Reversible Reactions

Reversible Reactions Go *Both Ways*

In a reversible reaction, the **products** can react with each other and **change back** into the reactants.

Reactants		Products
A + B	$\rightleftharpoons$	C + D

So there are actually two reactions happening at once: $A + B \rightarrow C + D$ and $C + D \rightarrow A + B$. This can affect the **yield** of a reaction, as some of the products will be converted **back** into reactants.

EXAMPLE: The industrial production of ethanol from ethene.

exothermic →

$$H_2C{=}CH_{2(g)} + H_2O_{(g)} \rightleftharpoons CH_3CH_2OH_{(g)}$$

← endothermic

Catalyst: H_3PO_4
Temperature: 300 °C
Pressure: 60 atm

Because the reaction is reversible you **don't** get a **high yield** — some of the ethanol **converts back** to ethene and water. But you can keep **removing** and **recycling** any ethene that you have left, so you can still end up with a good overall yield.

Reversible Reactions Reach an *Equilibrium*

If a reversible reaction is taking place in a **closed system** it will eventually reach a state of **equilibrium**.

A **closed system** is one where nothing can **get in** or **out**.

1) When a reaction **begins** there will be a **high concentration** of **reactants**, and a **low concentration** of **products** in the system. So the **forward** reaction will be **fast**, and the **reverse** reaction quite **slow**.
2) The concentration of **reactants** will gradually **decrease**, while the products build up. So the **forward** reaction will start to **slow down** while the **reverse** reaction **speeds up**.
3) After a while the forward reaction and the reverse reaction end up going at the **same rate**. From this point on the **concentration** of the **reactants** and **products won't change**.
4) This is called **dynamic equilibrium**. The forward and reverse reactions are **both still happening** — some reactant is being made into product, and some product is being made into reactant.
5) But since these processes are going at **exactly the same rate**, it seems as if nothing's happening.

Dynamic equilibrium — like walking up a down escalator...

1) Compare the rates of the forward and backward reactions of a reversible reaction at the following points:
   a) At the start of the reaction.
   b) At equilibrium.
2) What is dynamic equilibrium?

Le Chatelier's Principle

***Position** of Equilibrium*

The **position** of equilibrium tells you the amount of **reactants compared** to the amount of **products** that are present when the reaction reaches an **equilibrium.**

Reactants   Products

$$A + B \rightleftharpoons C + D$$

If the position of equilibrium lies on the **left-hand side**, there are **more reactants** than products in the reaction mixture.

If the position of equilibrium lies on the **right-hand side**, there are more **products** than reactants in the reaction mixture.

*Changing **Conditions** Changes the **Equilibrium Position***

Altering the conditions of a reversible reaction can **move** the position of equilibrium in one direction or the other. Careful control of the conditions can result in a higher yield (more of the products).

Look at the production of ethanol from ethene again as an example:

exothermic →

$$H_2C{=}CH_{2(g)} + H_2O_{(g)} \rightleftharpoons CH_3CH_2OH_{(g)}$$

← endothermic

1) If you increase the **pressure**, conditions will favour the forward reaction and **more ethanol** (CH_3CH_2OH) will be formed.
   This is because there are **more molecules** of gas on the **left-hand side** than on the right-hand side — two molecules of $H_2C{=}CH_2$/H_2O react to form **only one** molecule of CH_3CH_2OH. This **reduces** the pressure.
2) Raising the **temperature** favours the **reverse** reaction. This is because it's **endothermic** (see page 41) and **absorbs** the extra heat energy, **lowering** the temperature.
3) **Removing ethanol** from the container as it forms will push the equilibrium to the **right** to try and make up for the change in concentration between the reactants and products.

These observations can be summarised by an important rule known as **Le Chatelier's Principle**:

A **reversible reaction** will move its **equilibrium position** to **resist** any **change** in the conditions.

Equilibrium reactions are so stubborn — always resisting change...

