fat or water. Fat-soluble vitamins have long carbon chains. Water-soluble vitamins have OH or NH groups in abundance to allow hydrogen bonding.

The structures of vitamins

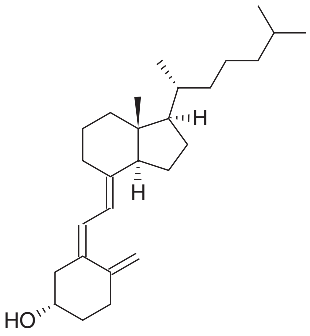
Vitamin A is fat soluble because the long carbon chain outweighs the single OH group.



Vitamin C is water soluble because of the large number of H bonding OH groups.



Vitamin D3 is fat soluble because the long carbon chain outweighs the single OH group.



Why are vitamins sensitive to heat?

Heat stops most vitamins from working effectively. This is because under high heat conditions the vitamin can oxidize and stop being the molecule it was before.

Why are vitamins so important?

As stated before vitamins are a group of biological molecules that the body cannot make. Therefore they have to be ingested as part of the diet. If the diet does not provide the vitamin then it can have serious long-term effects on health. Malnutrition is the consequence of this, and in certain parts of the world certain disease are prevalent because of a lack of vitamins. There are lists available on the internet, but this can be overcome by eating fresh food wherever possible, taking vitamin supplements, adding the missing vitamin into basic foodstuffs and genetic modification of food.

CORE
SPREAD 11: Biochemistry and the environment

Xenobiotics refer to chemicals that are found in an organism that are not normally present there. Biodegradable/compostable plastics can be consumed or broken down by bacteria or other living organisms.

Host–guest chemistry involves the creation of synthetic host molecules that mimic some of the actions performed by enzymes in cells, by selectively binding to specific guest species, such as toxic materials in the environment.

Enzymes have been developed to help in the breakdown of oil spills and other industrial wastes.

Enzymes in biological detergents can improve energy efficiency by enabling effective cleaning at lower temperatures. Biomagnification is the increase in concentration of a substance in a food chain.

Xenobiotics

These are chemicals that are found in an organism that are not normally present there. This covers such things as antibiotics that are taken by humans but not originally present. The term “xenobiotics” can also cover the presence of these compounds in water treatment and sewage, allowing the molecules to enter the food chain and cause other environmental problems. Because they are developed from fungi they are difficult to remove, so they are very similar to “natural” substances found in the water.

Xenobiotics and biomagnification

Biomagnification occurs when the concentration of a xenobiotic substance, such as DDT or mercury, in an organism exceeds the background concentration of the substance in its diet. This increase can occur as a result of:

- Persistence—where the substance can’t be broken down by environmental processes
- Food chain energetics—where the substance concentration increases progressively as it moves up a food chain
- Low or non-existent rate of internal degradation or excretion of the substance—often due to water-insolubility

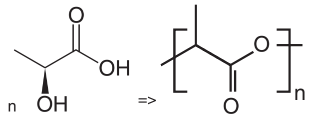
The following is an example showing how bio-magnification takes place in nature: An anchovy eats zoo-plankton that have tiny amounts of mercury that the zoo-plankton has picked up from the water throughout the anchovies lifespan. A tuna eats many of these anchovies over its life, accumulating the mercury in each of those anchovies into its body. If the mercury stunts the growth of the anchovies, that tuna is required to eat more little fish to stay alive. Because there are more little fish being eaten, the mercury content is magnified.

Biological magnification often refers to the process whereby certain substances such as pesticides or heavy metals move up the food chain, work their way into rivers or lakes, and are eaten by aquatic organisms such as fish, which in turn are eaten by large birds, animals or humans. The substances become concentrated in tissues or internal organs as they move up the chain. Bioaccumulants are substances that increase in concentration in living organisms as they take in contaminated air, water or food because the substances are very slowly metabolized or excreted.

Biodegradable and compostable plastics

Biodegradable plastics are plastics that are capable of being broken down by bacteria or other living organisms. Compostable plastics take the process one step further, not only are they biodegradable but the breakdown produces hummus. Although biodegradable plastics can be made from most polyesters (the ester linkage can be hydrolyzed), compostable polymers need to be made from starch.

The best example is polylactic acid that is derived from corn starch.



Host–Guest Chemistry

This is an idea where synthetic host molecules are created that mimic the actions of enzymes in cells. In this way they can selectively bind to specific guest species. In the IB DP context it can be used to remove toxic materials from the environment.

Host–guest systems have been utilized to remove hazardous materials from the environment. They can be made in different sizes and different shapes to trap a variety of chemical guests. One application is the ability of p-tert-butycalix[4]arene to trap a caesium ion. Caesium-137 is radioactive, and there is a need to remove it from nuclear waste in an efficient manner. Host–guest chemistry has also been used to remove carcinogenic aromatic amines from water. These waste materials are used in many industrial processes and found in a variety of products such as pesticides, drugs and cosmetics.

Host–guest complexes include biological systems, such as enzymes and their substrates, with enzymes being the host and the substrates the guest. In terms of coordination chemistry, metal–ligand complexes can be thought of as host–guest species, where large ligands act as hosts for metal cations. If the host possesses a permanent molecular cavity containing specific guest binding sites, then it will generally act as a host both in solution and in the solid state and there is a reasonable likelihood that the solution and solid state structures will be similar to one another. On the other hand, the class of solid state compounds only exhibit host–guest behavior as crystalline solids since the guest is bound within a cavity that is formed as a result of a hole in the packing of the host lattice. Such compounds are generally termed clathrates from the Greek klethra, meaning "bars."

Enzymes

Enzymes are very useful for environmental situations. They have been added to detergents (biological detergents) to help break down food stains, especially proteins. As they are ineffective over 40°C they help reduce energy costs by cleaning effectively at much lower temperatures. Enzymes have recently been used as part of oil spill eaters, chemicals designed to ingest crude oil from spillage and turn them into CO_2 and H_2O. It can also be used on other hazardous soils. It works by turning the oil into a natural food source for the bacteria in the area.

CORE
SPREAD 12: Green chemistry

Green chemistry, also called sustainable chemistry, is an approach to chemical research and engineering that seeks to minimize the production and release to the environment of hazardous substances.

A reminder of green chemistry principles:

1. **Prevention**
   It is better to prevent waste than to treat or clean up waste after it has been created.
2. **Atom economy**
   Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. **Less hazardous chemical syntheses**
   Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

4. **Designing safer chemicals**
   Chemical products should be designed to affect their desired function while minimizing their toxicity.
5. **Safer solvents and auxiliaries**
   The use of auxiliary substances (e.g., solvents and separation agents) should be made unnecessary wherever possible and innocuous when used.
6. **Design for energy efficiency**
   Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.
7. **Use of renewable feedstocks**
   A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
8. **Reduce derivatives**
   Unnecessary derivatization (use of blocking groups, protection/deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.
9. **Catalysis**
   Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. **Design for degradation**
    Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.
11. **Real-time analysis for pollution prevention**
    Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
12. **Inherently safer chemistry for accident prevention**
    Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions and fires.

    The disposal, manufacture and administration of drugs and medicines can affect the environment. It is also expected that drug manufacturers should adhere to the green chemistry principles above. There are a few specific examples.

Atom economy

Atom economy is a measure of efficiency in green chemistry.

It is in the data book and defined as:

$$\%\ \text{Atom economy} = \frac{\text{Molar mass of desired product}}{\text{Molar mass of all reactants}} \times 100$$

A green chemistry goal is to focus on reactions with near 100% atom economy. This means reactions that only produce one product, the desired one. Addition reactions in organic chemistry are good examples of 100% atom economy reactions and are keenly sought after in green circles. As addition polymerization gives 100% atom economy they are considered desirable in such terms, especially if the monomer can be sourced from something other than crude oil.

HL
SPREAD 13: Advanced proteins

Inhibitors play an important role in regulating the activities of enzymes.

Amino acids and proteins can act as buffers in solution.

Protein assays commonly use UV–Vis spectroscopy and a calibration curve based on known standards.

Proteins

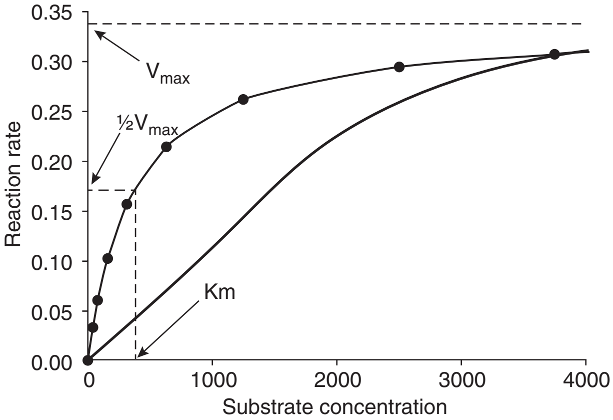
What are inhibitors?

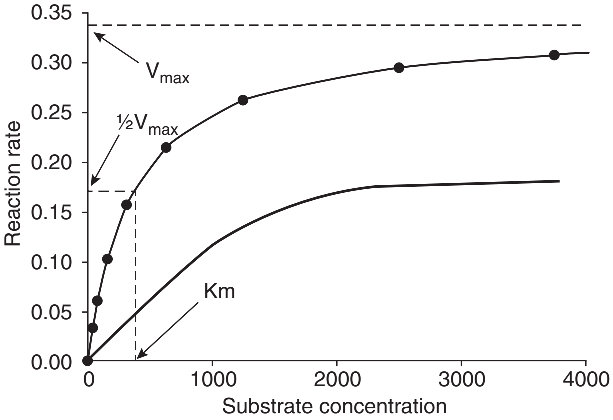
These are chemicals that bind to enzymes and reduce their activity. There are two types:

Competitive and non-competitive inhibitors

Competitive inhibitors compete for the active site of the enzyme. If you are imagining the lock and key idea then the competitive inhibitor is like another key that takes up the space in the lock. A non-competitive inhibitor binds to another part of the enzyme, but its presence can deform the shape of the active site. They are non-competitive because they do not compete for the active site.

Their effect on the rate is as follows:
Competitive





The non-competitive has a more permanent effect on the rate.

NOTE: THESE DIAGRAMS NEED TO BE RE DRAWN WITH A BETTER DOTTED LINE ON.

Maximum rate and the Michaelis constant

The maximum rate or V_{max} of a reaction is the maximum rate that can be achieved at infinite substrate concentration. The difference between enzyme catalyzed reactions and other kinetic reactions is that there are only finite number of active sites available on an enzyme. There will be a point when all the active sites are occupied, and increasing the concentration will make no difference to the rate of reaction. This is fairly easy to do, simply requiring you to extrapolate from the *y* axis.

The Michaelis constant is the value when the substrate concentration [S] equals the half V_{max}. Again this is easy to calculate from the graph, see above. The magnitude of the Michaelis constant tells you how much affinity the enzyme has for the substrate, because a low Michaelis constant (K_m) shows that low concentrations can get maximum activity.

As you can see from the graphs above, as V_{max} is affected in non-competitive inhibition it is possible to work out which type of inhibition is happening in any experiment. If K_m is the same in both experiments it is non-competitive. If K_m increases then it is competitive inhibition.

Protein concentration analysis

Protein concentration can be determined using a UV–Vis spectrometer. They work on the following principle: that when electromagnetic radiation (light, etc.) is passed through a substance some of the radiation is absorbed. If the intensity of the incoming radiation is I and the intensity of the outgoing tradition is I_0 then the absorbance of the material is related to the two factors:

In fact it is: $A = \log I_0/I$

So a substance where 83% of the light has been absorbed has absorption of … (no units).

So what? Well the Beer–Lambert law uses this to work out the concentration of the substance from this because (in simple terms) the more concentrated the substance the less absorption. There is a direct relationship. So:

$$A = \log I_0/I = ecl$$

Where

e = molar absorption constant
c = concentration
l = path length.

So we can rearrange this to be:

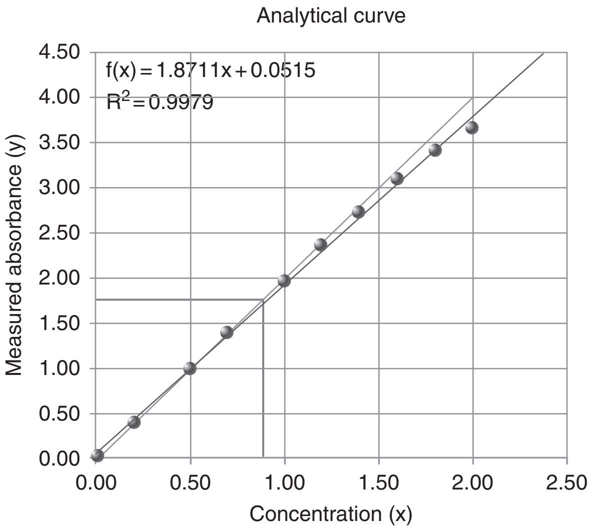
$$E = A/lc$$

Graphical analysis

The most common task involving this is to work out the concentration from a previously worked out calibration curve. A plot of absorbance over concentration should give a straight line if it obeys the Beer–Lambert Law.

Example:

The plot below is a calibration curve for a protein.



A sample of a protein was put into a UV–Vis spectrometer and gave an absorbance of 1.75. Using the calibration curve work out the concentration of this protein.

Reading off the graph at 1.75 absorbance we can see that the concentration must be 0.9 moldm^{-3}.

Complications could include full solution calculations so make sure you read the question properly before committing to an answer.

HL
SPREAD 14: Buffer solutions

Buffer solutions were mentioned in the acid and base topic, but here we put numbers in!

Blood is a buffer solution; buffer solutions are important in biological systems. The pH of buffer solutions can be calculated using a modification of an equation called the Henderson–Hasselbach equation (in your data book).

$$\text{pH} = \text{p}K_a + \log_{10} [\text{conjugate base}]/[\text{acid}]$$

Although an easier version to use in exams is:

$$[\text{H+}] = K_a [\text{acid}]/[\text{conjugate base}]$$

One of the most important buffer solutions is the one between hydrogen carbonate ions and carbonic acid

$$H^+_{(aq)} + HCO_3{}^-_{(aq)} \rightleftarrows H_2CO_{3(aq)} \rightleftarrows H_2O_{(l)} + CO_{2(g)}$$

Example
The concentration of hydrogen carbonate ions is 1.000 moldm^{-3}. The concentration of carbonic acid is 0.1103 moldm^{-3}. What is the pH of blood? $K_a = 4.3 \times 10^{-7}$

$[H^+] = 4.3 \times 10^{-7} \times 0.113/1.00$
$[H=] = 4.859 \times 10^{-8}$
$\text{pH} = -\log 4.859 \times 10^{-8}$
$= 7.313$

Be prepared to use any data given to work out the pH, although this is the most common one.

HL
SPREAD 15: Nucleic acids

Nucleotides are the condensation products of a pentose sugar, phosphoric acid and a nitrogenous base—adenine (A), guanine (G), cytosine (C), thymine (T) or uracil (U).

Polynucleotides form by condensation reactions.

DNA is a double helix of two polynucleotide strands held together by hydrogen bonds.

RNA is usually a single polynucleotide chain that contains uracil in place of thymine, and a sugar ribose in place of deoxyribose.

The sequence of bases in DNA determines the primary structure of proteins synthesized by the cell using a triplet code, known as the genetic code, which is universal.

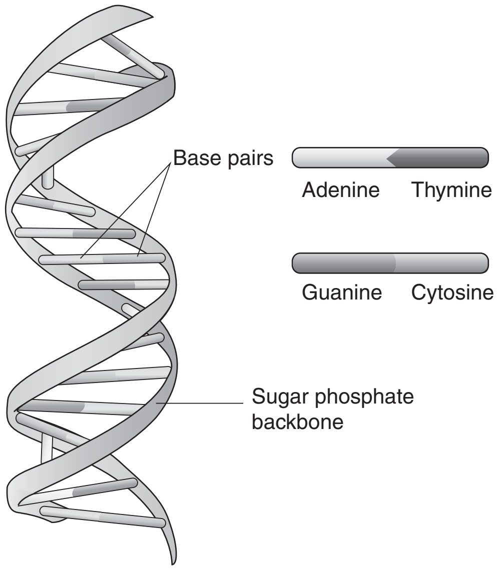
Genetically modified organisms have genetic material that has been altered by genetic engineering techniques, involving transferring DNA between species.

DNA: What's all the fuss about?

DNA or deoxyribonucleic acid is a very large molecule that, to put it very simply, carries all the genetic information required for an organism. DNA is found in all cells and is uniquely arranged for each individual organism.

