Chem Factsheet

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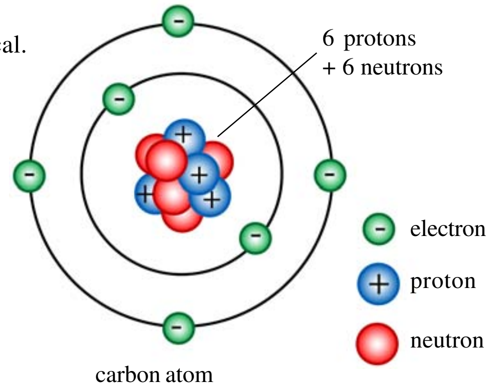
Basic atomic structure

Chemists have long believed that all matter is composed of "atoms". At GCSE you will have learned that these atoms are considered to be:

1. Spherical.



carbon atom

2. Very small.
3. Composed of sub-atomic particles called protons, electrons and neutrons with relative masses 1, 0 and 1 respectively and relative charges 1+, 1- and 0 respectively.
4. Characterised by the number of protons present.
5. Structured so that the protons and neutrons are positioned in a very small central nucleus.
6. Structured so that the electrons are orbiting in 3D shells about the nucleus.
7. Structured so that 2 electrons can occupy the first shell, 8 in the second and 8 in the third.
8. More stable if the outer electron shell is "full" – 2 electrons for the first shell but 8 for others.

These points constitute a "model" of atomic structure – in other words a physical picture of the constitution of an atom that has been derived and modified using experimental evidence. It superseded previous models as new evidence was produced and will be further modified and advanced as further new evidence emerges – any model must be formulated to be consistent with experimental observations!

This FactSheet aims to describe how the "scientific method" led to this basic model of atomic structure.

What is the Scientific Method?

In simple terms this can be represented as the sequence of *"ask a question" (e.g. how are atoms structured?) experiment, observation, analysis and finally, conclusion*. The "conclusion(s)" is/are, in this case, some aspect of how atoms are structured. They must consistent with the experimental observations and, better still, allow new predictions to be made which can then be tested by *further* experimental work. For example, the basic model presented above, can be used to explain how atoms bond together to make larger structures or explain the patterns in the Periodic Table.

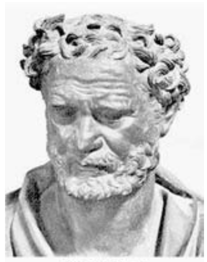
But this is not the end! Science is forever advancing and the "GCSE model of atomic structure" has now been replaced and, as science advances further, it is almost inevitable that new models will emerge!

How Big are Atoms?

From about the 1920's, X-ray crystallography and related techniques allowed atomic radii to be measured. They fall in the approximate range 30 – 300pm (1 pm (picometre) = 10^{-12}m). Hydrogen is the smallest and atoms like caesium are amongst the largest. On average, about 500,000,000 atoms could be laid end-to-end inside one centimetre!

Very Early Ideas about Atomic Structure

The ancient Greek philosopher, Democritus, claimed that all matter is made up of particles that he called "atomos" – Greek for *indivisible*. This is the origin of the idea of an atom.


Democritus
ca. 460 – 370BC

However, he went on to make what now appear to be outrageous claims about the natures and interactions of these particles. For instance:

1. Atoms are indestructible
2. Atoms are always in motion
3. Atoms exist in an infinite number of kinds, differing in shape and size
4. The "solidness" of matter depends on the shape of the atoms involved – e.g. water "atoms" are smooth and slippery while salt "atoms", because of their taste, are sharp and pointed
5. Atoms can combine to larger, more solid substances using tiny hooks and eyes or balls and sockets.

Clearly, this does not correspond to current ideas. For instance, he made no distinction between atoms and molecules. However, even though he did not get involved in experimental work, he did establish the idea that matter is particulate rather than continuous and that the particles show various degrees of motion.

Antoine Lavoisier


Antoine
Lavoisier
1743 - 1794

Further progress in developing atomic theory did not occur until the *science of chemistry* began to develop in the late 18th century. In 1789, Lavoisier adopted an experimental approach and, from his experimental data, formulated the *law of conservation of mass* (total mass of reactants = total mass of products). More importantly, he also defined an *element* as a substance that could not be further broken down by chemical methods.

John Dalton


John Dalton
1766 - 1844

In 1805, John Dalton (an English teacher and philosopher – not a scientist!) applied the *concept of atoms* to explain why elements always react in small whole number ratios. He is widely considered to be the founder of modern atomic theory wherein he proposed that:

1. Each element consists of tiny particles called atoms.
2. Atoms cannot be divided.
3. Atoms in one element are unique to that element.

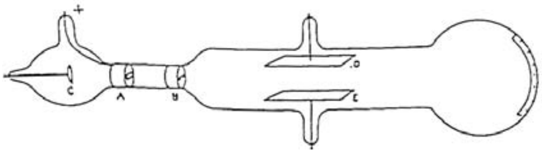
4. Atoms can join together to form chemical compounds.
5. Each different atom/element could be represented by a symbol.
6. Each different atom/element had a characteristic atomic mass.