1) You are making ethanol from ethene and steam using the reaction shown above. **What will happen to the yield of ethanol if you increase the amount of steam in the reaction mixture?**
2) Ammonia is produced industrially using the following reversible reaction:

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

   The forward reaction is exothermic and the backwards reaction is endothermic.
   How will the position of the equilibrium change if you:
   a) Increase the temperature of the reaction?
   b) Remove some ammonia from the reaction?

Equilibrium and Yield

Deciding on the **Best Conditions** to Use

Thanks to Le Chatelier's principle (see page 35) you might think it would be **easy** to work out the **optimum conditions** for a reversible reaction. But in real life it's not quite that simple.

For most reversible reactions that are used on an industrial scale there are other factors, such as **cost** and **time**, that need to be taken into account.

Have a look at the conditions used for the production of ethanol from ethene again:

$$H_2C{=}CH_{2(g)} + H_2O_{(g)} \rightleftharpoons CH_3CH_2OH_{(g)}$$

exothermic (forward) → ; ← endothermic (reverse)

Catalyst: H_3PO_4
Temperature: 300 °C
Pressure: 60 atm

Temperature:

1) **Lowering the temperature** would favour the forward reaction and so it should increase the **yield** of ethanol.
2) But lowering the temperature also means that fewer of the particles in the reaction mixture will have **enough energy** to react (see page 32). The particles will also be moving **more slowly**, so there will be **fewer collisions**. So lowering the temperature will **slow down** the **rate** of both the forward and reverse reactions.
3) A low temperature would make the forward reaction **too slow** to be useful. So a compromise temperature of **300 °C** is used.

Pressure:

1) **Increasing the pressure** would favour the forward reaction and increase the **rate** of reaction (as the particles will be **closer together** so will collide **more frequently**). This would increase the **yield** of ethanol.
2) But producing high pressures uses a lot of **energy** and **costs** a lot of money. You'd need some pretty strong equipment to stand up to the high pressures too — and that would be expensive to buy and maintain.
3) To make the reaction economic, a moderately high pressure of **60 atm** is used.

Concentration:

1) Ethanol is **removed** from the reaction vessel as it is produced.
2) This reduces the concentration of products so the equilibrium shifts to favour the **forwards reaction**. This **improves** the **yield** of ethanol.

Catalyst:

1) Using a solid **phosphoric acid(V)** catalyst **increases** the rate of **both** the forward and the backward reactions.
2) The catalyst has **no effect** on the **position** of the equilibrium — it just means the equilibrium is reached **faster** and the **temperature** and **pressure** at which the reaction can happen, at a reasonable rate, are **reduced.**

I should put a dodgy pun here, but I won't yield to the pressure...

1) Explain why the reaction above is not run industrially at a temperature of 40 °C.
2) Explain why the reaction above is not run industrially at a pressure of 500 atm.

The Mole

A Mole is a Number of Particles

If you had a sample of a substance, and you wanted to **count** the number of atoms that were in it, you'd have to use some very **big numbers**, and spend a very long time counting. So you need a **unit** to describe the **amount** of a substance that you have — that unit is the **mole**.

> **One mole** of a substance contains **6.02×10^{23}** particles.
> 6.02×10^{23} mol^{-1} is known as **Avogadro's constant**.

The particles can be **anything** — e.g. atoms or molecules (or even giraffes).
So 6.02×10^{23} atoms of **carbon** is 1 mole of carbon,
and 6.02×10^{23} molecules of CO_2 is 1 mole of CO_2.

Molar Mass is the Mass of One Mole

> **One mole** of atoms or molecules has a **mass in grams** equal to the **relative formula mass** (A_r or M_r) of that substance.

For **carbon**, A_r **= 12.0** so 1 mole of carbon weighs **12 g** and the **molar mass** is **12 g mol^{-1}**.
For **CO_2**, M_r **= 44.0** so 1 mole of CO_2 weighs **44 g** and the **molar mass** of CO_2 is **44 g mol^{-1}**.
So, **12.0 g** of **carbon** and **44.0 g** of **CO_2** must contain the **same number of particles**.