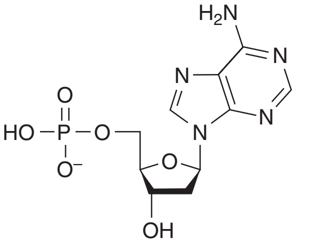
Structure

It is well known that it has a double helix structure with ladder-like rungs, which are held together by hydrogen bonds. The structure of the two strands making up the helix is made from a repeating pattern of nucleotides. Nucleotides are base-sugar-phosphate units.



The diagram above will help. The center part is the sugar deoxyribose. The left part is the remnants of phosphoric acid. The third part is the base (more later). The nucleotide is made by the condensation reaction.

Note also the negative charge on the phosphate ion. This gives DNA an overall negative charge.



What are the bases?

There are four bases found in DNA:

Adenine (A)
Guanine (G)
Cytosine (C)
Thymine (T)

The nucleotides then combine together, and the helix is held together by hydrogen bonds. Any combination up the helix is possible, but the bases can only combine ACROSS in certain combinations.

Adenine can combine with guanine.
Cytosine can combine with thymine.

DNA is very stable. Why is that?

There are strong interactions between the stacked bases and across the helix. These interactions can be hydrophobic and hydrophilic. Guanine pairs with cytosine (three hydrogen bonds in center of DNA strand) and thymine pairs with adenine (two hydrogen bonds in center of DNA strand). As the number of DNA nucleotides in the DNA chain increases, the strength of the bonding between the two complementary strands of deoxyribonucleotides increases as well because of the hydrogen bonds working together. Between nucleotides in a DNA strand (1/2 of a double helix); there are also phosphodiester bonds between deoxyribose and phosphate, which keep the individual nucleotides together in a strand.

So what is RNA?

RNA is similar to DNA but is a single strand. It also differs from DNA because it has the base uracil (U) instead of thiamine. It has the sugar ribose instead of deoxyribose in its nucleotide. It is used in protein synthesis in cells, as well as other biological functions.

Knowing the difference between RNA and DNA is important.

How does DNA replicate?

- DNA is stored in chromosomes, which are found in the nucleus of a cell. In humans there are 23 chromosomes containing DNA. Other organisms have other amounts of chromosomes.
- The DNA is packed efficiently with the help of proteins called histones. Histones have a positive charge and can bind with the negative charge on the phosphate ions on the DNA.
- When replication is due to occur the DNA strand unzips, the H-bonds break. New sugar-base units are picked up to replicate the old strand, the old strand is reformed and the new strand is an exact copy of the old one. The fact that bases can only combine with certain bases ensures exact replicas.

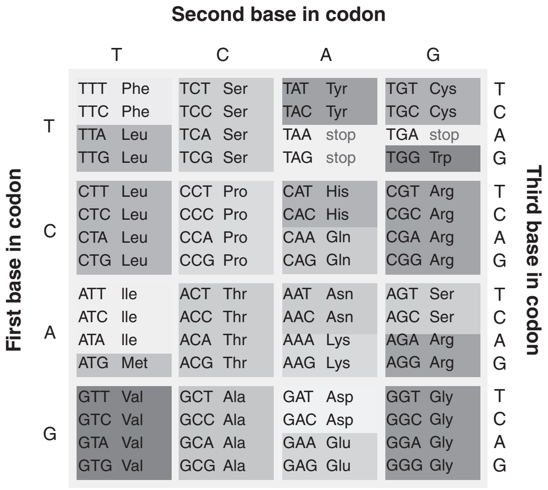
Protein synthesis

- The DNA is unzipped as before, but this time an enzyme reads the strand and produces an RNA strand (with the uracil replacing the thiamine).
- The new strand goes into the cytoplasm and encounters ribosomes. Here the protein is made using the instructions to make the correct sequence of amino acids needed for the protein.

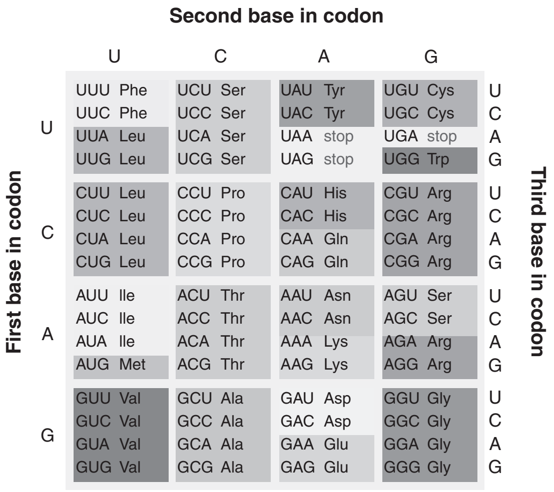
How does a sequence of bases make up a sequence of amino acids?

There are four bases in RNA. There are 20 amino acids used in proteins. Combining three bases gives you 64 different permutations (4^3). These are known as the triplet code, also known as codons. This is more than enough to make 20 amino acids. More than one codon can code one amino acid. This is a good thing because it can protect against mutation. There are also terminator codons (e.g., UAA, UAG) that tell the ribosomes to stop building the change, listed as STOP in the tables.

The table below lists all the possible permutations for DNA. You would be expected to be able to use this to work out code. Below that is RNA.



First base in codon	Second base in codon: T	C	A	G	Third base in codon
T	TTT Phe	TCT Ser	TAT Tyr	TGT Cys	T
	TTC Phe	TCC Ser	TAC Tyr	TGC Cys	C
	TTA Leu	TCA Ser	TAA stop	TGA stop	A
	TTG Leu	TCG Ser	TAG stop	TGG Trp	G
C	CTT Leu	CCT Pro	CAT His	CGT Arg	T
	CTC Leu	CCC Pro	CAC His	CGC Arg	C
	CTA Leu	CCA Pro	CAA Gln	CGA Arg	A
	CTG Leu	CCG Pro	CAG Gln	CGG Arg	G
A	ATT Ile	ACT Thr	AAT Asn	AGT Ser	T
	ATC Ile	ACC Thr	AAC Asn	AGC Ser	C
	ATA Ile	ACA Thr	AAA Lys	AGA Arg	A
	ATG Met	ACG Thr	AAG Lys	AGG Arg	G
G	GTT Val	GCT Ala	GAT Asp	GGT Gly	T
	GTC Val	GCC Ala	GAC Asp	GGC Gly	C
	GTA Val	GCA Ala	GAA Glu	GGA Gly	A
	GTG Val	GCG Ala	GAG Glu	GGG Gly	G



First base in codon	Second base in codon: U	C	A	G	Third base in codon
U	UUU Phe	UCU Ser	UAU Tyr	UGU Cys	U
	UUC Phe	UCC Ser	UAC Tyr	UGC Cys	C
	UUA Leu	UCA Ser	UAA stop	UGA stop	A
	UUG Leu	UCG Ser	UAG stop	UGG Trp	G
C	CUU Leu	CCU Pro	CAU His	CGU Arg	U
	CUC Leu	CCC Pro	CAC His	CGC Arg	C
	CUA Leu	CCA Pro	CAA Gln	CGA Arg	A
	CUG Leu	CCG Pro	CAG Gln	CGG Arg	G
A	AUU Ile	ACU Thr	AAU Asn	AGU Ser	U
	AUC Ile	ACC Thr	AAC Asn	AGC Ser	C
	AUA Ile	ACA Thr	AAA Lys	AGA Arg	A
	AUG Met	ACG Thr	AAG Lys	AGG Arg	G
G	GUU Val	GCU Ala	GAU Asp	GGU Gly	U
	GUC Val	GCC Ala	GAC Asp	GGC Gly	C
	GUA Val	GCA Ala	GAA Glu	GGA Gly	A
	GUG Val	GCG Ala	GAG Glu	GGG Gly	G

Genetic modification

Genetically modified organisms have genetic material that has been altered by genetic engineering techniques, involving transferring DNA between species. This can create “better” examples of the original organism. This can cause better resistance to certain diseases, or produce longer shelf life, or better flavor. Beneficial vitamins or anti carcinogens can be added to the food.

The concerns are that this is uncertain science; there could be transfer to normal crops with unknown effects. Allergic reactions could increase, and such modification is/can have unknown effects on ecosystems as a whole.

HL
SPREAD 16: Biological pigments

Biological pigments are colored compounds produced by metabolism.

The color of pigments is due to highly conjugated systems with delocalized electrons, which have intense absorption bands in the visible region.

Porphyrin compounds, such as hemoglobin, myoglobin, chlorophyll and many cytochromes, are chelates of metals with large nitrogen-containing macrocyclic ligands.

Hemoglobin and myoglobin contain heme groups with the porphyrin group bound to an iron (II) ion.

Cytochromes contain heme groups in which the iron ion interconverts between iron (II) and iron (III) during redox reactions.

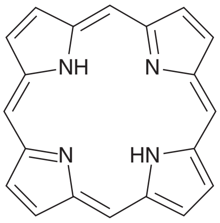
Anthocyanins are aromatic, water-soluble pigments widely distributed in plants.

Carotenoids are lipid-soluble pigments and are involved in harvesting light in photosynthesis. They are susceptible to oxidation, catalyzed by light.

Biological pigments are colored compounds produced by metabolism. They can appear in animals and plants. The color of these biological pigments is due to them having function groups with double bonds in: C=C, C=O, N=N, preferably many of them in the molecule. This is known as conjugated pi system. Benzene rings are a good example. These conjugated molecules are able to absorb light in the visible or UV region. In this context such highly conjugated systems with delocalized electrons are called chromophores, which have intense absorption bands in the visible region. In conjugated chromophores, the electrons jump between energy levels that are extended pi orbitals, created by the series of alternating single and double bonds. The greater the conjugation the more likely they are to be colored. Something with one double bond like ethene absorbs in the UV region and is therefore colorless.

Examples of biological pigments

Porphyrin compounds



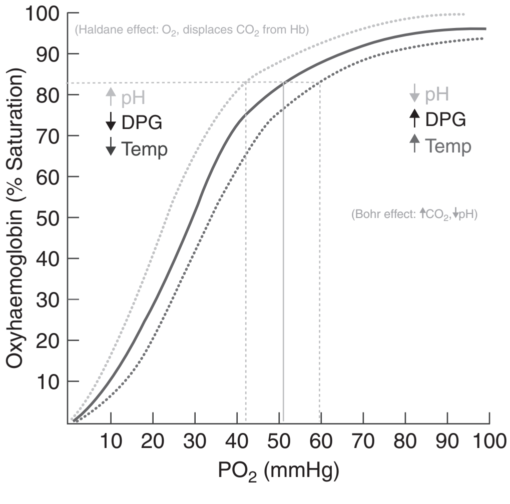
As you can see the porphyrin ring has a lot of conjugation. Pigments with this structure include hemoglobin, myoglobin and chlorophyll. In the hemoglobin there is the heme group, which is a derivation of the porphyrin group with an iron (II) ion bonded in the middle as a complex ion via dative covalent bonds in an octahedral shape. The spare places are used to bind to the rest of the hemoglobin protein and to the oxygen molecule it is to transport. Such metal organic structures are called chelates. When hemoglobin takes up oxygen the iron ion moves a bit and the hemoglobin molecule changes shape, and this allows another oxygen atom to bond easily. The binding is therefore a cooperative process although the maximum number of oxygens that can attach is four.

In the blood of a fetus the hemoglobin has a slightly different structure. This allows it to bind more effectively to oxygen than regular hemoglobin, which means the fetus can take oxygen from the blood of the mother.

Carbon monoxide can also bind preferably to the Iron (II) ion than oxygen. It can be seen as a competitive inhibitor, in this case with lethal consequences. Any inhalation of carbon monoxide can mean that the body does not get enough oxygen and can cause death.

Myoglobin is very similar and found in muscles of vertebrates.

Oxygen binding



This is the name given when the oxygen joins to the iron (II) ion. Each hemoglobin molecule has the capacity to carry four oxygen molecules. How much of that capacity is filled by oxygen at any time is called the oxygen saturation. Expressed as a percentage, the oxygen saturation is the ratio of the amount of oxygen bound to the hemoglobin, to the oxygen-carrying capacity of the hemoglobin. The oxygen-carrying capacity of hemoglobin is determined by the type of hemoglobin. The partial pressure of the oxygen is also a factor. As the partial pressure increases there comes a point when all sites on the molecule are used up and no more can be added. This explains the sigmoidal shape of hemoglobin's oxygen dissociation curve.

Oxygen saturation of hemoglobin is affected by:

Temperature—at higher temperature more oxygen is released from hemoglobin.
pH—low pH causes more oxygen to be released.

Carbon dioxide—similar as its increased pressure as an exhaled gas causes more oxygen to be deposited. It also lowers the pH (see above).

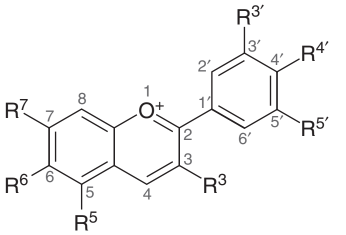
Cytochromes

Cytochromes are another heme-based porphyrin complex. This time the iron (II) can be oxidized to iron (III) and reduced back. This redox behavior ultimately helps the process of making Adenosine Triphosphate (ATP), the energy driver in cells.

Chlorophyll is another heme-based molecule, this time with a magnesium bonded in the center. As you will be aware this molecule is crucial in photosynthesis in plants and is green in color.

Anthocyanins

Anthocyanins are aromatic, water-soluble pigments widely distributed in plants. Their specific color depends on metal ions and pH. The basic structure is below, see the conjugation. Depending on pH the oxygen numbered 1 can EITHER have a positive charge (acidic) and causes the molecule to have less conjugation. This affects the color produced as light absorption is different. This can go some way to explaining the different colors of flowers depending on the pH.



Carotenoids

Carotenoids are lipid-soluble pigments and are involved in harvesting light in photosynthesis. They are susceptible to oxidation, catalyzed by light.

HL
SPREAD 17: Stereochemistry in biomolecules

With one exception, amino acids are chiral, and only the L-configuration is found in proteins.

Naturally occurring unsaturated fat is mostly in the cis form, but food processing can convert it into the trans form.

D and L stereoisomers of sugars refer to the configuration of the chiral carbon atom furthest from the aldehyde or ketone group, and D forms occur most frequently in nature.

Ring forms of sugars have isomers, known as α and β, depending on whether the position of the hydroxyl group at carbon 1 (glucose) or carbon 2 (fructose) lies below the plane of the ring (α) or above the plane of the ring (β).

Vision chemistry involves the light activated interconversion of cis- and trans-isomers of retinal.

We've seen in the Organic Chemistry section that stereoisomerism is common in organic molecules. To recap, there is *E*/*Z* (and the simpler cis-trans), and optical isomerism. Let's look at a few molecules.

Amino acids

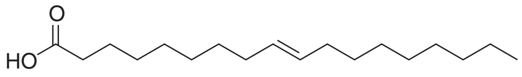
Amino acids have the general formula:

$H_2N–C^* (RH) – COOH$

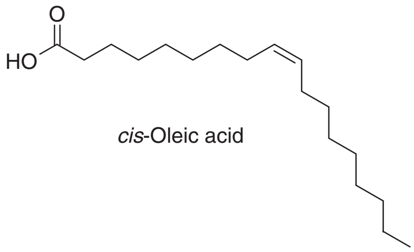
The carbon is chiral in nearly all amino acids (the exception is glycine, where the R group is a hydrogen). This means that there are two enantiomers of each amino acid. Curiously only one isomer (the same one, the L-isomer) tends to appear in nature when used in proteins.

Fats

We've also seen that unsaturated fatty acids contain double bonds. This means that they can display cis-trans isomerism, see below. The cis form is the most likely to be found in nature. Trans fatty acids can be formed when the cis form is hydrogenated partially. Apart from the health implications for trans fatty acids (increased risk of heart disease) you can see below how the trans molecule is flatter. This allows it to pack together better and form stronger intermolecular forces. This means that the trans form has a higher melting point. The higher melting point is a good thing as it allows a fat in a natural liquid form (an oil) to become a solid, which allows them to be used as an alternative spread to butter.



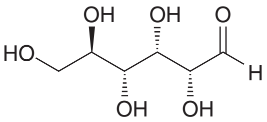
trans-Oleic acid



cis-Oleic acid

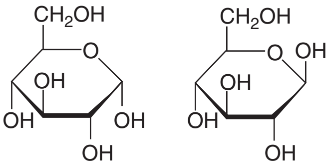
Sugars

Let's keep it simple first of all. Below is glucose in its straight chain form. You will see it contains a lot of chiral centers (4).



Chemists like to classify molecules as either D or L forms but which carbon to choose? It's the one furthest from the aldehyde or ketone.

It is harder to see in the ring form. Below are two forms of D glucose. In these diagrams it's the carbon below the CH_2OH.



Sugars can also be classified by the carbon NEXT to the O group on the other side (known as the first carbon). This would classify as either alpha or beta. The left example is the alpha as the OH lies below the plane of the ring. The other is beta.

