The Atomic Theory

The idea that the elements are capable of being split up into very tiny particles was first evolved by the Greeks. The word atom comes from the greek word **atomos** which means indivisible and the idea that the elements are made up of atoms is called the *atomic theory*.
A scientific theory is a scientific idea which has been accepted by scientists after due consideration. When an idea is first proposed it is called a *hypothesis* (note. theories are not facts but thoughts). A scientific law is a generalised statement of observed facts.

The Laws of Chemical Combination

Lavoisier (1774) showed that when tin is made to react with air in a closed vessel the weight of the vessel before and after heating is the same.

> **Law of Conservation of Mass:** The mass of a system is not affected by any chemical change within the system.

When various metals are oxidised one part by weight of oxygen always combines with the same number of parts by weight of the metal.

> **Law of Definite Proportions:** A particular chemical compound always contains the same elements united in the same proportions by weight.

Two elements can also combine to form more than one compound. For example, the different weights of oxygen which can combine with the same weight of nitrogen are integral multiples of 8.

> **Law of Multiple Proportions:** If two elements combine to form more than one compound the different weights of one which combine with the same weight of the other are in the ration of small whole numbers.

> **Law of Reciprocal Proportions:** The weights of two (or more) substances which react separately with identical weights of a third are also the weights which react with each other, or simple multiples of them.

The combining weights are called the *Equivalent Weights of the elements*. These four laws led to the atomic hypothesis proposed by Dalton (1803)

- The chemical elements consist of small particles, called *atoms*, which cannot be subdivided by chemical means.
- All the atoms of an element are identical.
- Chemical compounds are formed by atoms joining together in simple proportions (1:1, 1:2, 1:3).

These suggestions could be tested by experiment and this method is called *the scientific method*.
Gay-Lussac (1805-1808) showed that when chemical reactions occur between gases there is always a simple relationship between the volumes of gases and the products if they are gasses.

1 volume of Hydrogen + 1 volume of Chlorine → 2 volumes of Hydrogen Chloride
2 volumes of Hydrogen + 1 volume of Oxygen → 2 volumes of Steam

The elements therefore combine in simple proportions and the number of atoms must be simply related.

2 atoms of Hydrogen + 2 atoms of Chlorine → 2 atoms of Hydrogen Chloride

Every atom of hydrogen and chlorine must therefore be split into half to form an atom of hydrogen chloride which contradicts Dalton's hypothesis.
Avogrado (1811) resolved this difficulty by assuming that gas atoms do not exist separately but as aggregates called *molecules*. He postulated that equal volumes of all gases under the same conditions contain the same number of molecules.

2 molecules of Hydrogen + 2 molecules of Chlorine → 2 molecules of Hydrogen Chloride

Then the ratio of the weight of a volume of gas to the weight of the same volume of a standard gas equals the ratio of the molecular weight of the gas to the molecular weight of the standard gas which in turn is equal to the ratio of their densities. Therefore molecular weight is proportional to density and so relative molecular and atomic weights can be determined from density measurements.
Because nearly all the elements form stable compounds with it oxygen was chosen as the standard and taken to have an atomic weight of 16. Experiments show that 1,008g of hydrogen combine with 8g of oxygen and that two atoms of hydrogen combine with one atom of oxygen to form water. Hence 1,008g of hydrogen contain twice as many atoms as 8g of oxygen. Now hydrogen is the lightest element, so if the standard is chosen so that the atomic weight of hydrogen is close to 1 there would be no element with an atomic weight less than 1.
The atomic weight of an element is a small integral of its equivalent weight and this integer is called the *valence*. The valence is the ratio of the atomic weight to the equivalent weight and the equivalent weight and the valence can be determined experimentally. The method of relative densities gives an approximate value for the atomic weights of non-volatile elements which have no gaseous compounds. The atomic weights of solids which have few or no volatile compounds can be found using Dulong and Petit's Law (atomic weight × specific heat = 6,4).

Weights and Sizes of Atoms and Molecules

Since the atomic weight of hydrogen was taken as 1,008 the molecular weight is 2,016 and the gram molecular weight (mole) is 2,016 g. The density of hydrogen is 0,09 g/litre at normal temperature and pressure (NTP) and the gram molecular volume is 22,4 litres. Experiments with other gases show the same gram molecular volume therefore one mole at NTP contains the same number of molecules which is Avogadros number and this has been determined by several methods. The weight of the lightest element is then found by dividing the atomic weight Avogadros number.

$$\frac{1,008}{6,02\times10^{23}} = 1,67\times10^{-27}\,\text{kg}$$

Now one mole of water occupies 18 ml so if each water molecule were cubic it would occupy

$$\frac{18}{6,02\times10^{23}} = 3\times10^{-26}\,\ell$$

and since the volume of a sphere is two thirds the volume of a cube the radius of the water molecule is of the order 2×10^{-10} m. The radius of a gas molecule can be calculated using the kinetic theory of gases, from viscosity, from the diffusion constant, and from thermal conductivity. The radius of the hydrogen atom comes out to be about $1,37\times10^{-10}$ m.