You can use molar mass in calculations to work out how many moles of a substance you have.
Just use this formula:

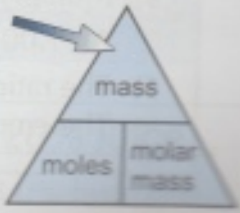
$$\text{Number of moles} = \frac{\text{Mass of substance (g)}}{\text{Molar mass (g mol}^{-1})}$$

g mol^{-1} is the same as g/mol.

EXAMPLE: How many moles of sodium oxide are present in 24.8 g of Na_2O?

Molar mass of Na_2O $= (2 \times 23.0) + (1 \times 16.0) = 62.0$ g mol^{-1}
Number of moles of Na_2O $= 24.8$ g $\div 62.0$ g mol^{-1} = **0.400 moles**

You can **rearrange** the formula above and use it to work out the mass of a substance or its relative formula mass (see page 3). It can help to remember this triangle:



EXAMPLE: What is the mass of 1.30 moles of magnesium oxide (MgO)?

Molar mass of MgO $= (1 \times 24.3) + (1 \times 16.0) = 40.3$ g mol^{-1}
Rearranging the formula, mass = moles × molar mass
So mass of MgO $= 1.30 \times 40.3 =$ **52.4 g** (3 s.f.)

Avocado's constant: how much I need to satisfy my guacamole craving

1) Find the molar mass of sulfuric acid, given that 0.700 moles weighs 68.6 g.
2) How many moles of sodium chloride are present in 117 g of NaCl?
3) I have 54.0 g of water (H_2O) and 84.0 g of iron (Fe). Do I have more moles of water or of iron?

Determination of Formulae from Experiments

Empirical and *Molecular* Formulae

The **empirical formula** of a compound is the **simplest ratio** of the atoms of each element in the compound.

The **molecular formula** of a compound gives the **actual number** of atoms of each element in the compound.

For example, a compound with the molecular formula C_2H_6 has the empirical formula CH_3. The **ratio** of the atoms is one C to every three Hs.

Calculating *Empirical* Formulae

Often, the only way to find out the formula of a compound is through **experimentation** and **calculation**. You can calculate the formula of a compound from the **masses** of the **reactants**. Here is a simple set of rules to follow when calculating a formula:

1) Write the **mass** or **percentage mass** of each element.
2) Find the number of **moles** of each substance by dividing by the atomic or molecular mass.
3) Divide all answers by the **smallest** answer.
4) If required: multiply to make up to **whole numbers**.
5) Use the **ratio** of atoms to write the formula (this gives the empirical formula).

EXAMPLE: Find the formula of an oxide of aluminium formed from 9.00 g aluminium and 8.00 g oxygen.

1) First write down the mass of each substance:
   Al: 9.00 g O: 8.00 g
2) Divide the mass by the atomic masses to find the number of moles of each substance:
   Al: 9.00 ÷ 27.0 = 0.333 moles O: 8.00 ÷ 16.0 = 0.500 moles
3) Divide by the smallest number, which is 0.333:
   Al: 0.333 ÷ 0.333 = 1.00 O: 0.5 ÷ 0.333 = 1.50
4) Multiply by 2 to give whole numbers:
   Al: 1.00 × 2 = 2 O: 1.50 × 2 = 3
5) The ratio of Al:O is **2:3**.
   The empirical formula is Al_2O_3.

Roman empirical formula — 1 Caesar, 3 gladiators & 8 straight roads...

