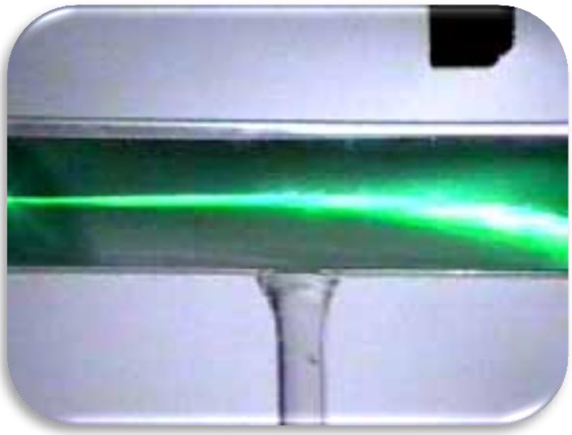
Chapter 1 (AS-Level)

Atomic Structure

Discovering the electron

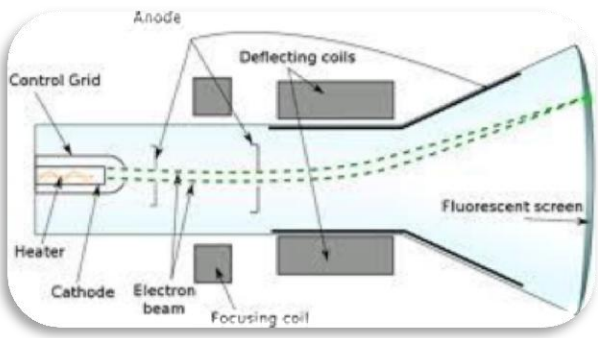
A. Study of Cathode rays

At normal pressures, gases are poor conductors, but at lower pressure they become better conductors of electricity. Scientists studied the effects of passing electricity through gases at low pressures.



A scientist named William Crookes saw that the glass of the containing vessel opposite the cathode glowed when the voltage applied was high.

A solid object placed between the cathode and the glass causes a shadow. They proposed that the glow was caused by rays coming from the cathode, called *cathode rays*.



There was some argument about whether the rays are waves or particles. The most important evidence is that they are deflected by magnetic fields, which is best explained by assuming that these are electrically charged particles.

The direction of deflection, which is towards the positive pole shows that they are negatively charged.

B. J.J. Thomson's e/m experiment

J.J. Thomson measured the deflection of a narrow beam of cathode rays in both magnetic and electrical fields. His results allowed him to calculate the charge-to-mass ratio (e/m) of the particles.

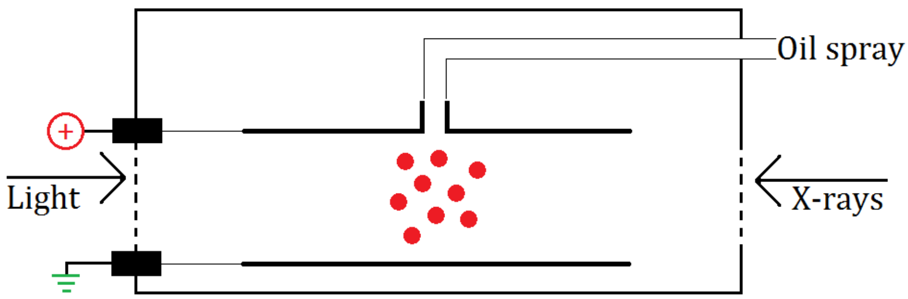
Their charge-to-mass ratio was found to be exactly the same, whatever gas or types of electrodes were used in the experiment.

The cathode ray particles had a very small mass, 1/2000 of a hydrogen atom. He decided to call them the *electrons*.

The name was suggested by George Johnstone Stoney for the "units of electricity.

C. Millikan's Oil drop experiment

The electron charge was first measured by the American Physicist Robert Millikan using his Oil drop experiment.



He gave the oil drops negative charge by spraying them into air ionized by X-rays. He adjusted the charge on the plates so that the upward force of attraction equaled the downwards force of gravity, and so the drop would stay stationary.