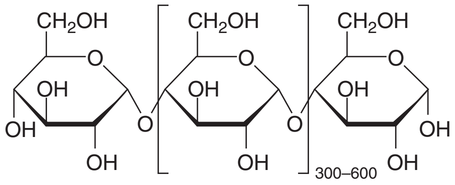
In fructose it is carbon (2) lies below the plane of the ring (α) or above the plane of the ring (β).

Cellulose and starch

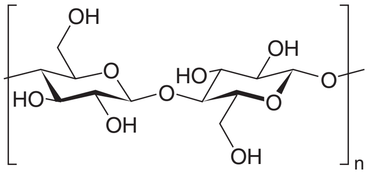
As we have seen these are polysaccharides both formed from glucose. Polysaccharides are polymers formed from the ring form of basic sugars, but the nature of the polysaccharide will depend on which OH on which carbon is used. This is very well illustrated with the cases of starch and cellulose.

Both are made from glucose.

Starch is formed from the alpha D form of glucose; note the O is below the plane to signify it is alpha.



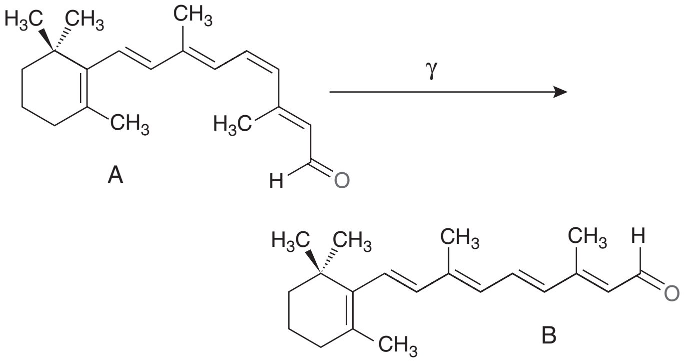
Cellulose is formed from the beta and the O is ABOVE the plane of the ring.



Starch, as we know is used to store sugars in the body. Cellulose is an essential component in the building of cell walls in plants. It is not digestible by animals but is useful to aid digestion and excretion.

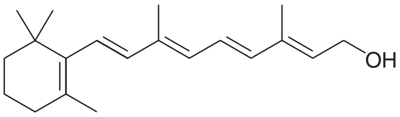
Vision chemistry

How do we see? It is complicated process that involves stereoisomers of a molecule called retinal. As you can see from the molecule below there are trans and cis forms. The molecules are in your data book.



When light shines on the eye the retina has to convert this into an electrical signal to send to the brain for translation. Here's how it works. The light converts retinal from the cis to the trans form. This causes the protein opsin to send a signal along the optic nerve to the brain. Opsin and retinal together are called rhodopsin.

Vitamin A is crucial in the process. Vitamin A is the chemical required to make retinal in the first place. Look how similar it is.



CHAPTER

15 Energy

This chapter covers material from Option C: Energy.

CORE
SPREAD 1: Energy sources, an introduction

A useful energy source releases energy at a reasonable rate and produces minimal pollution.

The quality of energy is degraded as heat is transferred to the surroundings. Energy and materials go from a concentrated into a dispersed form. The quantity of the energy available for doing work decreases.

Renewable energy sources are naturally replenished. Nonrenewable energy sources are finite.

Energy density = energy released from fuel/volume of fuel consumed.

Specific energy = energy released from fuel/mass of fuel consumed.

The efficiency of an energy transfer = useful output energy/total input energy × 100%.

What is an energy source?

A useful energy source releases energy at a reasonable rate and produces minimal pollution.

Renewable energy sources are naturally replenished. Nonrenewable energy sources are finite.

Examples include:

Nonrenewable

Type of fuel	Where it is from	Advantages	Disadvantages
Coal (fossil fuel)	• Formed from fossilized plants and consisting of carbon with various organic and some inorganic compounds. • Mined from seams of coal, found sandwiched between layers of rock in the earth. • Burnt to provide heat or electricity.	• Ready-made fuel. • It is relatively cheap to mine and to convert into energy. • Coal supplies will last longer than oil or gas.	• When burned coal gives off atmospheric pollutants, including greenhouse gases.
Oil (fossil fuel)	• A carbon-based liquid formed from fossilized animals. • Lakes of oil are sandwiched between seams of rock in the earth. • Pipes are sunk down to the reservoirs to pump the oil out. • Widely used in industry and transport.	• Oil is a ready-made fuel. • Relatively cheap to extract and to convert into energy.	• When burned, it gives off atmospheric pollutants, including greenhouse gases. • Only a limited supply.

Type of fuel	Where it is from	Advantages	Disadvantages
Natural gas (fossil fuel)	• Methane and some other gases trapped between seams of rock under the earth's surface. • Pipes are sunk into the ground to release the gas. • Often used in houses for heating and cooking.	• Gas is a ready-made fuel. • It is a relatively cheap form of energy. • It is a slightly cleaner fuel than coal and oil.	• When burned, it gives off atmospheric pollutants, including greenhouse gases. • Only limited supply of gas.
Nuclear	• Radioactive minerals such as uranium are mined. • Electricity is generated from the energy that is released when the atoms of these minerals are split (by nuclear fission) in nuclear reactors.	• A small amount of radioactive material produces a lot of energy. • Raw materials are relatively cheap and can last quite a long time. • It doesn't give off atmospheric pollutants.	• Nuclear reactors are expensive to run. • Nuclear waste is highly toxic, and needs to be safely stored for hundreds or thousands of years (storage is extremely expensive). • Leakage of nuclear materials can have a devastating impact on people and the environment. The worst nuclear reactor accident was at **Chernobyl**, Ukraine in 1986.
Biomass	• Biomass energy is generated from decaying plant or animal waste. • It can also be an organic material which is burned to provide energy, e.g., heat, or electricity. • An example of biomass energy is oilseed rape (yellow flowers you see in the UK in summer), which produces oil. • After treatment with chemicals it can be used as a fuel in diesel engines.	• It is a cheap and readily available source of energy. • If the crops are replaced, biomass can be a long-term, sustainable energy source.	• When burned, it gives off atmospheric pollutants, including greenhouse gases. If crops are **not replanted**, biomass is a nonrenewable resource.
Wood	• Obtained from felling trees, burned to generate heat and light.	• A cheap and readily available source of energy. • If the trees are replaced, wood burning can be a long-term, sustainable energy source.	• When burned it gives off atmospheric pollutants, including greenhouse gases. • If trees are **not replanted** wood is a nonrenewable resource

Renewable

Solar	• Energy from sunlight is captured in solar panels and converted into electricity.	• Potentially infinite energy supply. • Single dwellings can have own electricity supply.	• Manufacture and implementation of solar panels can be costly.
Wind	• Wind turbines (modern windmills) turn wind energy into electricity.	• Can be found singularly, but usually many together in wind farms. • Potentially infinite energy supply.	• Manufacture and implementation of wind farms can be costly. • Some local people object to on-shore wind farms, arguing that it spoils the countryside.
Tidal	• The movement of tides drives turbines. • A tidal barrage (a kind of dam) is built across estuaries, forcing water through gaps. • In future underwater turbines may be possible out at sea and without dams.	• Ideal for an island such as the UK. • Potential to generate a lot of energy. • Tidal barrage can double as a bridge, and help prevent flooding.	• Construction of barrage is very costly. • Only a few estuaries are suitable. • Opposed by some environmental groups as having a negative impact on wildlife. • May reduce tidal flow and impede flow of sewage out to sea.
Wave	• The movement of seawater in and out of a cavity on the shore compresses trapped air, driving a turbine.	• Ideal for an island country. • More likely to be small local operations, rather than done on a national scale.	• Construction can be costly. • May be opposed by local or environmental groups.

Geothermal	• In volcanic regions it is possible to use the natural heat of the earth. • Cold water is pumped underground and comes out as steam. • Steam can be used for heating or to power turbines creating electricity.	• Potentially infinite energy supply. • Used successfully in some countries, such as New Zealand and Iceland.	• Can be expensive to set up and only works in areas of volcanic activity. • Geothermal and volcanic activity might calm down, leaving power stations redundant. • Dangerous elements found underground must be disposed of carefully.
Hydrological or hydroelectric power (HEP)	• Energy harnessed from the movement of water through rivers, lakes and dams.	• Creates water reserves as well as energy supplies.	• Costly to build. • Can cause the flooding of surrounding communities and landscapes. • Dams have major ecological impacts on local hydrology.

Energy density

Energy density relates the mass of the fuel to the volume it takes up. The higher the energy density, greater the energy may be transported or stored for the same volume. It is an important consideration in fuel choice. The formula is below:

Energy density = Energy released from fuel/volume of fuel consumed

To compare two fuels diesel and liquid hydrogen, the energy densities of them are below:

Liquid hydrogen	4.5 mJ/l
Diesel	37.3 mJ/l

Specific energy

This relates the energy released to the mass:

Specific energy = Energy released from fuel/mass of fuel consumed

This makes different reading to before:

Hydrogen	141.86 MJ/kg
Diesel	46.2 MJ/kg

Application of these two similar but different formula needs to be carefully considered to what context the fuel is to be used. Is weight or volume the most important factor in your choice of fuel?

Fuel efficiency

Efficiency can also be looked at if you know the input energy and how much energy has been given out.

$$\text{The efficiency of an energy transfer} = \frac{\text{Useful output energy}}{\text{Total input energy}} \times 100\%$$

CORE
SPREAD 2: Fossil fuels

Fossil fuels were formed by the reduction of biological compounds that contain carbon, hydrogen, nitrogen, sulfur and oxygen.

Petroleum is a complex mixture of hydrocarbons that can be split into different component parts called fractions by fractional distillation.

Crude oil needs to be refined before use. The different fractions are separated by a physical process in fractional distillation. The tendency of a fuel to auto-ignite, which leads to “knocking” in a car engine, is related to molecular structure and measured by the octane number.

The performance of hydrocarbons as fuels is improved by the cracking and catalytic reforming reactions.

Coal gasification and liquefaction are chemical processes that convert coal to gaseous and liquid hydrocarbons.

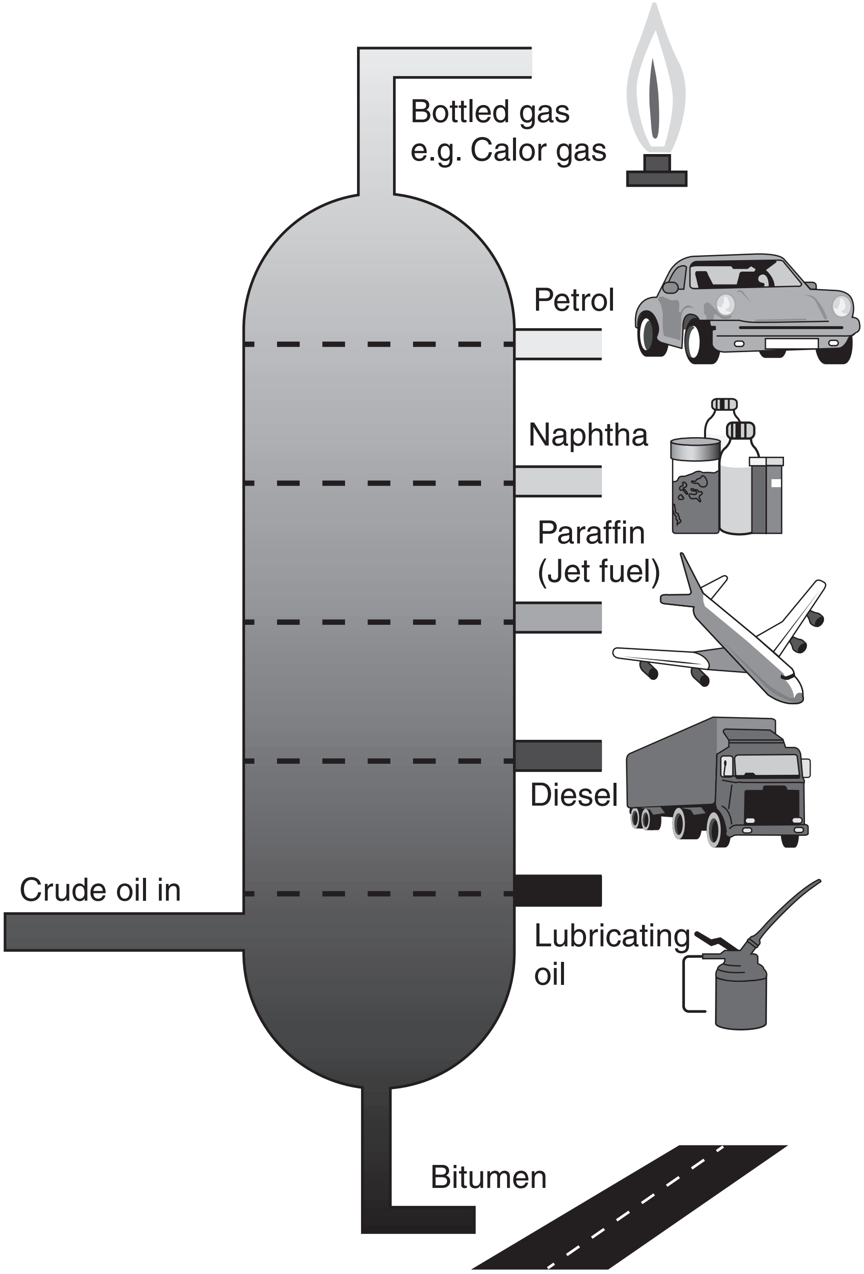
A carbon footprint is the total amount of greenhouse gases produced during human activities. It is generally expressed in equivalent tons of carbon dioxide.

What is a fossil fuel?

Fossil fuels were formed by the reduction of biological compounds that contain carbon, hydrogen, nitrogen, sulfur and oxygen. Our current sources of fossil fuels were formed by these reactions millions of years ago, the process of course continues today but is very slow and of no use to us to solve our energy problems.

Many of our fossil fuels come from a complex mixture of hydrocarbons called petroleum. It is also known as crude oil. It is of no use on its own and needs to be refined before it is useful.

As petroleum is a mixture it can be fractionally distilled to separate all the useful fractions. You have probably studied this before in your pre BDP studies.



The gasoline or petrol fraction is the most useful for use in cars. The fraction has around eight carbons in the alkanes. There are still a few problems.

What are they?

The tendency of a fuel to auto-ignite leads to “knocking” in a car engine. This is related to its molecular structure and measured by the octane number. The more branched the hydrocarbon, the higher the octane number. A glance at octane numbers will show that the more branching, increases the octane number and increases the efficiency of the combustion in the engine. Also the longer the chain, the lower the octane number; however, gasoline needs to be a liquid so chain length factors are restricted to the ones most suitable.

How do we produce branched hydrocarbons?

There are three types of cracking on the syllabus. Each produces shorter chain alkanes and alkenes from long chain alkanes.

1) Catalytic cracking: The hydrocarbons are passed over a silica/alumina catalyst at 1000°C. This tends to produce shorter alkanes and alkenes, which can be used to manufacture plastics.

For example,

$C_8H_{18} \Rightarrow C_6H_{14} + C_2H_4$

2) Catalytic reforming: This takes regular straight chain alkanes and branches them. This improves the octane number.

Octane ⇒ 2,3 dimethyl hexane

3) Cyclisation: This produces cyclic hydrocarbons from straight chain alkanes. To join up the chain it must also produce hydrogen. This can be used in the Haber process or in margarine manufacture.

Hexane ⇒ Cyclohexane + hydrogen

Is there another way of making hydrocarbons for fuels?

Yes: Coal gasification and liquefaction are chemical processes that convert coal to gaseous and liquid hydrocarbons. Coal gasification is a process that turns coal (in situ) into a variety of gases, including CO_2, methane and water. It is carried out at high temperature and pressures. Although it would be nice to include an equation here the complicated chemical formula potentially of coal and the mass of products make it difficult. However, the IB might ask you to write an equation based on information given.

Coal liquefaction

This is a similar process to gasification but converts coal directly into liquid hydrocarbons. There are a variety of ways of doing this. One way involves reacting the coal with hydrogen and a suitable catalyst.

$n\,C + (n + 1)\,H_2 \rightarrow C_nH_{2n+2}$

Finally, well I know all about the pros and cons of fossil fuels but is there a quantitative measure?

You mean the carbon footprint. Carbon footprint is a horribly abused phrase, so it is worth spelling out exactly what it means.

When talking about climate change, *footprint* is a metaphor for the total impact that something has. And *carbon* is a shorthand for all the different greenhouse gases that contribute to global warming.

The term *carbon footprint*, therefore, is a shorthand to describe the best estimate that we can get of the full climate change impact of something. That something could be anything—an activity, an item, a lifestyle, a company, a country or even the whole world.

A carbon footprint is the total amount of greenhouse gases produced during human activities. It is generally expressed in equivalent tons of carbon dioxide. You might be asked to calculate something to do with carbon footprint, but you would have to be given a lot of information as the calculation is an inexact science.