1) Find the empirical formulae of the following oxides:
   a) An oxide containing 12.9 g of lead to every 1.00 g of oxygen.
   b) An oxide containing 2.33 g of iron to every 1.00 g of oxygen.
   (Relative atomic mass values: Pb = 207.2, O = 16.0, Fe = 55.8)
2) Calculate the empirical formula of the carboxylic acid that is comprised of 4.30% hydrogen, 26.1% carbon and 69.6% oxygen.
   (Relative atomic mass values: H = 1.0, C = 12.0, O = 16.0)

Calculation of Molecular Formulae

Use the *Relative Formula Mass* to Work Out the Molecular Formula

To find the **molecular formula** from the **empirical formula**, you need to know the **relative formula mass** (see page 3) of the compound. This will usually be given to you in the question. Read through the example below and then try the questions.

EXAMPLE: Calculate the molecular formula of a hydrocarbon molecule if the compound contains 85.7% carbon and it's relative formula mass is 42.0.

First calculate the empirical formula:
In 100 g of the compound, there will be:
C: 85.7 g H: (100 g – 85.7 g) = 14.3 g

Hydrocarbons only contain carbon and hydrogen, so any mass that isn't carbon will be hydrogen.

Number of moles of each compound:
C: 85.7 ÷ 12.0 = 7.14 H: 14.3 ÷ 1.0 = 14.3
Divide by the smallest number (7.14):
C: 7.14 ÷ 7.14 = 1 H: 14.3 ÷ 7.13 = 2
So the ratio of C:H is **1:2**.
The empirical formula is **CH_2**.

Calculate how many multiples of the empirical formula the molecular formula contains:
The empirical formula (CH_2) has a relative mass of 12.0 + 1.0 + 1.0 = 14.0.
The molecular formula has a relative mass of 42.0.
42.0 ÷ 14.0 = 3
To find the molecular formula, multiply each of the values in the empirical formula by 3:
C: 1 × 3 = 3 H: 2 × 3 = 6
The molecular formula is **C_3H_6**.

The example above uses **percentage compositions** rather than the **mass** of each element in the compound. You can calculate the **percentage composition** yourself using the formula:

$$\text{percentage composition of element X} = \frac{\text{total mass of element X in compound}}{\text{total mass of compound}} \times 100\%$$

The percentage composition of my fridge is 80% cheese & 20% juice...

1) Calculate the molecular formula of a compound containing 52.2% carbon, 13.0% hydrogen and 34.8% oxygen if the relative formula mass of the compound is 46.0.
(Relative atomic mass values: C = 12.0, H = 1.0, O = 16.0)
2) Calculate the molecular formula of a hydrocarbon with a relative formula mass of 78.0 that contains 92.3% carbon.
(Relative atomic mass values: C = 12.0, H = 1.0)
3) Find the percentage composition of oxygen in each of the following compounds:
a) Ethanol (C_2H_5OH).
b) Nitric acid (HNO_3).
c) Propanone (C_3H_6O).

Atom Economy

A Higher **Atom Economy** Means Less **Waste**

1) Lots of reactions make **more than one product**.
   Some of them will be **useful**, but others will just be **waste**.
2) The **atom economy** of a reaction tells you how much of the **mass** of the reactants is converted into **useful products**, and how much is wasted during a reaction.

$$\text{atom economy} = \frac{\text{total } M_r \text{ of desired products}}{\text{total } M_r \text{ of all products}} \times 100$$

3) If a reaction has **100% atom economy** then **all** the atoms in the reactants have been turned into **useful** (desired) **products**. The higher the atom economy, the 'greener' the process.

EXAMPLE: Calculate the atom economy of the reaction to make hydrogen gas from methane and steam: $CH_{4(g)} + H_2O_{(g)} \rightarrow CO_{(g)} + 3H_{2(g)}$.