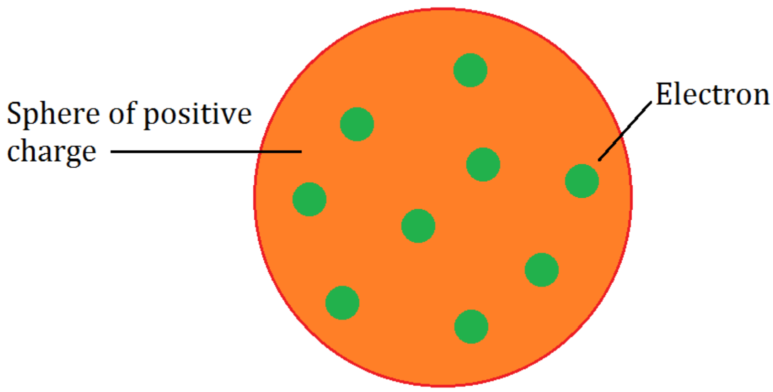
Calculations on the forces allowed him to find the charges on the drops. These were multiples of the charge on an electron.

He found that the electron had a charge of 1.602 x 10^{-19} C (coulombs). They had a mass of 9.109 x 10^{-31} kg, which is 1/1837 of the mass of a hydrogen atom.

Discovering the protons and neutrons

The new atomic models; the Plum-Pudding, and the Nuclear Atom

New discoveries needed new atomic models. If there are negatively charged electrons in all neutral atoms, then there must be a positively charged particle to cancel them out.

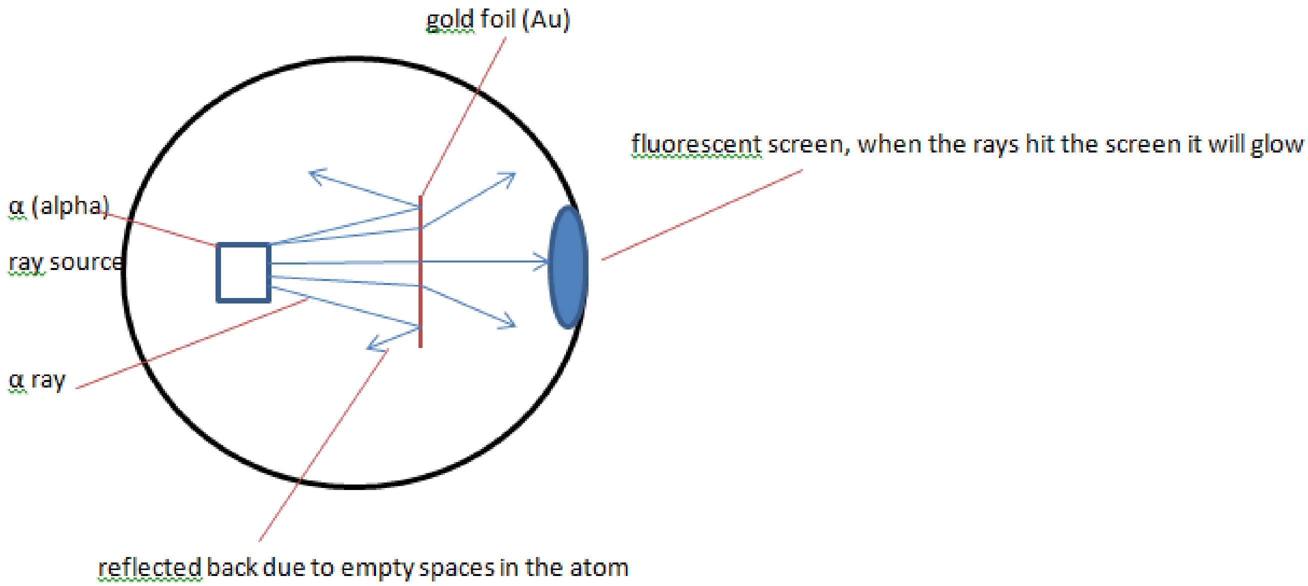


For some time, the most favored was the J.J. Thomson's "Plum-Pudding" model, in which the electrons were embedded in a "pudding" of positive charge.