CORE and HL
SPREAD 3: Nuclear energy, an introduction

The fusion of hydrogen nuclei in the sun is the source of much of the energy needed for life on Earth. There are many technological challenges in replicating this process on Earth but it would offer a rich source of energy. Fission involves the splitting of a large unstable nucleus into smaller stable nuclei.

NOTE: This section contains both Core and HL material. The HL material is in **BOLD**.

What is nuclear radiation?

As we know atoms contain protons, neutrons and electrons in varying numbers as noted on the periodic table. Some atoms are more stable than others. In order to achieve stable configurations they "spit" out particles and other radiation from their nucleus. These are classified in three ways.

Alpha α—this consists of a particle made up of two protons or two neutrons, essentially a helium nucleus. Alpha particles are slow and heavy and have little penetrating power.

A typical decay pattern would be

$$^{241}_{95}\mathrm{Am} \rightarrow {}^{237}_{93}\mathrm{Np} + {}^{4}_{2}\alpha$$

Note, the number of protons and neutrons goes down.

Beta β—Protons and neutrons are made of combinations of even smaller particles, called "quarks." Under certain conditions, a neutron can decay, to produce a proton plus an electron. The proton stays in the nucleus, whilst the electron flies off at high speed. Atoms with a high ratio of neutrons to protons often emit beta radiation. Beta particles are smaller and have a greater range.

A decay pattern would be:

$$^{90}_{38}\mathrm{Sr} \rightarrow {}^{90}_{39}\,\mathrm{Y} + \beta$$

Note that as the number of protons goes up, the number of neutrons reduces so mass number stays the same.

Gamma γ—This is a wave, not a particle and so can be emitted from many sources of radiation in addition to alpha and beta. They are highly penetrative.

Half-life

Half-life ($t_{½}$) is the amount of time required for a quantity to fall to half its value as measured at the beginning of the time period. While the term "half-life" can be used to describe any quantity which follows an exponential decay, it is most often used within the context of nuclear physics and nuclear chemistry—that is, the time required, probabilistically, for half of the unstable, radioactive atoms in a sample to undergo radioactive decay. Half-lives are quoted for radioactive isotopes

Using the equation given in the data book you can work out the percentage and amount of radioactive material left after a certain period of time.

Radioactive decay is a first order reaction:

λ = ln2/Half-life

Where λ is the decay constant. More likely you will be asked to work out a half-life from a decay constant, so:

$t½$ = ln2/λ

More manipulating of the math and we get an equation which will help us work out number of atoms left after a certain period of time

The nuclear half-life equation is:

$$N_t = N_0\, e^{-\lambda t}$$

(Note that the number "*e*" is the "natural" exponential, because it arises naturally in math and the physical sciences [i.e., in "real life" situations], just as *pi* arises naturally in geometry. It is 2.71828.)

N_0 **= the initial quantity of particles**
N_t **= the number of particles left at a given time**
λ **is the decay constant and it is worked out using**
0.693/half-life
t **= time**

An example:

A sample of radium contains 6.64×10^{23} atoms. It emits alpha particles and has a half-life of 1620 years. How many atoms are left after 100 years?

First let us work out λ:

$$0.693/1620 = 0.000427$$

Multiply by $t = -0.000427 \times 100 = 0.0427$

So plugging into the original equation:

$$N_t = 6.64 \times 10^{23}\, e^{-0.0427} = 6.36 \times 10^{23} \text{ particles}$$

You might be expected to manipulate the equation above to find either the time or the amount or percentage of particles reaming, but the math principles are the same.

CORE

SPREAD 4: Nuclear fusion

Light nuclei can undergo fusion reactions as this increases the binding energy per nucleon.

Fusion reactions are a promising energy source as the fuel is inexpensive and abundant, and no radioactive waste is produced.

Absorption spectra are used to analyze the composition of stars.

OK so nuclear fusion, what is it?

Well nuclear means of the nucleus and fusion means joining together. It is when two nuclei join together to make a bigger nucleus The process only takes place at a very high energy, but when it does happen a lot of energy is also released. If a way could be found to carry out nuclear fusion at low temperatures, then the energy problems of our world would be solved. Especially as there would be no radioactive water. Sadly, this seems a long way off. The reaction works according to Einstein's $E = mc^2$ formula. When the fusion occurs, a little bit of the atoms' mass is turned into kinetic energy in the form of heat energy.

Let us get a bit more technical. The particles in a nucleus (protons and neutrons) are collectively called nucleons (we're in physics territory here). They all have mass but their collective mass DOES NOT ADD UP to the mass of the nucleus. **The difference between them is the binding energy; the energy is required to split up the nucleus into protons and neutrons**. Binding energy increases as mass number increases up until iron, which is the most stable nucleus. That means by fusing two nuclei together you increase the binding energy, or if you prefer, the amount of energy needed to smash them up. There is a release of energy as nucleon is given off as mass and energy are essentially interchangeable here. **The Mass Defect is this difference in mass of the nucleus and the sum of the masses of its individual nucleons.**

$${}^{2}_{1}\mathrm{H} + {}^{3}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{1}_{0}n$$

Binding energy per nucleon

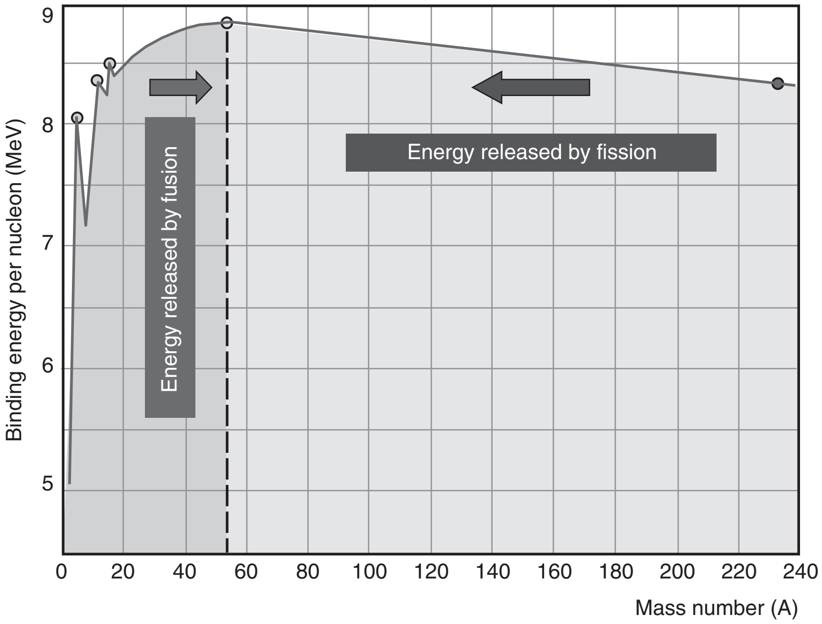
This is simply the binding energy in MeV (mega electron volts) divided by mass of the nucleons.

Binding energy is easily calculated as 931 MeV is assumed to be the binding energy per atomic mass unit. So you subtract the nuclear mass from the nucleon mass and multiply by 931 to get the answer in column 4.

Try it with the examples below:

Element	Mass of nucleons (u)	Nuclear mass (u)	Binding energy (MeV)	Binding energy per nucleon (MeV)
Deuterium	2.01594	2.01355	2.23	1.12
Helium 4	4.03188	4.00151	28.29	7.07
Lithium 7	7.05649	7.01336	40.15	5.74
Beryllium 9	9.07243	9.00999	58.13	6.46
Iron 56	56.44913	55.92069	492.24	8.7906
Silver 107	107.86187	106.87934	915.23	8.55
Iodine 127	128.02684	126.87544	1072.53	8.45
Lead 206	207.67109	205.92952	1622.27	7.88
Polonium 210	211.70297	209.93683	1645.16	7.83
Uranium 235	236.90849	234.99351	1783.80	7.59
Uranium 238	239.93448	238.00037	1801.63	7.57

Helium 4 has particularly high binding energy and the fusion of this is of particular interest.



Most fusion reactions happen in stars which are made up mainly of hydrogen and helium nuclei. This can be shown by looking at the characteristic atomic absorption spectra of stars. See Chapter 2 for more information on the lines in AA spectra.

CORE and HL
SPREAD 5: Nuclear fission

Heavy nuclei can undergo fission reactions as this increases the binding energy per nucleon.

^{235}U undergoes a fission chain reaction: $U^{235}{}_{92} + n^{1}{}_{0} \rightarrow U^{236}{}_{92} \rightarrow X + Y +$ neutrons.

The critical mass is the mass of fuel needed for the reaction to be self-sustaining.

^{239}Pu, used as a fuel in "breeder reactors," is produced from ^{238}U by neutron capture.

Radioactive waste may contain isotopes with long and short half-lives.

Half-life is the time it takes for half the number of atoms to decay.

What is nuclear fission?

Nuclear fission is the opposite of nuclear fusion. This is where nuclei split up releasing a variety of particles and a lot of energy. The reaction can occur naturally in radioactive decay situations, or it can be provoked by a nuclear reaction. Nuclear fission is possible because in heavy nuclei (above iron) the binding energy (the measure of stability of a nucleus) increases as the atom gets smaller. The technical way of expressing this is that the binding energy per nucleon increases.

Fission chain reaction examples:

Uranium when bombarded with neutrons will undergo fission producing two new elements and more neutrons (often this written with an intermediate $U^{236}{}_{92}$):

$$^{235}_{92}\mathrm{U} + ^{j}_{0}n \rightarrow ^{142}_{58}\mathrm{Ba} + ^{91}_{36}\mathrm{Kr} + 3^{l}_{0}n$$

The expelled neutrons can be used to continue the process in what is known as a chain reaction.

You might be expected to write nuclear equations like this given simple information.

The CRITICAL MASS is the amount of fuel (isotope here) that is needed for the chain reaction to be self-sustaining.

Breeder reactors

These are nuclear reactors that take nonfissile Uranium 238 and bombard it with neutrons. The process causes beta particles to be emitted (add the section from elsewhere on these equations). As a beta particle emits a neutron and effectively adds a proton, eventually you end up with Plutonium 239. It is easier to make Plutonium 239 this way (it is a very effective material) than to refine Uranium 235.

Storage and disposal of nuclear waste

There are two types of ionizing radiation:

Low-level waste, which includes items like rubber gloves, and other protective clothing give off small amounts of ionizing radiation for a short time.

This sort of waste can be disposed of in the sea, where it can be diluted, although this is not the best practice anymore. It can be stored in "ponds" for a period where its radiation can lose a lot of its activity before it is put into the sea. Other alternatives include storing it in concrete-lined vaults.

High-level waste, which generally includes the samples of the isotopes themselves, gives off much larger amounts of radiation over a longer period of time.

This is harder to dispose of. If recycling can be carried out, or further processing, then this will happen. The remainder will often be vitrified. The waste is dried in a furnace and made into a material like glass. This is solidified and stored in steel tubes. As the radiation can last thousands of years, storage of such waste is long-term problem. Currently it is stored in remote regions of high geological stability.

The length of the half-life of an isotope is a huge factor, with plutonium 239 having a half-life well over 20,000 years, so the process has to be permanent. Other factors to seriously consider include terrorist theft of Pu and U for making of nuclear bombs, see the Alexandr Litvninenko case and plant meltdown cases like Fukushima and Chernobyl. The health risks are well-known and include increased risks of cancer.

Ionizing radiation is dangerous because it produces oxygen-free radicals like superoxide O_2 and hydroxyl OH. These initiate chain reactions that can damage DNA and enzymes in the body.

Fuel enrichment with uranium

Natural uranium contains 99% of Uranium 238, a not particularly radioactive element and less than 1% Uranium 235, which is very useful for nuclear fission. The problem is separating the two isotopes, as they weigh very nearly the same. The methods employed successfully involve converting the uranium into the very heavy gas uranium hexafluoride (UF_6), which is covalently bonded compared to the UO_2 ionic substance it is derived from. From this you can either use a diffusion method or gas centrifuge. The U^{235} left is called enriched uranium. The remaining U^{238} is called depleted uranium.

Diffusion

Diffusing the gas across a semi-permeable membrane will cause a slight separation of the two isotopes. Thermal diffusion is better because the U^{235} will move to the hot plate, the U^{238} away from the hot plate.

The rate of diffusion can be calculated using Graham's Law:

$$\frac{\mathbf{Rate}_1}{\mathbf{Rate}_2} = \sqrt{\frac{M_2}{M_1}}$$

So, with uranium,

Rate 1/rate 2 = square root 352 (RMM U^{238}F6/RMM $U^{235}F_6$)

1.004/1

As you can see it is not a huge difference.

Gas centrifuge

This is a machine that spins the gas. The centrifugal forces act upon the differently weighing particles. The U^{238} particles collect on the edges of the centrifuge. The less dense U^{235} collects closer to the center.

CORE
SPREAD 6: Solar energy

Light can be absorbed by chlorophyll and other pigments with a conjugated electronic structure.

Photosynthesis converts light energy into chemical energy: $6CO_2 + 6H_2O \Rightarrow C_6H_{12}O_6 + 6O_2$

Fermentation of glucose produces ethanol, which can be used as a biofuel: $C_6H_{12}O_6 \Rightarrow 2C_2H_5OH + 2CO_2$

Energy content of vegetable oils is similar to that of diesel fuel but they are not used in internal combustion engines as they are too viscous.

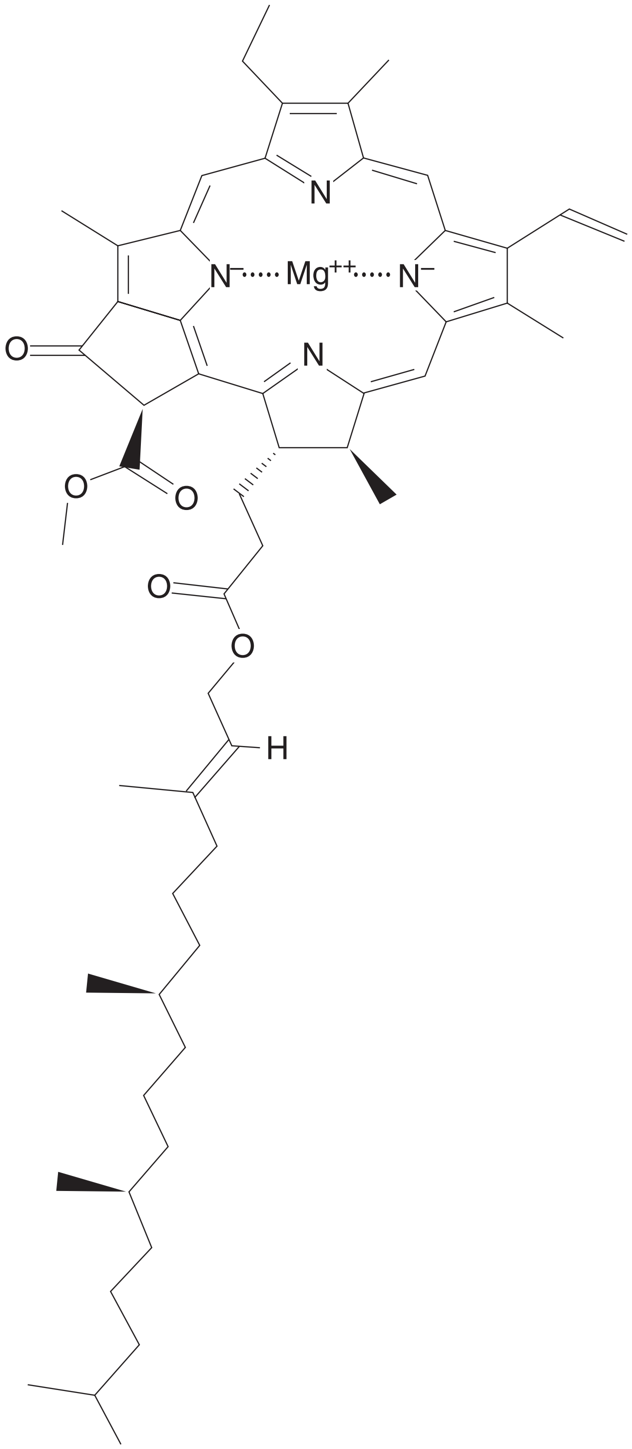
Transesterification between an ester and an alcohol with a strong acid or base catalyst produces a different ester: $RCOOR^1 + R^2OH \Rightarrow RCOOR^2 + R^1OH$

In the transesterification process, involving a reaction with an alcohol in the presence of a strong acid or base, the triglyceride vegetable oils are converted to a mixture mainly comprising of alkyl esters and glycerol, but with some fatty acids.

Transesterification with ethanol or methanol produces oils with lower viscosity that can be used in diesel engines.