First identify the useful product, which in this reaction is hydrogen gas.

$$\text{atom economy} = \frac{\text{total } M_r \text{ of desired products}}{\text{total } M_r \text{ of all products}} \times 100$$

$$= \frac{M_r \text{ of } H_2}{(M_r \text{ of } H_2) + (M_r \text{ of } CO)} \times 100$$

$$= \frac{3 \times (2 \times 1.0)}{3 \times (2 \times 1.0) + 1 \times (12.0 + 16.0)} \times 100 = \frac{6.0}{6.0 + 28.0} \times 100 = \mathbf{17.6\ \%}$$

High Atom Economy is Better in Industry

1) **Industrial reactions** are designed to be as **cheap** and **green** as possible. Generally, reactions with high atom economies are the **most efficient** processes as there is **minimal waste**.
2) The reactions with the **highest** atom economy are the ones that only have **one product**. These reactions have an atom economy of **100%**.
3) Reactions with low atom economies **use up resources** very quickly. They also make lots of **waste** materials that have to be **disposed** of somehow. That tends to make these reactions **unsustainable** — the raw materials run out and the waste has to go somewhere.
4) For the same reasons, low atom economy reactions aren't usually **profitable**. Raw materials are **expensive to buy**, and waste products can be expensive to **dispose of**.
5) The best way around the problem is to find a **use** for the waste products or to find a reaction with a **better** atom economy to make the same product.

Atom (Economy) — upgrade to Superior for only £16.99...

1) a) Ethanol can be made from bromoethane in the following reaction:
   $CH_3CH_2Br + NaOH \rightarrow CH_3CH_2OH + NaBr$.
   What is the atom economy of this reaction?

   b) In industry, ethanol is made from ethene and steam using the following reaction:
   $CH_2CH_2 + H_2O \rightarrow CH_3CH_2OH$.
   Suggest why this reaction is used, rather than the reaction in part a).

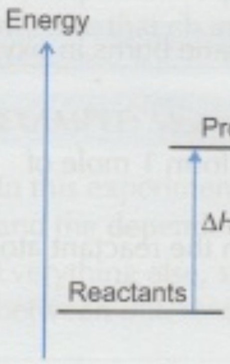
Endothermic and Exothermic Reactions

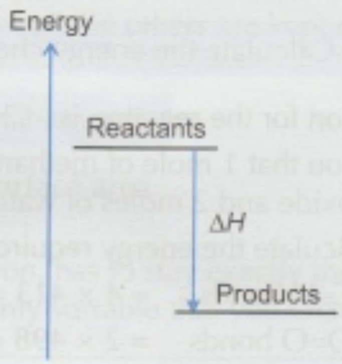
In an **exothermic** reaction, **heat** energy is **given out** (the room temperature rises).
In an **endothermic** reaction, **heat** energy is **taken** from the surroundings (the room temperature drops).

Making and Breaking Bonds

1) It takes energy to **break bonds**. When two atoms joined by a bond are **separated**, the energy required to do this must be provided from the surroundings.
2) However, energy is **released** when bonds are made. When two atoms become **joined together** by forming a bond, energy is **released** to the surroundings.
3) In a reaction, if more energy is taken in to break bonds than is given out when bonds are made, the process is **endothermic** — it will take in heat energy. The overall **enthalpy change** of the reaction (ΔH) is **positive.**
4) But, if more energy is given out when bonds are made than is taken in when bonds are broken, the process is **exothermic** — it will give out heat energy. The overall **enthalpy change** of an exothermic reaction (ΔH) is **negative.**

Reactions can be Represented by Energy Level Diagrams





In an **endothermic** reaction, the reactants **take in** energy from the surroundings. The products therefore have **more energy** than the reactants, and ΔH is **positive.**

In an **exothermic** reaction, the reactants **release** energy to the surroundings. The products therefore have **less energy** than the reactants and ΔH is **negative.**

After that I think I need a cup of tea. It'll help improve my energy level...

1) Are the following reactions exothermic or endothermic?
   a) burning coal
   b) sodium hydrogencarbonate + hydrochloric acid (temperature drops)
   c) acid + hydroxide (gets hotter)
   d) methane + steam (cools as they react)
2) a) Draw an energy level diagram for the following reaction:
   $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O \quad \Delta H = -2809 \text{ kJ mol}^{-1}$
   You should label the products, reactants and enthalpy change on your diagram.
   b) Is the reaction in part a) endothermic or exothermic?