Periodic Table (Mendeleeff 1869)

The elements when arranged according to atomic weight show a periodicity in their properties. The arrangement corresponds with their valences. It was at first difficult to see why Lithium, Potassium and Sodium should show similar properties.

Faradays Laws of Electrolysis

> The chemical action of an electric current is directly proportional to the quantity of electricity which passes through a solution.
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> The weights of the substances deposited by the same quantity of electricity are proportional to their chemical equivalents.

Stoney (1874) made the hypothesis that there was a fundamental unit of electricity and he suggested the name *electron*. To account for electrolysis Arrhenius (1880) believed that electrolytes contained electrically charged particles called *ions*.
The total amount of electric charge associated with one mole of a gas is similar to that carried by univalent ions in one mole of salt solution. If the molecules of gas are assumed to be singly ionised they seem to carry the same charge as univalent ions in solution.
Now when an electric current passes through a low pressure gas a glow is seen on the glass opposite to the cathode. This glow was attributed to rays coming from the cathode and hence were called *cathode rays*. Thomson (1897) showed that cathode rays consisted of negatively charged particles and determined their charge to mass ratio. He showed that they travelled at speeds about 0,1c and that the value of the charge to mass ratio was about 1/1800 of the hydrogen ions in electrolysis. If the charges are the same the mass of the cathode rays is about 1/1800 the mass of the hydrogen atom.
When UV light falls on certain metals negatively charged particles with the same charge to mass ratio as cathode rays are ejected (Hertz 1887). The same result was found for the charged particles emitted in thermionic emission.
In 1896 Bequerel discovered radioactivity the spontaneous disintegration of atoms with the emission of postively charged α-particles, negatively charged β-particles, and neutral *gamma*-rays.
These discoveries seemed to indicate that atoms contained negative and positive charges and were not as indivisible as first thought. An early theory regarded the atom as a positively charged sphere in which the negatively charged particles were distributed. By 1900 atoms were thought to have a diameter of about 10^{-10} m and to be neutral i.e. to have the same number of positive and negative charges. The negative charges were the electrons and the mass of the atom was thought to be many times the mass of the electrons. An early theory by Thomson regarded the atom as a positively charged sphere in which the negatively charged particles were distributed.

In 1900 the average charge on an electrolytic ion was found and between 1905 and 1908 the average charge on gaseous ions was found. Milikan (1909-1917) obtained a value for the charge on the electron.
The scattering of charged particles such as α-particles can be described in terms of the electrostatic forces between the particles and the charges which make up the atom. For the Thomson atom the average deflection should be very small. However, Geiger (1910) found that 1:8000 α's were scattered through an angle greater than 90^o. Rutherford (1911) proposed a new atomic model by assuming that all the positive charge was concentrated in a minute nucleus (from the Latin word for a nut or kernel) and that the electrons were distributed over a sphere of radius comparable to the atomic radius. Geiger and Marsden (1913) found that the experimental facts fitted this model.
If the coulomb force holds up to small distances from the nucleus then an estimate of the nuclear radius can be found from α-particle scattering experiments. The radius of the silver nucleus was estimated to be of the order of 10^{-15} m which is very small compared to the atomic radius. Thus in 1913 the atom was regarded as consisting of a positively charged nucleus (about 10^{-15} m in radius) surrounded by the electrons distributed in a volume (about 10^{-10} m in radius). The charge on the nucleus was Ze where Z is a positive integer and e is the electronic charge. Moseley showed that Z was equal to the atomic number which determines the position of the element in the periodic table. Thus the atomic properties are determined by the number of electrons in the atom.

Classical Physics (prior to 1900)

- Light and other electromagnetic radiation carries energy and momentum
- If a charged particle is accelerated it emits electromagnetic radiation at a rate proportional to the acceleration squared.
- If an accelerated charged particle oscillates with simple harmonic motion it emits radiation with a frequency equal to the frequency of the simple harmonic motion.

Classical physics (newtonian mechanics, E-M theory and thermodynamics) could not explain atomic phenomena. An atom could not exist as stationary positive and negative charges, and if the electrons circle the nucleus they would be subject to a constant acceleration, the centripetal acceleration, and hence would radiate E-M radiation. The energy of the system would then decrease and the atom would collapse. But these predictions do not agree with the experimental facts — atoms last for an extremely long time. Classical physics also could not account for the atomic line spectra of the elements nor for X-ray spectra.