Note, this topic contains both Core and HL material. The HL material is written in **bold.**

Chlorophyll



Chlorophyll is a very important molecule in plants. As you probably know the molecule is responsible for photosynthesis:

$6CO_2 + 6H_2O \Rightarrow C_6H_{12}O_6 + 6O_2$

Chlorophyll is the molecule that allows the conversion of light energy into stored chemical energy in glucose. It works because (as you can see in the molecule) it contains a conjugated system of alternating double and single bonds. This sort of system is very good at absorbing light of a particular wavelength. **The longer the conjugated system, the longer the wavelength of light it can absorb**. Any system containing such a structure will have similar colored effects. Beta Carotene is another good example. Parts of a molecule that contain such systems are called chromophores.

What has this got to do with energy?

Well if you can use the sun's energy to create glucose then you can harvest the plant and use the glucose to ferment to ethanol and then you have a biofuel:

$$C_6H_{12}O_6 \Rightarrow 2C_2H_5OH + 2CO_2$$

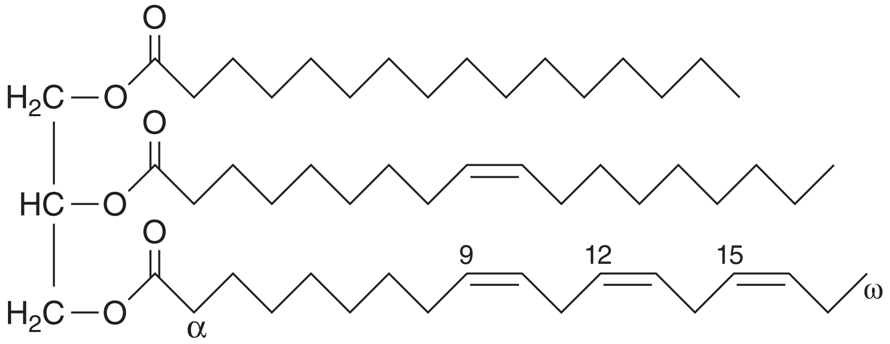
This is the same process used to ferment sugar into alcohol to make alcoholic beverages. Yeast is used to convert the glucose into ethanol, so the process has to take place below 27°C.

Uses of vegetable oils as fuel

Vegetable oils contain a similar amount of energy to diesel oil and seem to be a good alternative to fossil fuels given the renewable nature of the raw material. The problem is that vegetable oils can be too viscous to use in conventional engines, although progress is being made. Vegetable oils are made from triglyceride esters.

One way of making the fuels less viscous is to use a transesterification reaction. This swaps the alcohol groups in the presences of a strong acid or a base.

Vegetable oils are known as fatty acids and can appear in a variety of forms. Often as a triglyceride ester seen below. By applying transesterfication to this molecule using ethanol or methanol as the alcohol, the long side chains can be separated and the chain length shortened and the viscosity decreased. This produces alkyl esters and glycerol.



Evaluation of the advantages and disadvantages of the use of biofuels

Clearly biofuels have the advantage of not being made from fossil fuels, and it can be argued that they are "carbon neutral." This is because although they combust to produce CO_2 like any regular fuel, this is offset by the removing of CO_2 by the growing process. Disadvantages include the huge amounts of land required to produce enough crop to make a decent amount of fuel. This could mean that land currently used for food crop is not used anymore. Either way there could be huge environmental problem. The process of getting the oil is a lot easier than using fossil fuels and can be done anywhere where there is reasonably fertile soil. Therefore, it would allow all countries in the world to be more in control of their fuel needs than be at the mercy of fuel oil–rich states.

HL
SPREAD 7: What is a semiconductor?

The electrical conductivity of a semiconductor increases with an increase in temperature whereas the conductivity of metals decreases.

The conductivity of silicon can be increased by doping to produce n-type and p-type semiconductors.

Solar energy can be converted to electricity in a photovoltaic cell.

DSSCs imitate the way in which plants harness solar energy. Electrons are "injected" from an excited molecule directly into the TiO_2 *semiconductor.*

The use of nanoparticles coated with light-absorbing dye increases the effective surface area and allows more light over a wider region of the visible spectrum to be absorbed.

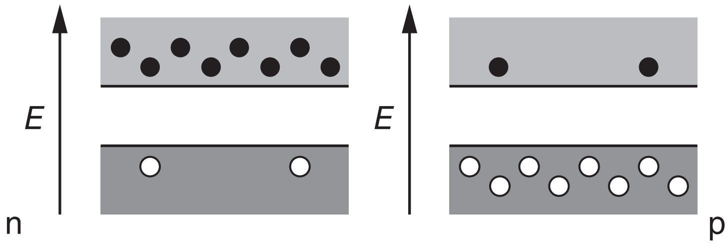
What is a semiconductor?

It is important that you are happy with exactly what a semiconductor is. You will be aware that metals conduct electricity because they have free electrons available to carry electric charge. You will also be familiar with the idea of nonmetals not being able to conduct electricity because the electrons are not able to move and carry electric charge. Silicon falls somewhere in the middle. It does not have free electrons to carry electric charge, but the energy needed to remove an electron is within the range of the energy in visible light. So if a voltage is applied to some silicon in sunlight it conducts electricity as the free electron can move around the lattice. The process is not very efficient. This is known as the photoelectric effect. The electrical conductivity of a semiconductor increases with heat, whereas the electrical conductivity of a metal decreases with heat.

How can we increase the conductivity of silicon and other semiconductors?

The process above can be made more efficient and useful by the process of "doping." This involves adding other atoms from either group 3 or group 5 to the silicon. If you add a group 3 element (e.g., Al, Ga, In) to the silicon the group 3 element takes the place of a silicon atom in the lattice (see diagram). The group 3 element has one less electron and leaves a "hole" in the lattice where the electron should be. The electron, excited by light moves around, leaving a hole (effectively an area of positivity) which can move along the lattice. This is a p-type semiconductor because it is a positive carrier.

If you add a group 5 element (As, P) you will be adding an extra electron to the lattice because they have an extra electron in their outer orbital. As it has an extra electron this allows the photoelectric effect to be more pronounced. It is an n-type semiconductor because the moving thing in the lattice is an electron (see diagram).



White hole, black electrons

So what is a photovoltaic cell?

Photovoltaic or solar cells operate on the principles above. Photons of light shine on the cell and this excites the electrons (or holes) to conduct electricity. This electric current can be used for a variety of applications.

Dye sensitized solar cells (DSSC)

They try and operate in the same way as chlorophyll works in plants. The technology uses organic dyes containing chromophore groups in a titanium dioxide nanoparticle layer. This has a huge surface area and allows a lot of light to be converted. In a typical photoelectric cell, the silicon acts as the receiver of the light and the transmitter. Here the dye excites the electrons which flow into the "semiconducting" titanium oxide and the electricity is generated.

1. The incident photon is absorbed by Ruthenium complex photosensitizers adsorbed on the TiO_2 surface.
2. The photosensitizers are excited from the ground state (S) to the excited state (S^*). The excited electrons are injected into the conduction band of the TiO_2 electrode. This results in the oxidation of the photosensitizer (S^+).

   $S + h\nu \rightarrow S^*$ (1)

   $S^* \rightarrow S^+ + e^-$ (TiO_2) (2)

3. The injected electrons in the conduction band of TiO_2 are transported between TiO_2 nanoparticles with diffusion toward the back contact (TCO). And the electrons finally reach the counter electrode through the circuit.
4. The oxidized photosensitizer (S^+) accepts electrons from the I^- ion redox mediator leading to regeneration of the ground state (S), and the I^- is oxidized to the oxidized state, I_3^-.

   $S^+ + e^- \rightarrow S$ (3)

5. The oxidized redox mediator, I_3^-, diffuses toward the counter electrode and then it is reduced to I^- ions.

   (4)$I_3^- + 2e^- \rightarrow 3I^-$

They are very efficient, they can work in low light, but the liquid electrolytic means that it cannot be operated at extreme temperatures (it could freeze). Also the volatile solvents used in the electrolyte mean spillages and breakages can be a hazard to human health. Also disposal.

CORE
SPREAD 8: Environmental impact—global warming

Greenhouse gases allow the passage of incoming solar short wavelength radiation but absorb the longer wavelength radiation from the Earth. Some of the absorbed radiation is reradiated back to Earth.

There is a heterogeneous equilibrium between concentration of atmospheric carbon dioxide and aqueous carbon dioxide in the oceans.

Greenhouse gases absorb IR radiation as there is a change in dipole moment as the bonds in the molecule stretch and bend.

Particulates such as smoke and dust cause global dimming as they reflect sunlight, as do clouds.

What are greenhouse gases?

Greenhouse gases allow the passage of incoming solar short wavelength radiation but absorb the longer wavelength radiation from the Earth. Some of the absorbed radiation is reradiated back to Earth.

We need global warming. We need greenhouse gases. Both have maintained a livable temperature on Earth for millions of years.

The Sun bombards Earth with shortwave ultraviolet and visible radiation. Most would be reflected straight back into space were it not for greenhouse gases in the atmosphere that absorb the radiation. The radiation hits the earth as UV but as it reflects back its infrared region.

This establishes an equilibrium between the energy reaching the earth from the sun and the energy reflected back. The problem is that man-made greenhouse gases could be upsetting the equilibrium causing more gases to exist in the atmosphere, so more heat trapped and the earth slowly warms.

The infrared light causes the bonds in greenhouse to bend and stretch as if they were in an infra spectrometer and the gases absorb this radiation. Molecules that contain bonds that are susceptible to IR stretching and bending are good greenhouse gases. So CO_2, methane and so on are all good gases. Nitrogen and oxygen are not (diatomic molecules do not respond to IR radiation). They absorb the radiation and there is a change on the dipole moment as they stretch and bend.

Sources, abundance and effects of greenhouse gases

Gas	Produced by	Abundance g	Global warming potential
CO_2	Burning of fossil fuels	0.03%	1
H_2O	Burning of fuels, evaporation	1%	0.1
CH_4	Farming decay products	Neg	30

Although CO_2 isn't a great greenhouse gas the huge amounts deposited into the atmosphere have caused its effect to be magnified.

Evidence of global warming

The arguments for and against and the evidence for the problem are well-known these days. The science is clear on the global warming potential of these gases. Conspiracy theorists and other skeptics tend to dwell on other factors and ignore the one factor which humans find very difficult to quantify: time. The process is very slow and happens gradually. I would guide you to Al Gore's "An inconvenient Truth." But there are glaring problems with the way he, a politician, presents his arguments.

CO_2 equilibrium with the oceans

The oceans contain a lot of carbon dioxide dissolved in them. There is another equilibrium set up between the atmospheric CO_2 concentrations and those in the atmosphere (heterogeneous). This too can be disturbed. The oceans have absorbed almost one-half (approximately 525 billion tons) of human-released CO_2 emissions since the Industrial Revolution. Although this has moderated the effect of greenhouse gas emissions, it is chemically altering marine ecosystems 100 times more rapidly than it has changed in at least the last 650,000 years. Recent studies suggest that the oceans are becoming less able to absorb as much carbon dioxide as they have in the past, decreasing their ability to buffer against climate change. By absorbing massive amounts of carbon dioxide, the pH (a measure of acidity) in ocean surface waters has dropped approximately 30%. As CO_2 dissolves in the ocean, the water becomes more acidic and the amount of dissolved carbonate available for calcium carbonate shell and skeleton formation—important to corals, plankton and shellfish—decreases.

The oceans are alkaline, meaning they are above 7 on the pH scale (7 is neutral, below 7 is acidic and above 7 is alkaline). Prior to industrialization, the pH of the oceans was on average about 8.2; however, since then, the average pH has dropped about 0.1 units. While this may seem like a small change, it actually represents a 26% increase in acidity.

The International panel on Climate Change (IPCC) determined that according to mid-range projections (522 ppm CO_2 in 2050) for future emissions of CO_2, the pH of the oceans will decline an additional 0.3–0.4 units by 2100, becoming 2 to 2.5 times more acidic than preindustrial levels. Marine life as we know it is not adapted to these conditions.

Particulates

There is a counter-problem to global warming: global dimming. This is when particulate matter (from volcanoes and soot, smoke and dust from industrial process) get into the atmosphere, causing greater cloud cover by complicated series of reactions. They can scatter the shortwave radiation from the sun before it gets to the surface and reflect it back into space. The drop in global temperatures widely associated with global warming skeptics between 1955 and 1976 has often been blamed on the huge amount of volcanic activity at that time spitting lots of sulfur particulates into the atmosphere. There are wild ideas of adding more particulates to the atmosphere to offset the problem associated with global warming!

Controlling CO_2 emissions

Efficiency and conservation

There are many energy efficiency and conservation practices that reduce the consumption of carbon-based fuels (e.g., natural gas, oil, coal or gasoline):decreasing carbon dioxide emissions, improving the efficiency of machines that run off fuels so that less fuel is needed recycling as much plastic as we can and so on.

Carbon-free and reduced-carbon energy sources

Another way to reduce carbon dioxide emissions is to use carbon-free or reduced-carbon sources of energy. Carbon-free sources of energy have their own associated impacts, but in general, these technologies generate energy without producing and emitting carbon dioxide to the atmosphere. Carbon-free energy sources include solar power, wind power, geothermal energy, low-head hydropower, hydrokinetics (e.g., wave and tidal power) and nuclear power. Alternatively, switching from high-carbon fuels like coal and oil to reduced-carbon fuels such as natural gas will also result in reduced carbon dioxide emissions.

Carbon capture and sequestration

A third option for reducing carbon dioxide in the atmosphere is carbon sequestration. Carbon sequestration involves the capture and storage of carbon dioxide that would otherwise be present in the atmosphere, contributing to the greenhouse effect. As described on the Carbon Sequestration Approaches and Technologies page, carbon dioxide can be removed from the atmosphere and retained (stored) within plants and soil supporting the plants. Alternatively, carbon dioxide can be captured (either before or after fossil fuel is burned) and then be stored (sequestered) within the earth. Methods include storing CO at the bottom of oceans or in abandoned mine shafts or reacting with metal oxides to form carbonates.

Cap and trade and market-based controls

In the face of growing concerns about global warming, efforts to reduce carbon dioxide emissions have introduced legal and economic carrot and sticks to prevent the excessive emission of greenhouse gases.

HL

SPREAD 9: Electrochemistry, rechargeable batteries and fuel cells

An electrochemical cell has internal resistance due to the finite time it takes for ions to diffuse. The maximum current of a cell is limited by its internal resistance.

The voltage of a battery depends primarily on the nature of the materials used while the total work that can be obtained from it depends on their quantity.

In a primary cell the electrochemical reaction is not reversible. Rechargeable cells involve redox reactions that can be reversed using electricity.

A fuel cell can be used to convert chemical energy, contained in a fuel that is consumed, directly to electrical energy.

Microbial fuel cells (MFCs) are a possible sustainable energy source using different carbohydrates or substrates present in waste waters as the fuel.

Electrochemical cells

What factors affect the voltage and current in a battery?

This section presupposes that you are familiar with the material on voltaic cells in the main section of the syllabus.

Voltage of a battery is of course dependent on the materials used to make the cell up. The bigger the electrode potential difference, the bigger the voltage—potentially. The Nernst equation is useful for working out the E_{cell} at nonstandard temperatures:

$$E_{\text{cell}} = E^{\ominus}_{\text{cell}} - \frac{RT}{zF}\ln Q$$

Most of this is fairly obvious, R being the gas constant, z being number of moles, T being temperature, F being the faraday constant. Q is reaction quotient, usually the concentration of the reduced species over the concretion of the oxidized species.

Example:

Work out the EMF of a cell containing 1.0 moldm^{-3} Zn¦Zn^{2+} and 0.5 moldm^{-3} Cu¦Cu^{2+}.

$$E_{\text{cell}} = E^{\ominus}_{\text{cell}} - \frac{RT}{zF}\ln Q$$

Voltage of cell (worked out in the usual way)

$0.76 + 0.34 = 1.10$

So E_{cell} = 1.10 − 8.31 × 298/2 × 96,500. ln 1.0/0.5
= 1.10 − 8.31 × 298/2 × 96,500. 0.69
= 1.10 − 2476/193,000. 0.69
= 1.10 − 0.012. 069
= 1.10 − 0.00828 = 1.09 volts

Total work obtained from a battery is dependent on the quantity of the materials making up the electrode. You get more current per unit time with more electrode material.

All batteries have an internal resistance. This is related to the time it takes for the ions to diffuse. This limits the maximum current of a battery. Internal resistance increases as batteries get older.