Then an experiment in 1909, by Hans Geiger and Ernest Rutherford, changed everything. They were investigating how alpha particles were scattered when they were fired at very thin sheets of different metals.

They detected alpha particles by flashes of light that were caused by the impact with a fluorescent screen. Some, however, were deflected with large angles.

The “Plum-Pudding” model couldn’t explain the surprising observations. However, Rutherford suggested that atoms consist of largely empty space and that the mass is largely concentrated into a very small, positively charged *nucleus*.



Most alpha particles pass through the empty space in the atom with very little deflection. When the alpha particle approaches on a path close to the nucleus, however, the positive charges strongly repel each other, and the alpha particle is deflected through a large angle.

Particles in the nucleus

The proton

Rutherford reasoned that there must be particles that are responsible for the positive charge. He and Marsden fired alpha particles through hydrogen, nitrogen and other elements.

They detected new particles with positive charge and the approximate mass of a hydrogen atom. He called these particles *protons*.

The proton has a positive charge of 1.602×10^{-19} C, equal in size but different in charge of that of an electron. It has a mass of 1.673×10^{-27} kg.

Each electrically neutral atom has the same number of protons as the number of electrons outside the nucleus.

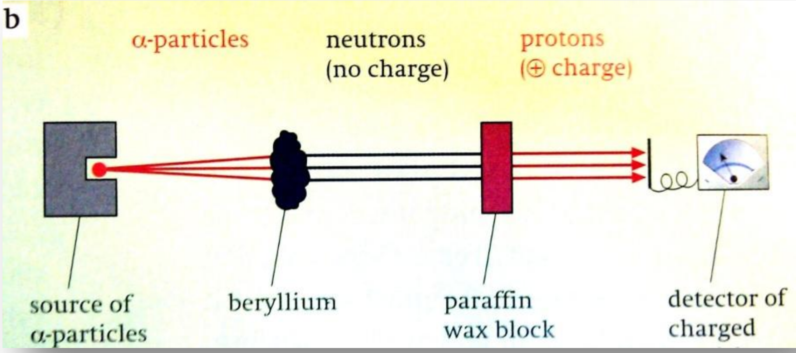
The neutron

The mass of the atom, which is concentrated in its nucleus, cannot depend only on protons, as they usually provide around half of the atomic mass.

Rutherford then proposed that there is another particle in the nucleus which has the same mass of the proton but with no electrical charge. As the particle is not charged, its detection was very difficult, not until 1932.

One of his co-workers, James Chadwick, produced sufficient evidence for the existence of the neutron.

Using the apparatus Chadwick bombarded a block of beryllium with alpha particles. No charged particles were detected on the other side of the block. However, when a block of paraffin wax was placed near the beryllium, charged particles were detected and identified as protons.

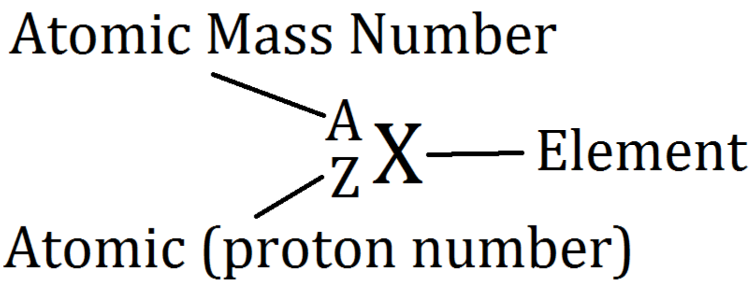


The alpha particles had knocked out neutrons from the beryllium, and in turn these knocked out protons out of the wax.

Order of discovery of subatomic particles

1. ***Electrons (cathode ray)***
2. ***Protons***
3. ***Neutrons (1932)***

Atomic and Mass numbers



Atomic Number (Z)

The difference between atoms of different elements is the number of protons in the nucleus of each atom.