Quantum Theory

This was introduced in 1900 by Planck because classical theory could not explain the dependence on the wavelength of the intensity of radiant energy emitted by a blackbody.
Thermal radiation is distributed over a continuous spectrum of wavelengths. At low temperatures it is chiefly infrared (long wavelength). At about 500^oC bodies begin to glow red-hot and around about 3000^oC the radiation contains enough of the short wavelengths to appear white-hot. A blackbody has an absorptivity of 1 and an emissivity of 1, i.e. it absorbs all the

radiation incident upon it and it is also the most efficient radiator. Stefan (1897) obtained an empirical rule

$$W = e\sigma T^4$$

where W is the rate of emission, e is the emissivity and σ is the Stefan-Boltzmann constant.
Boltzmann (1884) derived an equation using thermodynamics. Wein (1893) assumed the radiation was produced by emitters or oscillators of molecular size, the frequency being proportional to their kinetic energy, and the intensity proportional to the number of oscillators with that energy. The Rayleigh-Jeans law

$$f(\lambda, T) = 8\pi kT\lambda^{-4}$$

was derived using classical dynamics and statistics. This equation fits the experimental data at long wavelengths but fails to account for the observed dependence on temperature.
Planck postulated that the oscillators could only have energies equal to ϵ_o, $2\epsilon_o$, $3\epsilon_o \ldots \mathrm{n}\epsilon_o$ where ϵ_o is a discrete, finite amount, or quantum of energy and $\epsilon_o = hf$.

$$f(\lambda, T) = \frac{8\pi hc\lambda^{-5}}{\mathrm{e}^{hc/\lambda kt} - 1}$$

The formula gave excellent agreement with the experimental results. However, the concept of discrete energy states or quanta was so different from classical theory that it was met with strong opposition.
Hertz (1887) had discovered that certain metals emit electrons when irradiated with UV light. In this effect, the photoelectric effect, the electron current is proportional to the intensity of the light. The light has to have a critical frequency before electrons are ejected, and light above this frequency immediately ejects electrons and this is independent of the intensity. These facts could not be explained on classical theory.
According to Einstein (1905) energy can be emitted and absorbed by a radiator only in units of hf and that light consists of quanta of energy (*photons*) which move through free space at the velocity of light. The energy of the photoelectron (E_e) is equal to the energy of the light quantum (hf) minus the amount of work (ϕ is called the *workfunction*) needed by the electron to escape from the metal.

$$E_e = hf - \phi$$

If the photon energy (hf) is less than the workfunction (ϕ) of the metal no electrons are ejected. The number of ejected electrons is proportional to the number of photons i.e. the light intensity. Milikan (1916) verified Einstein's theory. Einstein also successfully applied the quantum theory to the specific heats of solids and polyatomic gases.

Atomic Spectra

The first problem that must be solved by a theory of atomic structure is the line, or emission, spectra which are produced when an electric discharge is produced in a gas or from a flame. Instead of a continuous band of colours, as in a rainbow or an incandescent solid, only a few colours appear in the form of bright, isolated, lines. The wavelengths of these lines are characteristic of the element and is a property of the atoms of that element. The spectrum of hydrogen in the visible and near UV region consists of a series of lines which come closer together has the wavelength decreases. In addition to emission spectra the elements have characteristic absorption spectra. The absorption occurs at wavelengths which correspond to the emission lines.

Balmar (1885) and Rydberg produced empirical formulae for the emission spectra of hydrogen. The Rydberg formula,

$$\frac{1}{\lambda} - R_H \left(\frac{1}{2^2} - \frac{1}{n^2} \right)$$

where R_H is the Rydberg constant, holds for the nine visible lines of hydrogen.
Bohr (1913) developed a theory of the atom which accounted for many of the properties of atomic spectra. Bohr applied the quantum theory to the Rutherford atom. He postulated that the atom consists of a number of states in which the emission of radiation corresponded to a transition between two states. The dynamic equilibrium of the system is governed by the ordinary laws of mechanics which do not hold in transitions. The different stationary states consist of electrons rotating about a positive nucleus in circular orbits where the angular momentum is quantised ($mvr = nh/2\pi$). From this theory the estimates of atomic radii are in good agreement with those obtained by other methods. According to Bohr a hydrogen atom radiates when an electron jumps from one stationary state to another of lower energy. Bohr's theory gives excellent agreement with the Rydberg constant and the wavelengths of the Balmar series but does not account for all atomic phenomena.

