1 The building blocks of the atom

1.1 The beginnings of atomic research

The word ‘atom’ is derived from the Greek ‘atomos’, meaning indivisible. In about the year 400 BC the Greek philosopher Democritus postulated that all matter was made up of minute particles which could not be destroyed or broken up. He was unable to perform any experiment to support his hypothesis, but this concept could account for the fact that different substances had different densities: the more the atoms were compressed the denser and heavier the substance became. A few Greek sages accepted the atomic theory of Democritus, but the great majority adopted the view of Aristotle, who believed that matter was continuous in structure, and this was also the opinion held by the alchemists in the Middle Ages. When modern scientific research began in the seventeenth and eighteenth centuries, the concept of atoms was revived and appeared in the writings of scientists, but it was generally mentioned incidentally and no attempt was made to use it to explain natural phenomena or to verify it experimentally.

John Dalton is regarded as the father of modern atomic theory. He was an English teacher who dabbled in chemistry as a hobby and became one of the founders of modern chemistry. The idea of atoms attracted him because he found that it could explain certain properties of gases. Later he realized that it also provided a simple explanation for the fact that elements combining to form compounds do so in fixed ratios by weight (the Law of Constant Proportions). In his book A new system of chemical philosophy, published in 1808, Dalton propounded his atomic theory, according to which all matter was composed of atoms, all the atoms of a particular element were identical, while the atoms of different elements differed in mass and in other properties. When two or more elements combined to form a compound, their atoms joined to form ‘compound atoms’, or molecules as they are called today. Dalton’s ideas fell on fertile ground. At that time the experimental methods in science were sufficiently advanced to take up the challenge of testing theories on the structure of matter, and the atomic theory
The building blocks of the atom

which was perfected by other chemists of the nineteenth century was based solidly on the science of chemistry.

The scientists of the nineteenth century succeeded in determining the mass ratios of the atoms of different elements, and to a close approximation also their absolute masses and sizes. By experiments which were both simple and ingenious, like measuring the area resulting from the spread of a drop of oil floating on water, or measuring the rate at which two different gases mix, they could establish that the diameter of an atom (and a molecule) is not much greater than, nor much less than, a hundredth of a millimetre of a centimetre, or $10^{-8}$ centimetres in scientific notation. This unit of length is called an angstrom (denoted Å) in memory of the nineteenth-century Swedish physicist A. J. Angström, who investigated the spectrum of the sun and the northern lights.

Michael Faraday’s researches on electrolysis at the beginning of the last century implied that the interatomic forces are essentially electric in nature, and yet, until the 1890s nothing at all was known about the internal structure of the atoms. They were regarded as tiny grains of matter, solid but elastic like billiard balls, and the name ‘atom’ – indivisible – was still appropriate. The first to discover anything about the internal structure of the atom was the British physicist J. J. Thomson, who is regarded as the discoverer of the electron.

The discovery of the electron

During the years 1894 to 1897 J. J. Thomson investigated the phenomenon of ‘cathode rays’ which had been discovered in 1858. To form these invisible rays an electric voltage was applied between two metal plates (electrodes) in a glass tube under high vacuum. The rays were emitted from the negative electrode – the cathode – and caused a glow when they impinged on the glass or a plate coated with zinc sulphide fixed inside the tube (see Fig. 1.1). Another British physicist, Sir William Crookes, had in the year 1879 postulated that the cathode rays were a stream of particles carrying negative electric charges. Thomson verified this by showing that the rays could be deflected from their straight path by a magnetic or an electric field, and that their behaviour under the influence of these fields was exactly what would be expected of a stream of negatively charged particles. By measuring the

*We shall frequently use powers of ten for writing very small (or very large) numbers. $10^2$ is $10 \times 10$ and $10^3$ is $10 \times 10 \times 10$, etc. Negative powers are defined by the formula: $10^{-8} = 1/10^8$
1.1 The beginnings of atomic research

Figure 1.1 Cathode rays. A beam of electrons emitted by the cathode (C) passes through a slit in the anode (A) and produces a spot of light on the fluorescent screen (F). One can deflect the beam by applying an electric or magnetic field.

deflection of the rays in combined electric and magnetic fields of different strengths he was able to calculate the speed of the particles as well as the ratio between the charge carried by each particle (e) and its mass (m), but no way could be found of calculating the charge and the mass separately. The ratio e/m of the particle was found to be independent of the type of metal of which the cathode was made or the residual gas in the tube. Moreover, in the year 1888 several scientists had observed that when various metals were illuminated with ultraviolet light they emitted negatively charged particles (see p. 36). Thomson repeated these experiments and found that the particles which the light knocked out of the metal surface were identical (in regard to their e/m ratio) to the particles constituting the cathode rays. Thus he reached the conclusion that these particles were present in all matter, and that by means of an electric voltage or irradiation with light they could be extracted from certain substances. The particles were given the name electrons. (Thomson was awarded the Nobel Prize in physics in 1906 for this discovery.)