Bond Energy

Average Bond Energy

Bonds between **different atoms** require different amounts of **energy** to break them. When the **same two atoms** bond in the same way, the amount of energy needed is always about the same. The average bond energy values for some common bonds are given below:

C–H 413	C–O 360	C=C 612
O=O 498	H–H 436	C=O 743
C–C 348	O–H 463	

All these values are in kJ mol^{-1}.

The values tell you that:

e.g. It takes 413 kJ of energy to break 1 mole of C–H bonds.
It takes 463 × 2 = 926 kJ to break 1 mole of water (which has 2 O–H bonds per molecule) into oxygen and hydrogen atoms.
743 × 2 = 1486 kJ are released when 1 mole of CO_2 (which has 2 C=O bonds) forms.

Calculating the Change in Energy

When a reaction takes place, the change in energy is simply:

sum of energy required to break old bonds – sum of energy released by new bonds formed

EXAMPLE: Calculate the energy change involved when 1 mole of methane burns in oxygen.

The equation for the reaction is: $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
This tells you that 1 mole of methane reacts with 2 moles of oxygen to form 1 mole of carbon dioxide and 2 moles of water.

Step 1: Calculate the energy required to break all of the bonds between the reactant atoms:
4 C–H bonds = 4 × 413 = 1652 kJ
2 O=O bonds = 2 × 498 = 996 kJ
Total = 2648 kJ

Step 2: Calculate the energy released by all the new bonds formed in the products:
2 C=O bonds = 2 × 743 = 1486 kJ
4 O–H bonds = 4 × 463 = 1852 kJ
Total = 3338 kJ

Step 3: Combine the two values to give the overall value for the energy change:
The overall energy change is: 2648 – 3338 = **–690 kJ mol^{-1}**.

The negative sign shows that energy is being released to the surroundings, indicating that this is an **exothermic** reaction. This is expected, since this is a combustion reaction.

Ian Fleming was like an exothermic reaction — he made lots of Bonds...

1) Calculate the energy change of the following reactions:
(Use the values for the average bond energies given at the top of the page).
a) burning 1 mole of propane $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$
b) burning 1 mole of ethanol $C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$
c) hydrogenation of 1 mole of ethene $C_2H_4 + H_2 \rightarrow C_2H_6$

Planning Experiments

Make Sure You **Plan** Your **Experiment Carefully**

To get accurate and precise results from your experiments, you first need to plan them carefully...

1) Work out the **aim** of the experiment.
2) Identify the **variables** (see below).
3) Decide what **data** to collect.
4) Decide the right **equipment** to use.
5) Plan how to reduce any **risks** in your experiment.
6) Write out a **detailed method**.
7) Carry out **tests** to address the aim of your experiment.

You Need to Control All the **Variables**

A **variable** is a quantity that might **change** during an experiment, for example temperature. There are two types of variables to know about when carrying out an experiment:

- The **independent variable** is the quantity that you **change**.
- The **dependent variable** is the thing that you measure.

When you plan an experiment you need to work out how you will **control** the variables so that the only one that changes is the one you're investigating — all the others are kept **constant**.

EXAMPLE: Measuring the effect of surface area on reaction rate.

In this experiment, the **independent variable** is the **surface area**, and the **dependent variable** is the **rate** of reaction.

Everything else, such as temperature and concentration, has to stay exactly the same between different experiments. Surface area is the only variable that you change.

Choose the Right **Equipment**

You need to think carefully about selecting the right **equipment** for your experiment...

1) The equipment has to be **appropriate** for the specific experiment — for example, in an experiment where you're collecting a **gas** the equipment you use needs to be properly **sealed** so that the gas can't **escape**.
2) The equipment needs to be the right **size**.
3) The equipment needs to be the right level of **sensitivity** — for example, if you want to measure out 4.2 g of a compound, you'll need a balance that measures to at least the nearest 0.1 g, not the nearest gram.