The atomic number shows:

- The number of protons in the nucleus
- The number of electrons in a neutral atom of that element
- The position of the element in the periodic table

Mass number (A)

It is useful to have a measure for the total number of particles in the nucleus of an atom. It is called the mass number. For any atom:

- The mass number is the sum of the number of protons and the number of neutrons in the nucleus

Behavior of protons, neutrons and electrons in electric fields

The three particles behave differently in electric fields due to a different charge on them and their relative masses.

Protons are attracted to the negative pole and electrons are attracted to the positive pole. Because electrons are much lighter, they are deflected more.Neutrons are not deflected as they have no charge on them.

Summary:

Particle Name	Relative Mass	Relative Charge
Proton	1	+1
Neutron	1	0
Electron	negligible	-1

Isotopes

In Rutherford's atomic model, the nucleus consists of protons and neutrons, each with a mass of one atomic unit. The relative atomic masses of elements should then be whole numbers. It was a puzzle why chlorine has a relative atomic mass of 35.5.

The answer is that atoms of the same element are not all identical.

These atoms that have the same proton number but a different mass number are called isotopes.

For example, hydrogen has three isotopes:

Isotope	Protium	Deuterium	Tritium
Symbol	$^{1}_{1}H$	$^{2}_{1}H$	$^{3}_{1}H$
Protons	1	1	1
Neutrons	0	1	2

Electrons in atoms

The electrons are involved in the changes that happen in chemical reactions, so if we knew everything about the arrangements of the electrons in atoms and molecules, we could predict most of the ways that chemicals behave, purely from mathematics.

There are some models that show how the electrons are arranged around the nucleus. The first and most simple one is that thy orbit the nucleus – which was rejected.

This is because the electrons would soon lose energy and fall down into the nucleus.

The second model is that they orbit around the nucleus, in shells or energy levels.

Arrangement of electrons: Energy levels and shells

In 1913, a Danish physicist Niels Bohr proposed his ideas about arrangements of the electrons in atoms.

The German physicist Max Planck had proposed in his Quantum Theory, that energy is atomic, and can only be transferred in packets, or quanta.

Bohr applied this theory to the energy of electrons. So he suggested that electrons can only have energy in quanta, and so they can only exist in *quantized levels of energy*.

If an electron gains or loses energy, it will travel up and down the energy levels, respectively, but cannot stay somewhere in between.

These energy levels are most commonly called as *shells*.

Shells are numbered 1, 2, 3, 4, etc. These numbers are known as the principal quantum numbers, which are given the symbol n. Such numbers correspond to the periods in the periodic table.

For a given element, electrons are added to the shells as follows:

- Up to 2 in shell 1
- Up to 8 in shell 2
- Up to 18 in shell 3

Ionisation energy

When an atom loses an electron it becomes a positive ion. We say that it has been ionized. Energy is needed to remove electrons and this is generally called *Ionisation Energy*.

The first ionisation energy of an element is the amount of energy needed to remove one electron from each atom in a mole of atoms of an element in the gaseous state.

The general symbol for ionisation energy is ΔH_i and for the first ionisation energy it is ΔH_{i1}.

$X_{(g)} \rightarrow X^{+}_{(g)} + e^{-}$

1M 1M

2^{nd} Ionization Energy/Enthalpy/Potential

$X^{+}_{(g)} \rightarrow X^{2+}_{(g)} + e^{-}$

1M 1M

3^{rd} Ionization Energy/Enthalpy/Potential

$X^{2+}_{(g)} \rightarrow X^{3+}_{(g)} + e^{-}$

1M 1M

Examples of ionisation energies of the element Nitrogen:

Electrons removed	1	2	3	4	5	6	7
N	1400	2860	4580	7480	9450	53300	64400

Trends in ΔH_i (Ionization energy):