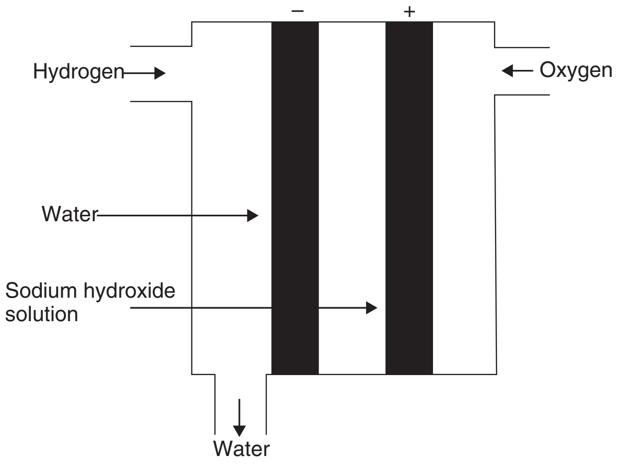
How a hydrogen-oxygen fuel cell works

The voltaic cells met on the core course were very simple. The chemical energy was stored in the voltaic cell (a series of these is called a battery). A fuel cell is a modified version of this where chemicals are continuously supplied to the cell. These chemicals react at the electrodes to produce electrical energy. Car companies are enormously interested in this idea, as it could be used to power environmentally friendly vehicles.

The ideal reaction for such cells is this one because the waste product is simply water:

$$2H_2 + O_2 \rightarrow 2H_2O$$

The fuel cell works like this:



- The basic cell has two porous platinum electrodes (although graphite is a cheaper alternative). The electrolyte is aqueous sodium hydroxide.
- Hydrogen is pumped through one side of the cell, oxygen to the other.

At the hydrogen electrode:

$$4H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$$

The electrons produced go round the circuit and do work (i.e., power the vehicle), then end up at the oxygen electrode.

At the oxygen electrode:

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

The hydroxide ions are recycled, which means the battery never needs to be recharged. Such cells are still expensive and potentially dangerous as hydrogen and oxygen have to be stored in the vehicle.

Note that the IB syllabus stresses the need for the candidate to write equations in for an acid solution too. The equations are below:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$
$$H_2 \rightarrow 4H^+ +4e^-$$

Methanol can also be used as a fuel in acid conditions. The equations are below:

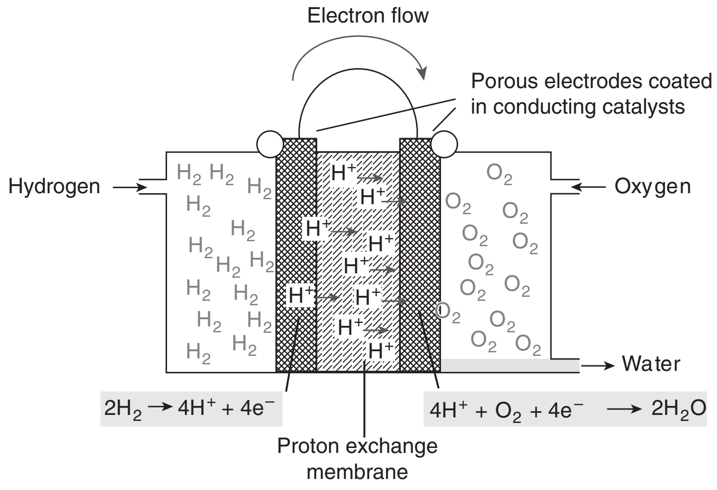
Anode	$CH_3OH + H_2O \rightarrow 6H^+ + 6e^- + CO_2$ Oxidation
Cathode	$\frac{3}{2}O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$ Reduction
Overall reaction	$CH_3OH + \frac{3}{2}O_2 \rightarrow 2H_2O + CO_2$ Redox reaction

These cells are limited in their power but have the advantage of not needing a supply of hydrogen. They are also quite inefficient.

SPREAD 10: Proton exchange membrane fuel cells (PEMFC)

These operate in a similar way chemically to a conventional fuel cell. The membrane here is made of a polymer that will conduct hydrogen ions but not allow gases to mix.

One of these types is called a Proton Exchange Membrane Fuel Cell (PEMFC), or a Polymer Electrolyte Membrane Fuel Cell (also PEMFC). There is a simplified diagram below:



Essentially, this has two metal electrodes covered with a fine layer of metal catalyst, for example platinum. This catalyzes the reactions at the two electrodes.

Sandwiched between these is a polymer-based membrane through which protons (hydrogen ions) can diffuse.

One electrode is exposed to hydrogen gas; the other to oxygen or air.

The catalyst on the electrode exposed to the hydrogen catalyzes the reaction:

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

You may notice that I have doubled that equation on the diagram above. I will explain why in a moment.

On the electrode exposed to the oxygen, this happens:

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

So, overall, at the left-hand electrode, hydrogen molecules ionize to give hydrogen ions and electrons.

Those hydrogen ions diffuse through the membrane to the right-hand electrode, where they react with oxygen to make water.

The overall reaction in the fuel cell can be found by adding the two equations together, but because of the need for four electrons at the right-hand electrode, the hydrogen equation has to happen twice.

$2H_2 \rightarrow 4H^+ + 4e^-$
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Giving:

$2H_2 + O_2 \rightarrow 2H_2O$

Notice that the only waste product from this cell is water.

I was going to show you how to use electrode potentials to find the EMF of a cell like this, but just realized that you can't do that! Standard electrode potentials relate to ions in solution. In this particular case you don't have solutions—certainly not at the electrode on the hydrogen side. We will look at electrode potentials in the next example instead.

Microbial fuel cells

These are cells where in anaerobic conditions the microbes in an aqueous sugar solution produce electrons instead of CO_2 and water. These electrons are transferred to an anode and the fuel cell operates under this principle. The carbohydrate can be changed as can the water to waste water and so on. It is a possible sustainable fuel cell for the future. Similar optimism hold for geobacter bacteria, found in so-called mud batteries. The bacteria found in mud convert substrates found in waste water to use as fuel which generates electricity. This could be used to clean up waste water in the future.

HL
SPREAD 11: Rechargeable batteries

Lead-acid battery

In a typical voltaic cell met on the core course, the cell provides electrical energy only for as long as the chemicals are present. Once used up, the cell is dead. It is not reversible. If these cells are made into a normal batter, then the batter is "dead" once used up. Rechargeable batteries do not have this problem: the reaction is reversible. The traditional rechargeable battery is the large lead-acid batteries found in cars.

The anode (+) is made of lead (IV) oxide.

The cathode (–) is made of lead.

The electrolyte is a sulfuric acid (H_2SO_4) solution.

When the battery is used, the lead electrode is oxidized to SOLID lead sulfate:

$Pb + SO_4^{2-} \rightarrow PbSO_{4(s)} + 2e^-$

The electrons travel around the circuit, do work and end up at the lead oxide electrode where …

The lead oxide electrode is reduced to SOLID lead sulfate.

$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_{4(s)} + 2H_2O$

It is important that you learn these two half equations
The overall equation is (gained from combining the two equations above):

$Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \rightarrow 2PbSO_4 + 2H_2O$

To recharge the battery the equation is reversed by using a battery charger or the car's alternator while in motion. Sulfuric acid gets used up and needs to be topped up occasionally. The high mass of the battery and the pollutant potential of both lead and sulfuric acid has provoked further research into rechargeable batteries.

Nickel-cadmium batteries and lithium ion batteries

In a nickel cadmium battery, the anode is made of nickel hydroxide and the cathode is made of cadmium hydroxide. The electrolyte is potassium hydroxide.

At the anode:

$NiO(OH) + H_2O + e^- \rightarrow Ni(OH)_{2(s)} + OH^-$

At the cathode:

$Cd(OH)_2 + 2e \Rightarrow Cd_{(s)} + 2OH^-$

Similarities and differences between fuel cells and rechargeable batteries

Fuel cells do not need recharging whereas batteries do. They do not produce poisonous pollutants whereas batteries do. However, fuel cells are much more expensive than rechargeable batteries at the current time.

Concentration cell

A concentration cell has the same electrodes and electrolytes on both sides of the cell; the only difference is the concentrations of the two electrolytes. This difference produces an electric current that can be deduced from the Nernst equation, see above.

Thermodynamic efficiency

Thermodynamic efficiency is a simple measure of the efficiency of a cell in percentage terms. It is

Thermodynamic efficiency = $\Delta G/\Delta H$

ΔG can be calculated by $\Delta G = -nFE$
Where n = number of moles, F = faraday constant and E is the electrode potential.

CHAPTER

16 Medicinal chemistry

This chapter covers the material covered in Option Module D: Medicinal Chemistry.

CORE
SPREAD 1: Pharmaceutical products and drug action

In animal studies, the therapeutic index is the lethal dose of a drug for 50% of the population (LD50) divided by the minimum effective dose for 50% of the population (ED50).

In humans, the therapeutic index is the toxic dose of a drug for 50% of the population (TD50) divided by the minimum effective dose for 50% of the population (ED50).

The therapeutic window is the range of dosages between the minimum amounts of the drug that produce the desired effect and a medically unacceptable adverse effect.

Dosage, tolerance, addiction and side effects are considerations of drug administration.

Bioavailability is the fraction of the administered dosage that reaches the target part of the human body.

The main steps in the development of synthetic drugs include identifying the need and structure, synthesis, yield and extraction.

Drug–receptor interactions are based on the structure of the drug and the site of activity.

Basics: What is a drug or medicine?

These are chemicals that have a known biological effect on humans or other animals. In the positive sense drugs and medicines are substances that can cure, prevent or help diagnose disease, or enhance physical well-being. Drugs of course can be misused for recreational purposes, especially hallucinogens.

All drugs have side-effects, an effect the drug has on the body that is secondary to the one intended. These can have adverse effects, or can be beneficial. Sometimes side-effects are of great concern, some will be minor. The seriousness of the disease the drug is being used for will affect the amount of side-effects tolerated in the drug.

Methods of administering drugs

It is important that drugs get into the blood stream as quickly as possible in order for them to reach the site where their effects will be needed. This can be via the stomach, lungs or directly into the bloodstream.

There are five common ways in which drugs can be administered.

- Orally—in the form of tablets or medicines.
- Inhalation—in the form of nasal sprays.
- Via the skin—for treatment of skin conditions and other localized irritation.
- Rectally—the anus has a good supply of blood vessels and so drugs work quicker; less nausea can be experienced with the more traditional oral route.
- Via injection.

Injection needs to be administered by professionals and falls into three further categories:

Subcutaneous—injected directly under the skin. This is used mainly for insulin injections for people with type 1 diabetes.
Intramuscular—injected into the muscle. Favored spots include the dorso-gluteal muscles in the buttocks and the deltoid muscle in the arm; this is the most common form of injection and is used for vaccines, sedatives and painkillers.
Intravenous—injected directly into a vein. These are often specialty pharmaceuticals and are commonly known as a "drip." This is the fastest way to administer drugs but also the most dangerous and highly skilled.

How do drugs work?

Drugs can kill foreign organisms, such as bacteria, worms and viruses. These are selectively toxic drugs.

Some drugs act by stimulating or depressing normal biological functions. These drugs often act on cell membranes through specific drug receptor sites. These interactions can either block the normal pharmacological response (depressing normal function)—this is an **antagonist,** or give the normal pharmacological response (initiates the normal function); this is an **agonist.**

Drug–receptor interactions are based on the structure of the drug and the site of activity.

What is the right drug for the job?

A few more definitions:

- Tolerance—the body can get used to the administered drug, which means more and more of the drug needs to be taken to have the desired effect. It is possible for a lethal dose to be administered.
- Addiction—is the compulsive need to use the drug to function normally. The user can suffer withdrawal symptoms if the drug is unavailable.
- Dosage—is the amount of the drug administered for therapeutic purposes.

The ideal drug is easy to take, needed only in small doses, is non-addictive, side-effect free and does not allow a tolerance to build up. Such perfect drugs do not exist, and judgments need to be made when developing drugs as to how serious the ailment is compared with any side-effects and other factors. This is known as the risk-to-benefit ratio. A hay-fever cure that causes severe addiction would not be on sale, yet a drug that can cure cancer can also cause severe side-effects because the life-saving benefits are worth it.

CORE
SPREAD 2: New drugs

Research and development of new drugs

Pharmaceutical companies are constantly searching for new and better drugs and spend billions testing and researching possible leads.

They will look at the following things in the first instance:

- Therapeutic index
- In humans this is the lethal dose of the drug in 50% of the population (LD50) divided by the minimum effective dose in 50% of the population. The effective dose being "bringing about a noticeable effect."

$$\text{Therapeutic index} = \frac{\text{TD50}}{\text{ED50}}$$

In animals this is the lethal dose of the drug in 50% of the population (LD50) divided by the minimum effective dose in 50% of the population.

$$\text{Therapeutic index} = \frac{\text{LD50}}{\text{ED50}}$$

Note the subtle difference. In a testing program the drug is tested on animals first in order to determine the toxic dose.

Once it gets past the animal testing stage it will be tested on humans to work out the toxic dose (not the lethal dose) and cross tested with a placebo to ensure the results are true. A placebo is a medically ineffective treatment designed to act as a control in such experiments.

The Therapeutic Window is the range of dosages between the minimum amounts of the drug that produce the desired effect and the amount that causes a medically unacceptable adverse effect.

It is considered morally questionable these days to test animals and humans excessively these days, and therefore for ethical and economic reasons such tests are now kept to a minimum.

Bioavailability

This is another factor to consider. It is the fraction of the administered drug that reaches the target part of the human body. Drugs administered intravenously have a bioavailability of 100%. Other methods will have less success.

Route	Bioavailability	Characteristics
Intravenous	100%	Most rapid
Intramuscular	$75 \leq 100\%$	Large volume may be injected but painful method
Subcutaneous	$75 \leq 100\%$	Smaller volume than IM, may be painful
Oral	$5 \leq 100\%$	Convenient, first pass metabolism occurs
Rectal	$30 < 100\%$	Less first pass metabolism than oral route
Inhalation	$5 < 100\%$	Rapid onset
Transdermal	$80 \leq 100\%$	Usually slow absorption, lack of first pass metabolism and prolonged duration of action

Howmed.net

Factors that affect it include the way the drug is administered as well as functional group and polarity. Specific examples are not needed here, but in simple terms, for example, if your drug is an ester it may be susceptible to hydrolysis by esterase enzymes in the body. Converting the ester to a ketone may prevent this if the effectiveness isn't impaired.

Does taking the drug with or without food affect the bioavailability? Grapefruit juice is a well-known inhibitor and affects bioavailability of many drugs.

As oral drugs have to pass through the intestinal wall their solubility in water is a great help.

The development of synthetic drugs

- Identify the need (often this can mean attempting to improve or modify a drug already in existence).
- Identifying the molecular structure that has the desired effect. This might involve testing a wide range of molecular compounds.
- Synthesis of the drug—development—best yields for manufacture, yield and extraction from natural sources.
- Preclinical trials to test toxicity in test tubes and on animals.
- Clinical trials on humans with placebos.
- Approval by development countries' drug administrations.

The process can take up to 20 years.

CORE
SPREAD 3: Aspirin

Mild analgesics function by intercepting the pain stimulus at the source, often by interfering with the production of substances that cause pain, swelling or fever.

Aspirin is prepared from salicylic acid.

Aspirin can be used as an anticoagulant, in prevention of the recurrence of heart attacks and strokes and as a prophylactic.

What are analgesics?

Analgesics are fancy word for pain killers. There are two types: mild and strong.

Mild analgesics like aspirin, acetaminophen (paracetamol) and ibuprofen work by inhibiting the enzyme that synthesizes prostaglandins, which produce fever, swelling and transmit pain from the site of injury to the brain.

Strong analgesics based on opiates, like morphine and codeine, interact with receptor sites in the brain and are much more powerful.

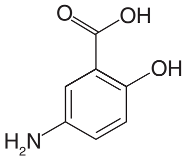
Aspirin

Aspirin is the pharmacological name for derivatives of salicylic acid and is a mild analgesic.

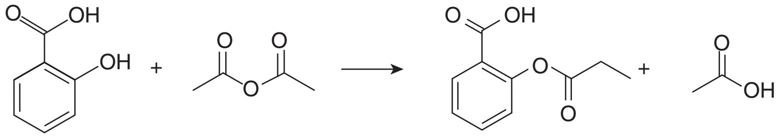
A pain killer aspirin also has "side effects" that are beneficial. It is an anticoagulant (thins the blood), so can be taken to prevent heart attacks. This also makes it a prophylactic (a drug taken to prevent disease). This blood thinning quality makes it less common as a pain killer these days as it can cause internal bleeding in the stomach and Reyes disease in children. There is a synergistic side-effect with alcohol (it enhances the effect) that can enhance the stomach bleeding.

Although aspirin is sparingly soluble it can be made much more soluble by turning it into the sodium salt of the ester. This increased solubility increases the bioavailability of the drug.

Aspirin traditionally is methyl salicylate, an ester, and is made by the esterification of salicylic acid, 2-hydroxybenzoic acid.