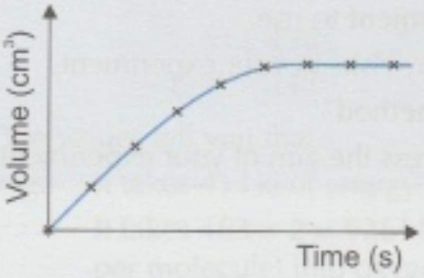
Reduce Risk — and play poker instead...

1) A student is measuring the effect of temperature on the time taken for a lump of magnesium to react completely in a sample of concentrated hydrochloric acid.
   a) What is the dependent variable in the student's experiment?
   b) Name two variables that the student should control to make the experiment a fair test.

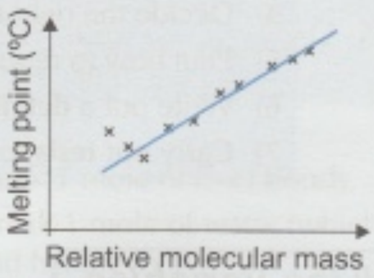
Presenting and Interpreting Data

You Can Represent Your Data in a **Table** or on a **Graph**

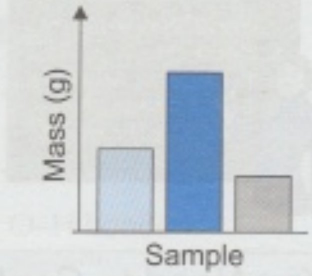
When you do an experiment, it's a good idea to set up a table to **record** your **results** in. Make sure you **include** enough **rows** and **columns** to **record all of the data** you need. Tables are good for **recording** data, but it can be easier to interpret your results if you **plot** them on a **graph**. Depending on the **type** of experiment, the **graph** you plot will vary:



Line graphs show how two sets of data are related.



Scatter plots show **trends** in data. Don't join all the points — just draw a **line of best fit**.



If one of your sets of data can be split into **groups**, draw a **bar graph**.

Repeating an Experiment Makes Your Results More **Reliable**

1) If you **repeat** an experiment, your results will usually **differ slightly** each time you do it. You can use the **mean** (or average) of the measurements to represent all these values. The more times you repeat the experiment the **more reliable** the average will be. To find the mean:

Add together all the data values then **divide** by the total number of values in the sample.

EXAMPLE: Calculate the mean result for the volume of hydrogen gas produced after 30 seconds in the reaction between hydrochloric acid and magnesium.

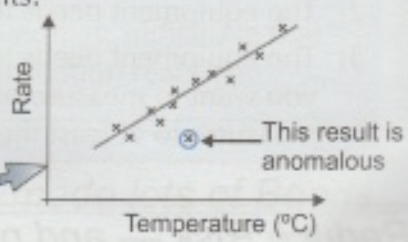
Run 1	Run 2	Run 3
23 cm^3	22 cm^3	25 cm^3

There are **three** values in this sample, so to find the mean result, just add together the results and divide by three:

$(23 + 22 + 25) \div 3 = \mathbf{23.3\ cm^3}$

2) Repeating experiments also lets you spot any **weird results** that stick out like a hedgehog in a tea cup. These are called **anomalous** results. For example — if one of the results above was only 5 cm^3, then something probably went wrong. You should **ignore** the anomalous result when you calculate the mean.

3) Anomalous results are really easy to spot on **scatter plots** and **line graphs** as they sit miles away from the line of best fit.



I was hoping for a nice result, but it ended up being mean...

1) Kay measured the volume of gas given off in a reaction. Her results were 22.0 cm^3, 23.0 cm^3, 22.0 cm^3, 19.0 cm^3 and 24.0 cm^3. Identify any anomalous results and calculate the mean.