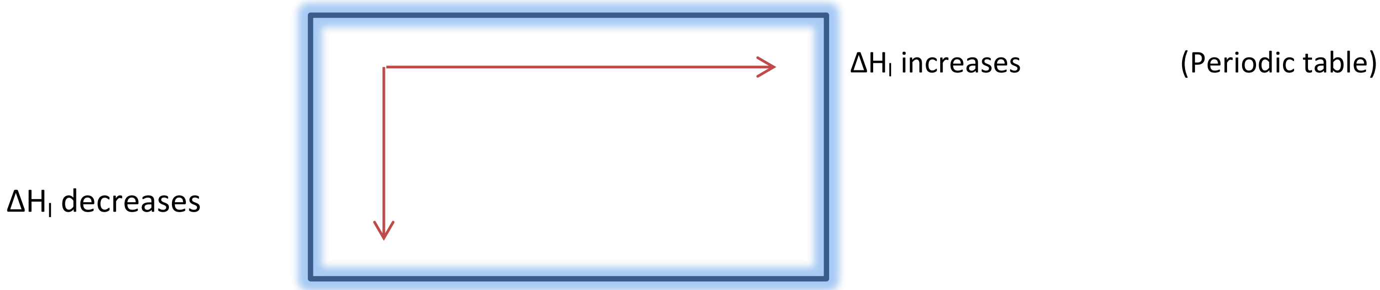
1) ΔH_I increases as more and more electrons are removed i.e. $\Delta H_{I2} > \Delta H_{I1}$.
2) There are one or more particularly large sizes of ΔH_I within the successive ΔH_I of each element (except for H and He), due to the jump from one energy level to another.

Factors affecting ΔH_I:

1) The size of the positive nuclear charge; the greater the positive nuclear charge the greater the ΔH_I.
2) The distance of electrons from nucleus; the further the e^- is from the nucleus, the weaker the attraction and therefore the smaller the ionization energy needed.
3) The shielding effect of inner electrons; as the number of inner shells increases, the ΔH_I decreases.

In general:

1. ***As we go from left to right across a period, the nuclear charge increases and atomic size decreases, ΔH_I increases.***
2. ***As we go down a group the shielding effect and atomic size increases and ΔH_I decreases.***



3. ***Electrons are in discrete energy levels (quantized) (or shells) characterized by their principal quantum numbers (n= 1,2,3,4, etc...)***
4. ***The nearest to the nucleus is shell 'K' with n=1, the next is 'L' with n=2. The furthest away from the nucleus has the highest energy (energy becomes higher)(less negative)***
5. ***The maximum number of electrons in an energy level (or shell) is given by the equation***

   $\#e = 2n^2$ where n is 'principal quantum number'

Need for a more complex model

The electronic configurations are not so simple. For some elements, like lithium to neon, their first ionization energies don't increase evenly.

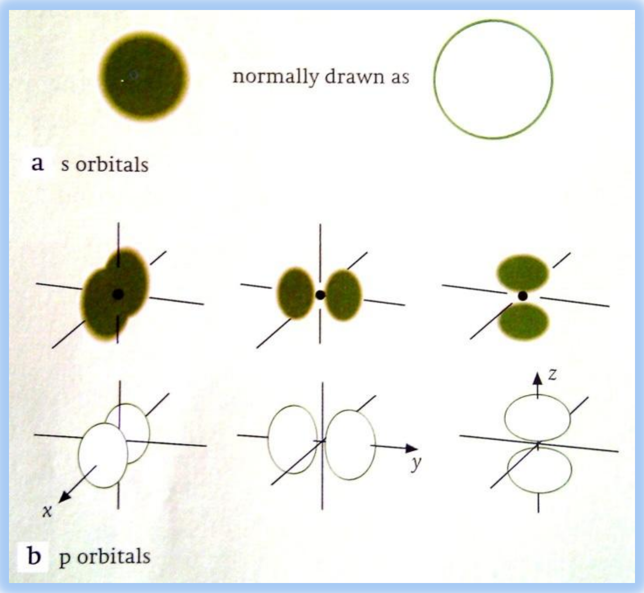
This, and other complications, shows the need for a more complex model of electronic configurations, other than the Bohr's model.

Bohr's model as shown by quantum mechanics:

1) Energy levels consist of one or more sub-levels which contains orbitals at different energies.

2) Sublevels are s, p, d, f types

- *S contains one orbital*
- *P contains three orbitals*
- *D contains five orbitals*
- *F contains seven orbitals.*



3) An orbital is a region in space around the nucleus where there is a high probability of finding a particular electron.