Salicylic acid is reacted with ethyl-anhydride (a more reactive type of carboxylic acid derivative) that does not go to equilibrium. The reaction is an esterification with the OH group of the salicylic acid reacting with the "acidic" ethanoic anhydride.



In the lab this would produce a crude product that would require recrystallization.

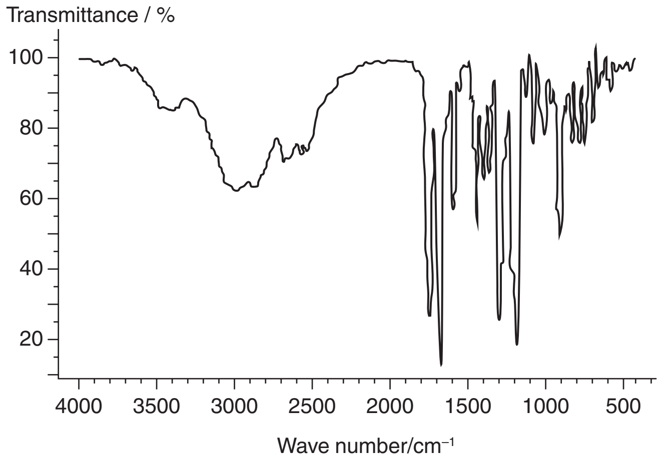
Recrystallization is the process of purifying a solid, the equivalent of distilling with an impure liquid.

The crude product is dissolved in the minimum amount of hot solvent (in this case, water) to dissolve it. The solution is filtered through a hot filter funnel and cooled rapidly to induce recrystallization. The product is then filtered and allowed to dry.

The melting point of the aspirin is a good way to ascertain its purity. Aspirin has a melting point between 138°C and 140°C. Salicylic acid has a melting point nearer 160°C. Pure aspirin will melt sharply at the desired temperature. Impurities will raise the melting point, and it will melt over a wider range.

Infrared spectroscopy

Below is an IR spectrum of aspirin. You can see the broad OH peak due to the acid group and the peak around 1750 because of the carbonyl group on the ester.



CORE
SPREAD 4: Penicillin

Penicillins are antibiotics produced by fungi.

A beta-lactam ring is a part of the core structure of penicillins.

Some antibiotics work by preventing cross-linking of the bacterial cell walls.

Modifying the side-chain results in penicillins that are more resistant to the penicillinase enzyme.

What are antibiotics?

Bacteria causes diseases in humans and animals. A bacterium is a single-celled organism. Bacteria can exist in the body quite benignly but some cause disease.

Streptococcus causes sore throats and pneumonia.

Bacilli causes tuberculosis.

Spirochete causes syphilis and gum infections.

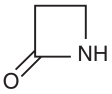
Antibiotics or antibacterials are chemicals that prevent the growth and multiplication of bacteria. Antibiotics were famously discovered by Alexander Fleming in 1928 and are derived from fungi. The most famous type are penicillins and their derivatives. The wide-spread use of antibiotics only began after World War II and now there is the possibility of overuse. Bacteria develop immunity/resistance to penicillins over time, and modifications of the molecule are needed to stay ahead of the game. Patient compliance with the dosages (seeing through a full course) and not over-proscribing are crucial to the continued effectiveness of antibiotics.

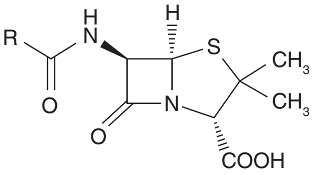
How do antibiotics work?

Penicillins work by preventing cross-linking in the cell wall of the bacteria, which stops it developing a proper cell wall and dying. Others perform other functions similarly lethal to bacteria.

What are penicillin molecules like?

Here is the basic molecule for penicillin. The beta-lactam ring is the crucial part as this is the part that interferes with the enzyme involved with cell wall construction.





The R group here is a side chain that can be modified to add variety to the types of penicillin out there.

The beta-lactam ring has an unusual square structure, where each bond is 90°. Due to its irregularity, the beta-lactam ring is very reactive. The ring opens and covalently bonds to the enzyme trans peptidase, responsible for the forming of bacterial cell walls. If bacterium is unable to build its cell wall, it bursts, disintegrates and dies.

CORE
SPREAD 5: Opiates

The ability of a drug to cross the blood–brain barrier depends on its chemical structure and solubility in water and lipids.

Opiates are natural narcotic analgesics that are derived from the opium poppy.

Morphine and codeine are used as strong analgesics. Strong analgesics work by temporarily bonding to receptor sites in the brain, preventing the transmission of pain impulses without depressing the central nervous system.

Medical use and addictive properties of opiate compounds are related to the presence of opioid receptors in the brain.

What are opiates?

Opiates are a class of naturally occurring analgesics that are derived from the opium poppy. They work very well and are used in cases where the patient is in extreme pain. This is because they are strong analgesics and bind to pain receptor sites in the brain, blocking the signals, which is much more effective than the localized pain interference of mild analgesics. The problem is that opiates can cause side-effects and severe addiction.

They can cause:

The inhibition of the coughing reflex.
A feeling of euphoria.
Constipation.
A lack of sex drive.
Severe addiction.
Tolerance that can lead to approaching the lethal dose.

Their use is limited because of these severe problems. Heroin is a failed drug and now is only used illegally. It is particularly addictive. Use of opiates is only sanctioned because of their tremendous pain reliving ability.

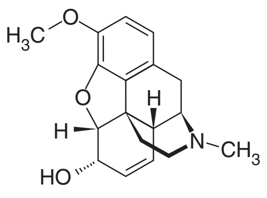
How do they work?

To do this it must cross the blood–brain barrier, a layer of tightly packed cells that make up the walls of brain capillaries and prevent substances in the blood from diffusing freely into the brain. How successful a drug is at crossing the blood–brain barrier depends on:

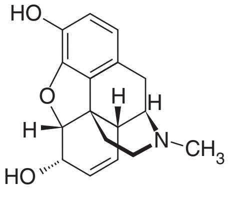
Its RMM—a low RMM is preferable
Chemical structure
High degree of lipid solubility

Ability to dissolve in water of the brain's interstitial fluid once through the barrier. As we will see opiates contain hydrogen bonding groups as well as long chains so will be able to cross the barrier.

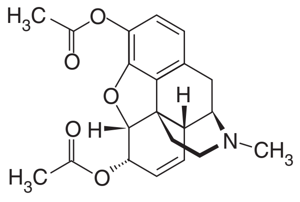
The structures of some opiates



Codeine



Morphine



Diamorphine 'Heroin'

Look at the similarity of the molecular structure! Morphine has two alcohol groups. Diamorphine (heroin) is the ester derivative of morphine. Codeine puts an ether group on one of the alcohol groups.

Synthesis of codeine and diamorphine from morphine

Morphine is the principle alkaloid (name of functional group) in opium that is extracted from the opium poppy. Diamorphine is made from morphine by treating morphine with ethanoic anhydride in a similar esterification reaction that makes aspirin from salicylic acid. Heroin's two acetyl groups make it more lipid soluble so travels through the blood–brain barrier better than morphine, so it is more rapid acting. Its severe addiction problems count against it.

Making codeine from morphine

Step 1 is to remove the protons on the alcohol groups by reacting with a base, followed by reaction with iodomethane. The mechanism would be nucleophilic substitution S_N2.

Codeine is a milder opiate and is often available over the counter. When it breaks down it metabolizes in the body, and one of its metabolites can be morphine, which is more powerful than codeine. This is an active metabolite.

CORE
SPREAD 6: pH regulation of the stomach

Non-specific reactions, such as the use of antacids, are those that work to reduce the excess stomach acid.

Active metabolites are the active forms of a drug after it has been processed by the body.

What is the problem?

The stomach is a vital part of the digestive system, which breaks down food into molecules that can be used by cells in the body. The stomach is a bag that secretes enzymes, mucus and hydrochloric acid, which are known as the gastric juices. The pH of the stomach is around 2. The stomach wall is protected by the mucus but excess acid in the stomach can cause pain, which we know as indigestion, or dyspepsia. Excess acid can be produced by over-eating, anxiety, smoking and alcohol consumption. The simple cure is to use antacids, which are effectively bases to regulate pH. They are non-specific drugs. More complicated cures are outline later.

What compounds can be used as antacids?

Non-toxic bases essentially.

These are the most common:

- Magnesium and calcium hydroxide ($Mg(OH)_2$ and $Ca(OH)_2$)
- Aluminium hydroxide ($Al(OH)_3$) although the toxicity of aluminium is a concern

- Sodium carbonate Na_2CO_3
- Sodium bicarbonate (bicarbonate of soda, sodium hydrogen carbonate) $NaHCO_3$

The bases all react with HCl in the way you would expect:

$Mg(OH)_2 + 2HCl \Rightarrow MgCl_2 + 2H_2O$
$Al(OH)_3 + 3HCl \Rightarrow AlCl_3 + 3H_2O$
$Na_2CO_3 + 2HCl \Rightarrow 2NaCl + CO_2 + H_2O$
$NaHCO_3 + HCl \Rightarrow NaCl + CO_2 + H_2O$

Calculations based on the most effective drug to combat indigestion by weight are fair game here.

Example
Which would be more effective in neutralizing stomach acid? 1.0 g of aluminum hydroxide or 1 g of sodium carbonate?

RMM = $Al(OH)_3$ = 78.01 $gmol^{-1}$
RMM Na_2CO_3 = 106.0 $gmol^{-1}$
Moles of $Al(OH)_3$ = 1/78.01 = 0.0128 moles
Moles of Na_2CO_3 = 1/106 = 0.0094 moles

According to the equations:

A total 0.0128 moles of $Al(OH)_3$ would neutralize 3 × 0.0128 moles of acid = 0.0384 moles of stomach acid.
So 0.0094 moles of Na_2CO_3 would neutralize 0.0189 moles of stomach acid.

Therefore aluminum hydroxide is more effective.

More specific drugs to regulate acid production

H2 receptor antagonists

These are drugs like ranitidine (Zantac). It was known that histamine regulated production of stomach acid, but antihistamines had no effect on production of acid. This was because there were two receptors on histamine, H1, which had no effect and H2, which did. These drugs worked successful on the H2 receptor.

Proton pump inhibitors

These are the best drugs available, they include omeprazole and esomeprazole. They block the gastric proton pump system, a system responsible for the acidification of the stomach, which produces enzymes that help produce the acid. While the drug is administered the enzymes are changed irreversibly and cannot produce acid.

CORE
SPREAD 7: Antiviral medications

Viruses lack a cell structure and so are more difficult to target with drugs than bacteria.

Antiviral drugs may work by altering the cell's genetic material so that the virus cannot use it to multiply. Alternatively, they may prevent the viruses from multiplying by blocking enzyme activity within the host cell.

What is a virus?

Viruses come in many different forms but essentially they consist of a core of DNA or RNA surrounded by a protein coat that protects these genes. They have no nucleus, they do not feed, excrete or grow. They can however replicate inside the cells of living organisms.

Viruses can only replicate inside a cell; they do this by injecting their DNA or RNA into the cytoplasm of the host cell. This allows the virus to take control over the cell causing the cell to die. This causes the symptoms of the viral infection, or the body's response to the viral infection is the symptoms. The virus produces millions of new viruses that can take over other cells in the live form.

This lack of basic cell structure makes it difficult to target drugs at specific viruses. In addition viruses mutate and are not the same year after year. The drug manufacturers are always playing catch-up finding cures for the last version of the virus, not the latest.

Examples of viral infections include the common cold, influenza, chicken pox and AIDS.

How do antiviral drugs work?

Many viral infections are easily dealt with by the body's own immune system, the common cold, chicken pox and mild influenza being cases in point. The speed with which a virus can replicate doesn't help the immune system.

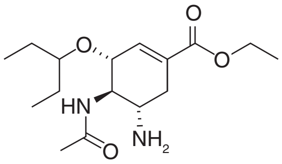
Some antiviral drugs work by modifying the cell's genetic material, so the virus cannot attack it and multiply. Others block enzyme activity in the cell preventing the virus from multiplying. Others prevent the virus from leaving the cell entirely.

Case study 1: Flu viruses

Influenza is a very common viral infection that causes headaches, fevers, sore throats and extreme fatigue. It can be a very serious condition, although it is often confused with the common cold, meaning the severity of the real condition is often underplayed. About a quarter of a million people die every year from severe cases of the disease. It is transmitted by respiration and is therefore easily passed on and the symptoms arrive very quickly.

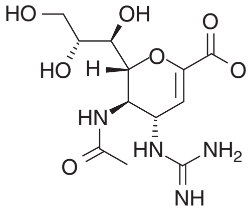
Oseltamivir (Tamiflu) is a common antiviral treatment. It is a good example of an ACTIVE METABOLITE because the drug itself is not virally effective; however, once in the liver it is hydrolyzed to its active metabolite, which is effective against the virus.

It works because Oseltamivir is a neuraminidase inhibitor, serving as a competitive inhibitor of the activity of the viral neuraminidase enzyme on the surface of normal host cells. By blocking the activity of the enzyme, Oseltamivir prevents new viral particles from being released and thus fail to facilitate virus release.



Note the amide, alkene, ester, amine and ether group.

Below is the structure for Zanamivir, another antiflu drug.



Note the proliferation of alcohol groups, as well as amines, amides, carbonyls and carboxylic acids. It works in a similar way to Tamiflu by binding to the active site of the neuraminidase protein, rendering the influenza virus unable to escape its host cell and infect others. It is also an inhibitor of influenza virus replication.

Case study 2: AIDS

Acquired Immune Deficiency Syndrome (AIDS) is caused by a virus containing RNA only. This virus is known as the human immunodeficiency virus (HIV) virus. There are two types: HIV 2, a mild version found mainly in Africa, and HIV 1, which is very virulent and found worldwide. The virus attacks white blood cells, which are used by the body to help protect itself against infection. With these white blood cells out of action the body cannot defend itself against disease. The infected person often dies of other diseases rather than AIDS itself.

Once infected (the diseases is usually transferred by sexual contact) the person develops mild flu like symptoms and then will often have no symptoms at all. Once inside the cell the virus makes DNA from its RNA template. This DNA is then integrated into the DNA of the host cell affecting its function.

RNA-based viruses like HIV are associated with a long incubation period. AIDS is the name for the final period when the immune system has broken down. Final period AIDS victims often suffer from pneumonia and viral-induced cancers.

Treatment

When first isolated HIV/AIDS was a disease that killed you there was a huge rush to get any kind of medication to help slow down the infection. Being a virus HIV mutates regularly and there are many different versions out there. The first drug to come to market was AZT in 1987. AZT worked by inhibiting the enzyme in the virus that turned the RNA in the HIV virus into DNA. As most cells do the reverse process, turn DNA into RNA, this doesn't affect the normal working of cells. Sadly AZT was not potent enough to prevent all RNA from replicating, and it had a lot of side-effects too.

Other places where an anti-HIV drug can work

Preventing the virus from entering the cell, these drugs could alter the binding site on the cell, thus not allowing the virus to bind to the receptor. These are known as entry inhibitors. One example is maraviroc.

Integrase inhibitors (also known as integrase nuclear strand transfer inhibitors or INSTIs) inhibit the viral enzyme integrase, which is responsible for integration of viral DNA into the DNA of the infected cell. There are several integrase inhibitors currently under clinical trial, and raltegravir became the first to receive FDA approval in October 2007. Raltegravir has two metal binding groups that compete for substrate with two Mg^{2+} ions at the metal binding site of integrase. As of early 2014, two other clinically approved integrase inhibitors are elvitegravir and dolutegravir.

Other possible sites for an antiviral to act include:

- Modifying the cell wall to prevent virus entry.
- Preventing the HIV virus from shedding its protective coat before RNA release.
- Altering the genetic nature of the virus to prevent production of new viral RNA.
- Preventing the virus from leaving the host cell. This is a possible pathway as flu treatments often work by this pathway.

The road to a fully effective treatment for HIV/AIDS is a long one and a lot of research still needs to be done.

CORE
SPREAD 8: Environmental impact of some medications

High-level waste (HLW) is waste that gives off large amounts of ionizing radiation for a long time.

Low-level waste (LLW) is waste that gives off small amounts of ionizing radiation for a short time.

Antibiotic resistance occurs when micro-organisms become resistant to antibacterials.

The synthesis, isolation and administration of drugs can have an effect on the environment.

A reminder of green chemistry principles:

1. **Prevention**
   It is better to prevent waste than to treat or clean up waste after it has been created.
2. **Atom economy**
   Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

3. **Less hazardous chemical syntheses**
   Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. **Designing safer chemicals**
   Chemical products should be designed to affect their desired function while minimizing their toxicity.
5. **Safer solvents and auxiliaries**
   The use of auxiliary substances (e.g., solvents and separation agents) should be made unnecessary wherever possible and innocuous when used.
6. **Design for energy efficiency**
   Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.
7. **Use of renewable feedstocks**
   A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
8. **Reduce derivatives**
   Unnecessary derivatization (use of blocking groups, protection/deprotection, temporary modification of physical/chemical processes, etc.) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.
9. **Catalysis**
   Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. **Design for degradation**
    Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.
11. **Real-time analysis for pollution prevention**
    Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
12. **Inherently safer chemistry for accident prevention**
    Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions and fires.