Wave-Particle Duality

Light is sometimes treated as a wave (reflection, refraction, diffraction and interference) and sometimes as a particle or photon (the photoelectric effect and the Compton effect). In the Compton effect the interaction between a photon and an electron is treated as an elastic collision between two particles. Electromagnetic radiation is regarded as having a dual nature the momentum (particle nature) is directly related to the wavelength (wave nature).
De Broglie (1924) suggested that matter also has a dual nature and that particles, like electrons, have a wavelength ($\lambda = h/mv$). Davisson and Germer (1927) showed that electrons show similar diffraction patterns as X-rays when they bombard crystals.
Bohr's quantum conditions also follow from the wave nature of the electron. By considering the electron orbit as a standing wave and using the De Broglie hypothesis the angular momentum is found to be quantised.

$$mvr = \frac{nh}{2\pi}$$

The Nucleus

Prout had suggested in 1816 that atoms are made up of elementary constituents.
All the atomic masses are close to integers and the presence of two or more isotopes results in fractional atomic weights. The lightest positive charge found had the mass of the hydrogen atom and carried a positive charge equal to the electronic charge. This led to the idea that all atoms were made up from hydrogen hence the name *proton* (which comes from the Greek word **protos** which means first) was given to indicate its importance. To account for atomic masses close to the integer A it was necessary to assume that atoms contained A protons but unfortunately the charge on the nucleus would have to be A which is not so. To overcome this difficulty it was then assumed that the nucleus contained electrons. This proton-electron hypothesis accounted for both α- and β-decay but a free electron confined to the nucleus would have to have energy close to 60 MeV and a speed near 0,999c. Electrons emitted in β-decay never have energies greater than 4 MeV so it seemed unlikely that the nucleus contained electrons. Rutherford (1920) suggested

that an electron and a proton might be closely combined so as to form a neutral particle called a *neutron*. This neutron being neutral would be extremely difficult to detect. However, Bothe and Becker (1930) discovered that when boron and beryllium were bombarded with α-particles a very penetrating radiation was produced. Curie and Joliot (1932) showed that when this radiation was allowed to fall on hydrogenous materials highly energetic protons were ejected. Chadwick (1932) showed that the radiation had a mass similar to the mass of the proton but with zero charge. Since this new particle was neutral it was identified as the neutron.
The neutron-proton hypothesis is consistent with the phenomenon of radioactivity. The electron cannot exist inside the nucleus and the β-particle is formed at the instant of emission when a neutron is considered to change into a proton and an electron. (Note - the free neutron is radioactive and decays into a proton by emitting a β-particle) An α-particle can be formed by two protons and two neutrons.
In considering nuclei of different elements to be composed of neutrons and protons the neutron is not regarded as a composite particle (consisting of a proton and electron) but as a fundamental particle like the proton. Because of the positive charge on the proton there must be electrostatic repulsive forces between the protons. From α-particle scattering experiments the atomic nucleus has a radius of about $10^{-15}\,\mathrm{m}$ and the mass of the hydrogen atom is of the order of $10^{-27}\,\mathrm{kg}$ which means it has a density of about $10^{18}\,\mathrm{kg/m^3}$. This great density suggests that there must be very strong attractive forces between protons, between neutrons, and between protons and neutrons which are more complex than gravitational or electromagnetic forces. The nuclear force must be short-range and fall off rapidly with distance from the nucleus where the coulomb forces dominate. The magnitude of the nuclear force means that it requires millions of times more energy to split it up into its constituents than it requires to separate an electron from it nucleus.
The emission of α- and β-particles gave rise to the ideas that atoms are made of smaller units and the scattering of α-particles gave rise to the idea of the nuclear atom. The analysis of the chemical properties of radioactive elements led to the discovery of isotopes. The bombardment of elements with very high energy α-particles from radioactive isotopes led to the discovery of the neutron and to the discovery of artificial radioactivity.

Fission

The discovery of fission was the result of attempts to make transuranic elements ($Z > 92$). In early experiments uranium was bombarded with neutrons and several β activities, distinguished by their half-lives, were detected. In addition to the elements which seemed to be real transuranic elements there were four which were thought to be isotopes of radium. Hahn and Strassman (1939) showed that these elements were isotopes of barium and lanthanum. The production of these isotopes required a reaction which split the nucleus into fragments. Other isotopes such as strontium, yttrium, krypton and xenon were found. These products had high energy and produced intense ionisation in gases. This was ample evidence that the nucleus had split into fragments and the reaction was called *fission*. In addition to the fragments neutrons and gamma rays were also produced. One of the striking properties of fission is the amount of energy, about 200 MeV, which is released per fission, and the fact that several neutrons are emitted results in a chain reaction which when allowed to proceed without control produces the atomic bomb (A-bomb, 1 kg of uranium is equivalent to about 20000 tons of the conventional explosive TNT) and when controlled in a nuclear reactor leads to nuclear power.