4) Orbitals have different 3D shapes, no exact boundaries. They are fuzzy like clouds, often called electronic clouds, drawn with boundaries to represent 90-95% of the space in which an electron exists.

5) S orbitals are spherical

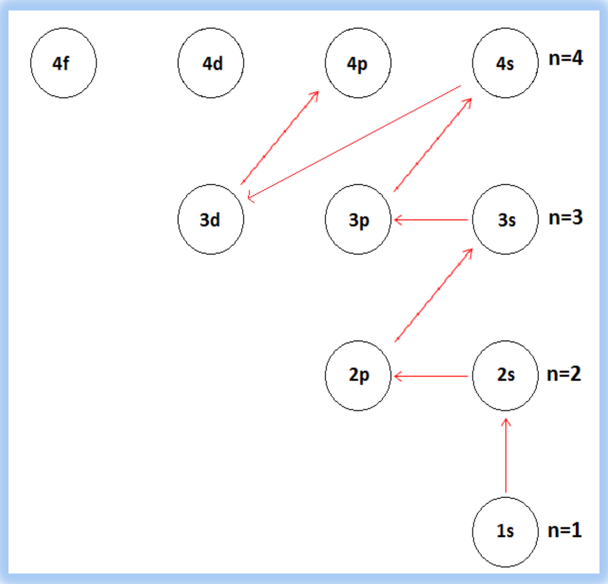
6) While P orbitals are dumbbell shaped with 2 lubes extending along X, Y and Z axes.

Filling the orbitals and electronic configurations

Three important rules:

1) Pauli Exclusion Principle.
   - Any orbital cannot hold more than 2 electrons, in this case they should be paired (spin-paired)
2) In filling shells and orbitals, the orbitals of the lowest energies are filled first. (i.e. the electronic configuration [distribution of electrons] should be given in its lowest energy state.
3) Orbitals of equal energies (degenerate orbitals) are filled singly first. Then you should double up with more electrons.

(Lowest energy state = Ground state)



Examples of electronic configuration of some elements:

First 18 elements:

1	H	$1s^1$
1	He	$1s^2$
3	Li	$1s^2\ 2s^1$
4	Be	$1s^2\ 2s^2$
5	B	$1s^2\ 2s^2\ 2p^1$
6	C	$1s^2\ 2s^2\ 2p^2$
7	N	$1s^2\ 2s^2\ 2p^3$
8	O	$1s^2\ 2s^2\ 2p^4$
9	F	$1s^2\ 2s^2\ 2p^5$
10	Ne	$1s^2\ 2s^2\ 2p^6$
11	Na	$1s^2\ 2s^2\ 2p^6\ 3s^1$
12	Mg	$1s^2\ 2s^2\ 2p^6\ 3s^2$
13	Al	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$
14	Si	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$
15	P	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$
16	S	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$
17	Cl	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$
18	Ar	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

Electronic configuration for some of the elements from 19 to 36:

19	K	$[Ar]\ 4s^1$
20	Ca	$[Ar]\ 4s^2$
21	Sc	$[Ar]\ 3d^1\ 4s^2$
		…
24	Cr	$[Ar]\ 3d^5\ 4s^1$
25	Mn	$[Ar]\ 3d^5\ 4s^2$
		…
29	Cu	$[Ar]\ 3d^{10}\ 4s^1$
30	Zn	$[Ar]\ 3d^{10}\ 4s^2$
31	Ga	$[Ar]\ 3d^{10}\ 4s^2\ 4p^1$
		…
35	Br	$[Ar]\ 3d^{10}\ 4s^2\ 4p^5$
36	Kr	$[Ar]\ 3d^{10}\ 4s^2\ 4p^6$

Some electronic configurations arrow in box form:

	1s	2s	2p		
H	↑				
He	↑↓				
Li	↑↓	↑			
F	↑↓	↑↓	↑↓	↑↓	↑
Ne	↑↓	↑↓	↑↓	↑↓	↑↓

		4s	3d					4p		
K	[Ar]	↑								
Sc	[Ar]	↑↓	↑							
Mn	[Ar]	↑↓	↑	↑	↑	↑	↑			
Ga	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑		
Kr	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

END OF LESSON