Types of waste

The disposal, manufacture and administration of drugs and medicines can affect the environment. It is also expected that drug manufactures should adhere to the green chemistry principles above. There are a few specific examples.

Nuclear waste

Radioactive samples can be used in the treatment of disease, often as tracers or locating agents. The radioactive sample can be detected by a scanner allowing a better idea of what the problem is. A good example is the barium meal, where a non-toxic sample of a radioactive barium compound is ingested. This allows the gastro intestinal tract to show up better under a scanner. Such uses cause nuclear waste to form.

Types of nuclear waste

There are two types of ionizing radiation:

- Low-level waste, which includes items like rubber gloves, and other protective clothing give off small amounts of ionizing radiation for a short time.

This sort of waste can be disposed of in the sea, where it can be diluted, although this is not best practice anymore. It can be stored in "ponds" for a period where its radiation can lose a lot of its activity before it is put into the sea. Other alternatives include storing it in concrete-lines vaults.

- High-level waste, which generally includes the samples of the isotopes themselves give off much larger amounts of radiation over a longer period of time.

This is harder to dispose of. If recycling can be carried out, or further processing then this will happen. The remainder will often be vitrified. The waste is dried in a furnace, and made into a material-like glass. This is solidified and stored in steel tubes. As the radiation can last thousands of years storage of such waste is a long-term problem. Currently it is stored in remote regions of high geological stability.

Antibiotic waste

As discussed antibacterial drugs kill infectious bacteria; however, over time some bacteria develop immunity to the antibiotic. This can happen by natural mutation and can be made worse by patients not taking the full course of antibiotics, leaving some bacteria in the system. The process of feeding antibiotics to healthy livestock has also exacerbated the problem, as their excreted waste matter can contain antibiotics that can get into the water supply. Another problem is the antibiotic waste that is disposed into water supplies, down the sink, for example, can mean that antibiotics end up in the sewage treatment plants. Here the antibiotics can encounter bacteria, and immunity can easily develop. Antibiotics are losing their effectiveness, and this is a major challenge in medicinal chemistry.

Solutions to the problem include further restricting the prescription of antibiotics for mild infections, restricting the use of "last-resort" antibiotics, insisting patients take their full course of antibiotics and better waste managements.

CORE
SPREAD 9: More on green chemistry

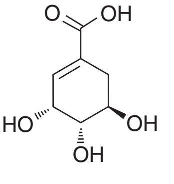
Solvent disposal

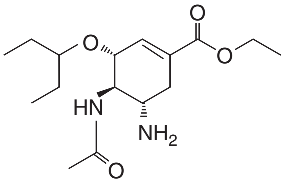
There are two problems with solvents. Firstly, the solvent itself may be toxic and can cause environmental damage if allowed to enter the water supply. Secondly, the chemical substance that was dissolved in the solvent might also cause large environmental problems. Thirdly, organic solvents are often flammable.

Dilution is not the answer. All solvents are treated as if they are concentrated. None must ever be put down the sink. All waste solvents must be stored carefully and collected by specialist waste disposal firms. Governments use heavy fine systems to enforce regulations. Your school or college will be also susceptible to the law, so think carefully about what you put down the sink next time you are carrying out laboratory work.

Tamiflu and green chemistry: A case study

Tamiflu, otherwise known as Oseltamivir, is an important drug in the fight against influenza. It is considered an important drug in the green chemistry world because its precursor is shikimic acid, see figure below.





It is found in the Star Anise plant found in Asia.

The synthesis of Tamiflu requires shikimic acid. This acid is extracted from the pods of star anise.

A 10-step process of complex chemical reactions results in the synthesis of Tamiflu. Some of the steps use potentially explosive azide chemistry; therefore, it is not a green process.

Not only is the process extremely long, taking approximately 6–8 months to complete, but 30 kg of star anise only produces 1 kg of shikimic acid. Hence, in order to be able to produce the quantities of Tamiflu required to fight a bird flu pandemic, either another source of shikimic acid must be found or another synthesis should be devised.

Roche, the manufacturer, and its partners are increasingly using fermentation processes to produce shikimic acid. This involves using a special strain of *E. coli* bacteria. When these bacteria are overfed sugar, they produce shikimic acid as a waste product. Scientists are working to improve the fermentation process and increase its efficiency so that it can be used to fully meet the shikimic acid requirements of Tamiflu production.

HL
SPREAD 10: Taxol—a chiral auxiliary case study

Taxol is a drug that is commonly used to treat several different forms of cancer.

Taxol naturally occurs in yew trees but is now commonly synthetically produced.

A chiral auxiliary is an optically active substance that is temporarily incorporated into an organic synthesis so that it can be carried out asymmetrically with the selective formation of a single enantiomer.

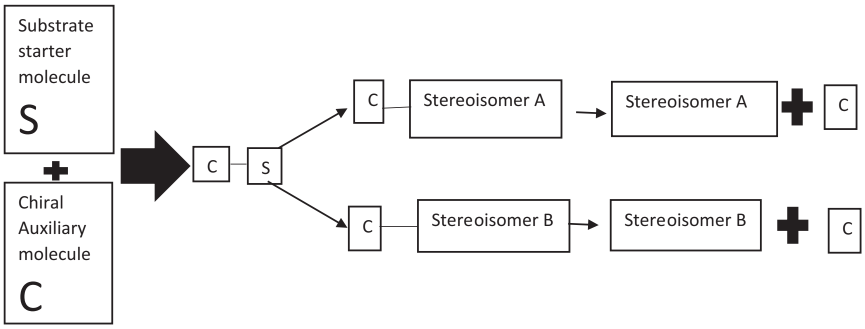
What is a chiral auxiliary?

Many drugs are complicated organic molecules. The more complicated the molecule the more likelihood there is that the molecule contains chiral centers. Chiral centers produce optical isomers, one of which might be effective; the other might be ineffective or, worse, cause horrific side-effects.

Enantiomers can be identified using a polarimeter (see Chapter 11). This makes use of the fact that optical isomers behave differently in plane polarized light. One enantiomer rotates the light in one direction (+), and the other rotates it in the opposite direction (−). Optical isomers (it's in the name!) are still classified by this + − nomenclature.

There are ways to deal with this problem: if the other enantiomer is medically inert then you can leave it in the medicine, but the dosage size would have to increase to make up the difference. Also, from a green chemistry perspective half the drug you manufacture is going to waste. Removing the isomer after manufacture is possible but technically difficult and expensive. It is better therefore to prevent the "wrong" isomer from forming in the first place. This is where chiral auxiliaries come in.

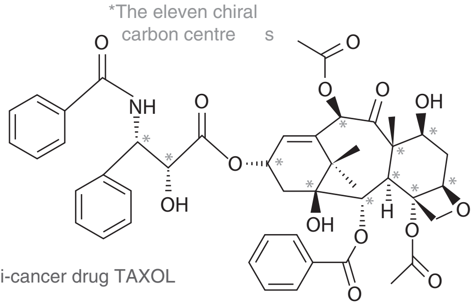
A chiral auxiliary is an optically active molecule that is temporarily incorporated into an organic syntheses so that it can be carried out asymmetrically, producing only the desired isomer. The auxiliary is then recycled after use.



Doc Brown

Case study: Taxol

Taxol is an anticancer drug, used in breast and ovarian cancers. Its structure is shown below. Note it has 11 chiral carbons! Manufacturing this from a raw material would be very difficult. The precursor can be derived from yew tree. It is impossible to provide all the raw material to supply what is required, especially as the tree dies in the harvesting process. Further advances allow yew tree needles to be farmed instead, but now the drug is manufactured in large fermentation tanks using specialist penicillin-type bacteria. This method removes the need to use a lot of toxic chemicals in the original pathway and, therefore, is a fine example of green chemistry at work.



The anti-cancer drug TAXOL

Taxol works by a complicated process but ultimately works to prevent mitosis, cell division. As cancer works by division of mutated cells it is a good treatment for breast, lung and ovarian cancers. The side-effects are nasty and can include hair loss, but they are worth for the fight against the disease.

HL
SPREAD 11: Nuclear medicine

Alpha, beta, gamma, proton, neutron and positron emissions are all used for medical treatment.

Magnetic resonance imaging (MRI) is an application of nuclear magnetic resonance (NMR) technology.

Radiotherapy can be internal and/or external.

Targeted alpha therapy (TAT) and boron neutron capture therapy (BNCT) are two methods that are used in cancer treatment.

What is nuclear radiation?

As we know atoms contain protons, neutrons and electrons in varying numbers as noted on the periodic table. Some atoms are more stable than others. In order to achieve stable configurations they "spit" out particles and other radiation from their nucleus. These are classified in three ways:

Alpha α—this consists of a particle made up of two protons or two neutrons, essentially a helium nucleus. Alpha particles are slow and heavy and have little penetrating power.

A typical decay pattern would be:

$$^{241}_{95}\text{Am} \rightarrow ^{237}_{93}\text{Np} + ^{4}_{2}\alpha$$

Note that the number of protons and neutrons goes down.

Beta β—protons and neutrons are made of combinations of even smaller particles, called "quarks." Under certain conditions, a neutron can decay to produce a proton plus an electron. The proton stays in the nucleus, whilst the electron flies off at high speed. Atoms with a high ratio of neutrons to protons often emit beta radiation. Beta particles are smaller and have a greater range.

A decay pattern would be:

$$^{90}_{38}\text{Sr} \rightarrow ^{90}_{39}\text{Y} + \beta$$

Note that when the number of protons goes up, the number of neutrons reduces, so mass number stays the same.

Gamma γ—this is a wave, not a particle and so can be emitted from many sources of radiation in addition to alpha and beta. They are highly penetrative.

Half-life

Half-life ($t_{½}$) is the amount of time required for a quantity to fall to half its value as measured at the beginning of the time period. While the term "half-life" can be used to describe any quantity, which follows an exponential decay, it is most often used within the context of nuclear physics and nuclear chemistry—that is, the time required for half of the unstable, radioactive atoms in a sample to undergo radioactive decay. Half-lives are quoted for radioactive isotopes.

Using the equation given in the data book you can work out the percentage and amount of radioactive material left after a certain period of time.

The nuclear half-life equation is:

$$N_t = N_0\, e^{-\lambda t}$$

Where:

N_0 = the initial quantity of particles

N_t = is the number of particles left at a given time
λ is the decay constant and it is worked out using
0.693/half-life
t = time

Example
A sample of radium contains 6.64×10^{23} atoms. It emits alpha particles and has a half-life of 1620 years. How many atoms are left after 100 years?

First let's work out λ

.693/1620 = 0.000427

Multiply by $t = -0.000427 \times 100 = 0.0427$

So plugging into the original equation:

$N_t = 6.64 \times 10^{23}\, e^{-0.0427} = 6.36 \times 10^{23}$ particles

You might be expected to manipulate the equation above to find either the time, or the amount or percentage of particles reaming, but the math principles are the same.

HL
SPREAD 12: Use of radioactive sources as medicine

Alpha sources

Radium 233 (half-life 11 days) are used in cancer treatments. They have low penetrative power but highly destructive and can be injected directly into tumors. This can cause the cancer cells to die with little damage to other neighboring cells. The half-life also allows them to disappear from the body relatively quickly.

Beta sources

One of the newest and most attractive medical radioisotopes is lutetium-177. With a half-life of about six and a half days, it is still active when it reaches the hospital, and can cause problems after treatment. It also emits mostly short-range, low-energy beta particles, so the damage to healthy tissue is minimal. It can be applied intravenously and has fewer side-effects than older radioisotope treatments.

Yttrium 90 is another source of beta radiation with a half-life of 64 hours. It is used in liver cancers.

Gamma sources

Gamma sources include Technetium-99, which is used as a "tracer" in medicine. This is a combined beta and gamma source, and is chosen because betas are less harmful to the patient than alphas (less ionization) and because Technetium has a short half-life (just over six hours), so it decays away quickly and reduces the dose to the patient. This tracer can be detected by scanners that allow tumors to be detected.

Internal and external radiotherapy

Internal radiotherapy implants are radioactive metal wires, seeds or tubes put into your body, inside or close to a tumor. This is called brachytherapy. The radioactive metal is called a source and is left inside the body for a period of time. In many types of cancer the source is taken out after a few minutes or a few days.

In some types of cancer, small metal implants are left in the body permanently. These implants are made of radioactive gold or contain radioactive iodine. They give a very high dose of radiation to the area of the cancer cells. For most types of implants the radioactivity only travels a few millimeters through body tissue and so it cannot be detected outside the body. For some people the radioactivity can be detected outside the body at first. They need to avoid close contact with people until the radioactivity drops to safe levels.

Radioactive liquids

Radioactive liquids to treat cancer are given either as a drink or by injection. Examples include:

- Radioactive phosphorus—used for blood disorders.
- Radioactive radium—used for prostate cancer that has spread to the bones.
- Radioactive strontium—used for secondary bone cancers.
- Radioactive iodine—used for benign (non-cancerous) thyroid conditions and thyroid cancer.

The radioactive part may be attached to another substance, which is designed to take the isotope into the tumor.

External radiotherapy destroys cancer cells using radiation aimed at a cancer from a machine. The types of radiation used include high energy X-ray beams or particle beams, such as protons or electrons. The most common types of external radiotherapy use photon beams (either as X-rays or gamma rays). The radiotherapy beams destroy the cancer cells in the treatment area.

Side effects

Hair loss, nausea, sterility, fatigue and damage to cell DNA.

Initial diagnosis

Often tumors are first identified using a Magnetic resonance imagery MRI scanner. These are essentially NMR machines, but the word “nuclear” in NMR can imply they are using ionizing radiation. They do not of course, as we have seen they use powerful magnets and radio waves. If a tumor is discovered it can be treated or traced more specifically with radioactive medicines.

Specific treatments

Targeted alpha therapy

Targeted therapy is used to keep cancer from growing and spreading. To become cancer cells, normal cells go through a process called *carcinogenesis*. Cancer cells may then grow into tumors or reproduce throughout a body system, like blood cancers do. Scientists have learned a lot about the molecules that are part of this process and the signals a cell gets to keep this process going. Targeted therapy disrupts this process. The drugs target certain parts of the cell and the signals that are needed for a cancer to develop and keep growing. These drugs are often grouped by how they work or what part of the cell they target. One innovative approach is the use of TAT to inhibit cancer growth, using an alpha particle emitting radioisotope such as ^{213}Bi. Because of its short range and high linear energy transfer (LET), alpha-particles may be particularly effective in the treatment of cancer, especially in inhibiting the development of metastatic tumors from micro-metastases.

Neutron capture therapy (**NCT**) is a noninvasive treatment for invasive malignant tumors such as primary brain tumors and recurrent head and neck cancer. **BNCT** is a highly selective type of treatment that can selectively target the tumor at the cellular level without causing radiation damage to the adjacent normal cells and tissues. However, the effectiveness of BNCT is dependent upon a relatively homogeneous distribution of ^{10}B within the tumor, and this is still one of the key stumbling blocks that have limited its success.

HL
SPREAD 13: Drug detection and analysis

Organic structures can be analyzed and identified through the use of infrared spectroscopy, mass spectroscopy and proton NMR.

The presence of alcohol in a sample of breath can be detected through the use of either a redox reaction or a fuel cell type of breathalyzer.

This section looks at the variety of techniques used in medicine and drug detection and analysis.

Detection

This is usually for forensic or criminal purposes, for example in detecting for illegal drugs in an athlete or breathalyzers for drink driving offences.

For alcohol detection a breathalyzer can either utilize the potassium dichromate oxidation reaction discussed in Chapter 11. The crystals will turn green in the presence of alcohol, or, alternatively a fuel cell can be used to generate an electric current when the alcohol is oxidized.

Infra-red spectroscopy can be used at the police station to detect the presence of certain bonds within the ethanol molecule. The technique can be made quantitative by converting the intensity of the signal to known standard.

Steroid detection by cheating athletes also requires sophist aced detection techniques. Gas chromatography can be used to separate the samples, followed by mass spectrometry to identify the steroid by mass to charge ratio values and other recognizable peaks.

Identification

Uses similar techniques, but can also utilize the more specific NMR techniques.

Isolation

The tradition methods of isolation include recrystallization and filtration, or for liquids, distillation. All will result from loss of the product. With distillation, especially fractional distillation, there are many things to consider, including the intermolecular forces of the liquids (how they mix); differences will mean that the mixture will not necessarily behave in an ideal way. (Your teacher may have mentioned Raoult's law.)

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