Interestingly, he listed "lime" (CaO) and "soda" (Na_2CO_3) as elements because he did not have the means to break them down to simpler substances. Nevertheless, a lot of his ideas have stood the test of time!

J. J. Thomson

J.J. Thomson
1856 - 1940

From 1897 to 1906, Joseph John Thomson investigated the properties of *cathode rays*. These are emitted from the negative electrode of a cathode ray tube (CRT) which allows a high voltage to be applied across a near- vacuum. By measuring deflections of the rays in either an electrical field or a magnetic field he was able to show that cathode rays are made up of very small *negatively* charged particles and that the same particles were produced no matter what trace gas was present in the tube.

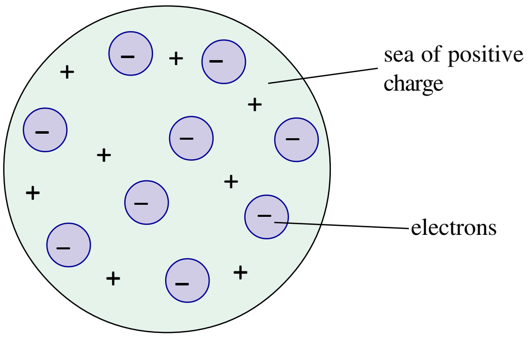


Thomson's CRT

Hence, since different elements in the CRT produced the same rays, he had shown that atoms are ***not*** indivisible, contrary to the ideas of the early Greeks and Dalton! He concluded that **all atoms** must contain these sub-atomic particles which he called *corpuscles* but which later became known as electrons.

He was also able to measure the mass of these particles as about 1/2000th of the mass of the lightest atom, H.

Plum pudding atom

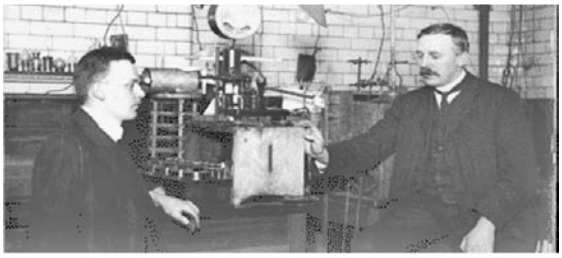


Following these findings, in 1904, Thomson proposed a "new" model of atoms where they are made up negative electrons moving around in a "sea of positive" charge which is equal, but opposite, to the total charge of the electrons in order to give the overall neutrality of the atom. This became known as his "*plum pudding atom*" – not very satisfactory considering the amount of detailed and precise experimental work done, because it implies that the very smallest of atoms (H) contains about 2000 electrons!

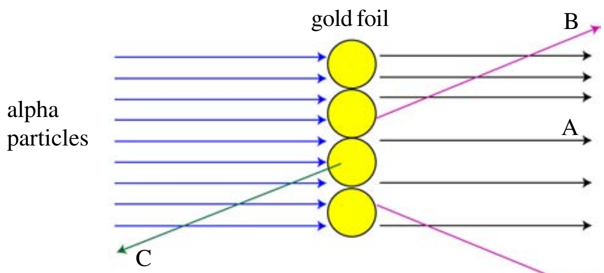
Ernest Rutherford

Ernest Rutherford
1871 - 1937

Surprisingly, Thomson's model remained unchallenged for quite some time until, in 1909, Rutherford (one of Thomson's own students!) examined experimental results produced by his own research students Geiger and Marden. He directed them to examine what happened when positively charged alpha-particles, with a relative mass of 4, (obtained from a radioactive source but not shown to be helium nuclei until much later) were directed towards a sheet of very thin gold foil. His idea was to test Thomson's model because Rutherford expected (by calculation) the α-particles to pass through the foil mostly unaffected.



Hans Geiger 1882 - 1945 Ernest Marsden 1889 - 1970



A Most pass through unaffected
B A few pass through but are deflected
C A very small number are reflected back towards the source

However, it was observed that, despite the fact that most particles did pass through the foil without deviation, a few were deflected through large angles and an even smaller number were deflected back towards the α-particle source.

Rutherford was very surprised by these observations, famously saying "it was almost as incredible as if you fired a 15 inch shell at a sheet of tissue paper and it came back and hit you".

Subsequently, Rutherford used these observations and associated measurements to show by calculation that the positive charge of the atom must be concentrated in a very small volume, much smaller than the total volume of the atom. This region was the birth of the idea of the nucleus!

Hence, in 1911, Rutherford proposed the "*nuclear atom"* as a model to supersede Thomson's plum pudding model. His model said:
1. the entire positive charge and most of the mass of an atom are *concentrated in a nucleus*, located at the centre of an atom.
2. negatively charged electrons *orbit the nucleus* – he imagined this by analogy with the orbits of the planets about the sun.
3. the total positive charge in the nucleus and the total negative charge in the orbits must *balance* to give a neutral atom.
4. most of an atom's volume is *empty space* between the minute nucleus and the electron orbits.

Note: It varies from one element to another, but the ratio of atomic diameter to nucleus diameter has been shown (by experiments similar to Rutherford's but using electron beams instead of α-particles) to be about 100,000:1. A reasonable picture of this ratio is provided by imagining an H atom to be represented as the size of Wembley Stadium. On the same scale, the nucleus would be represented by a pea at the centre spot!

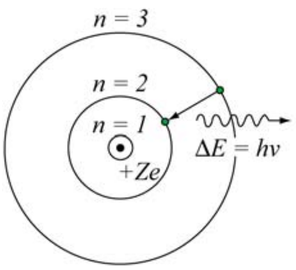
In 1911 Antonius van den Broek, after analysing X-rays emitted by various elements, suggested that the total nuclear charge of different elements was equal to the element's position in the Periodic Table – in other words equal to its atomic number. This was confirmed by Henry Moseley in 1913. Finally, following Rutherford's discovery and characterisation of the proton in 1917, it was realised that the atomic number of an element is equal to the number of protons in its nucleus.

Niels Bohr

Niels Bohr
1885 - 1962

In 1885 Johann Balmer had observed that hydrogen could be caused to emit *specific frequencies (f)* in the visible part of the spectrum by a suitable input of energy. In 1913, Bohr suggested that, in order to account for these observations, the electrons of an atom must be in *specific shell-like orbits* around the nucleus, each associated with a *fixed energy level*. The electrons levels are said to be quantised and are numbered 1, 2, 3 etc away from the nucleus.

This allows Balmer's emission spectrum to be explained. The "Balmer frequencies" in the visible region are caused by electrons from level 2 being excited by an energy input and so jumping up to levels 3, 4, or 5 etc. This would be unstable and the electron can revert to level 2 by emitting energy in the form of visible light.



If E_n represents the energy of the n^{th} electron shell, then
Lower frequency emitted (f_1) = $E_3 - E_2/h$
(where h = Planck's constant)

Next frequency emitted (f_2) = $E_4 - E_2/h$

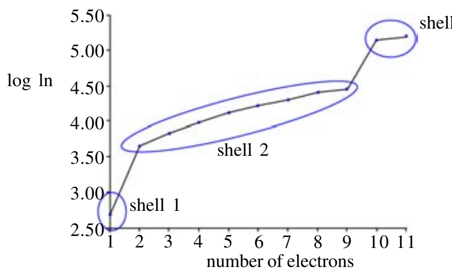
Next frequency emitted (f_3) = $E_5 - E_2/h$ etc.

Furthermore, Bohr said that, since the emission frequencies get closer and closer together, then the energy levels must also get closer and closer together as distance from the nucleus increases.

Successive Ionisation Energy Patterns

The n^{th} ionisation energy (I_n) of an atom is the energy needed to remove the n^{th} electron from one mole of gaseous atoms/ions.

e.g. $Na(g) \rightarrow Na^+(g) + e^-$; I_1[Na]
$Ca^{3+}(g) \rightarrow Ca^{4+}(g) + e^-$; I_4[Na] etc.



A sodium atom has 11 electrons and, according to Rutherford's model, it should get steadily more difficult to remove successive electrons from an increasingly positive particle. However, as seen in the graph of $I_1 - I_{11}$ for sodium, even there is an overall increasing trend the significant steps between I_1 and I_2, and then between I_9 and I_{10}, in the graph contradict Rutherford's model. However, it is consistent with Bohr's model because electrons being removed from an energy level nearer to the nucleus will be much more difficult to remove because they are nearer to the positive nucleus and less shielded from the nuclear attraction by inner energy levels.

Furthermore, when these results are compared with similar graphs for other elements, it can be shown that the inner energy level never has more than 2 electrons and the next, never more than 8. These are the numbers familiar from the "GCSE" model of the atom!

James Chadwick

James Chadwick
1891 - 1974

Rutherford was worried as to why protons in the nucleus do not "fly apart" as a result of mutual repulsions and why they could not account for overall atomic masses. In 1921 he postulated that another particle – the *neutron* – with no electrical charge and similar mass to the proton, must be present in the nucleus which could somehow compensate for the repelling effects and also account for the "missing" mass. In 1932, Rutherford's theory about the existence of neutrons in the nucleus was proved by James Chadwick using experiments involving the bombardment of beryllium with alpha particles. Chadwick's discovery was a remarkable feat since neutral particles are very difficult to detect and monitor. However, it was vitally important in reinforcing Rutherford's ideas and accounting for atoms of the same element being able to have different masses – isotopes!

This is not the entire story! Many contributors have not been mentioned and much more sophisticated models of atomic structure have since emerged in response to further experimental work – sub-shells, orbitals, the electron as a wave, mathematical models etc. These are for future study but, in the meantime, the model discussed so far allows most aspects of A-level chemistry (e.g. periodicity and bonding) to be accounted for.

Acknowledgements: *This Factsheet was researched and written by Mike Hughes.* ***Curriculum Press, Bank House, 105 King Street, Wellington, Shropshire, TF1 1NU. ChemistryFactsheets*** *may be copied free of charge by teaching staff or students, provided that their school is a registered subscriber. No part of these Factsheets may be reproduced, stored in a retrieval system, or transmitted, in any other form or by any other means, without the prior permission of the publisher.* ***ISSN 1351-5136***