When enough experimental results have been accumulated in a new area of physics, the scientists usually try to utilize these results to construct a description of the physical world, which they call a model. On the strength of Thomson’s findings, the first experiment-based model for the structure of the atom was put forward in 1902. This model was proposed by the British physicist Lord Kelvin, but as it was based on Thomson’s experiments and was enthusiastically supported by him, it came to be known as Thomson’s model. (Since this model was later rejected in favour of a better one, its authors apparently did not insist on getting the credit for it.) According to the model, the atom was a positively charged sphere about 1 Å in diameter in which electrons were embedded like plums in a pudding. The total charge of the negative electrons was equal to the positive charge of the sphere, and so the atom as a whole was electrically neutral. It was already known
The building blocks of the atom

Figure 1.2

Millikan’s experiment to measure the charge of an electron.

that atoms could be transformed into electrically charged bodies (ions) by various means (for example by irradiation with X-rays). According to Thomson’s model, ionization of an atom (converting it into an ion) is simply the removal of an electron from it. The atom is then left with a positive charge equal in magnitude to the charge of the electron. This explanation of the ionization process provided the basis for the first estimate of the electron charge and hence also its mass (since the ratio $e/m$ was known). The mass was found to be 2000 times smaller than that of the hydrogen atom – the lightest of the elements.

The first accurate measurement of the electron charge was made by the American physicist R. A. Millikan (Nobel laureate for 1923) in a brilliant experiment in the year 1909. By means of X-ray irradiation he charged minute droplets of oil and observed them with a microscope as they floated between two parallel charged plates (see Fig. 1.2). By measuring the speed at which the droplets fell under different electric field strengths he could calculate their charges. All the charges he measured turned out to be integral multiples of a fundamental charge whose magnitude was $1.6 \times 10^{-19}$ coulombs.* It could be assumed that this charge was the charge of a single electron. From now on we shall denote the magnitude of this charge by the letter $e$. (The charge of the electron is $-e$, and the electron itself will be denoted $e^-$.) In more accurate experiments $e$ was found to equal $1.6021 \times 10^{-19}$ coulombs. It also turned out that the charge of most observed positively and negatively charged particles is $\pm e$. (The charge of some short-lived particles is an integral multiple of $e$.) All measured electric charges are in fact multiples of $e$, but because of the minuteness of this fundamental charge scientists did not detect this fact as long as

* The unit of electric charge is called after the French physicist Charles de Coulomb. When a wire is carrying an electric current of one ampere, a charge of one coulomb passes its cross-section each second.
1.1 The beginnings of atomic research

they were dealing with 'large' charges. (Even one-millionth of a coulomb contains more than a million million fundamental charges.) Millikan's success in measuring the charge of the electron made it possible to find its mass as well (since the ratio $e/m$ was known). The mass was found to be $9.11 \times 10^{-28}$ grams, or 1/1840 of the mass of a hydrogen atom.

Rutherford’s experiment

In the first decade of the twentieth century several other models of the atom were proposed. These models were based on a variety of combinations of positive and negative charges, and what all of them had in common was a lack of any experimental basis. The first model based on experiment was that of the illustrious New Zealand-born physicist, Ernest Rutherford. In 1910 Rutherford’s laboratory at Manchester University was engaged in research on the scattering of alpha particles in their passage through matter. Alpha particles are heavy particles – about four times as heavy as the hydrogen atom – with a charge of $+2e$, and are emitted from certain radioactive substances (see below). When a beam of alpha particles strikes a very thin metal foil, it penetrates and passes through it. In the process some of the particles are deflected from their straight path, much as bullets fired into an avenue of trees might be deflected by ricocheting off the tree trunks. Rutherford’s students measured the percentage of particles deflected at different angles as the beam passed through a thin gold leaf. They placed a plate coated with zinc sulphide behind the leaf (see Fig. 1.3) and with the aid of a microscope counted the number of scintillations in a given period. Every scintillation was evidence of an alpha particle striking the plate. They then shifted the plate to a different angle and counted the scintillations in the same period. Through such measurements they hoped to learn something about the internal structure of the atom.

In these experiments only small angles of scattering were examined, because it was assumed that the heavy and fast-moving alpha particles could not change direction to any great extent on their way through the thin leaf. But one day Hans Geiger, a German researcher in Rutherford’s group, was looking for a research topic for his student E. Marsden, and Rutherford suggested he might check if any of the alpha particles were deflected through large angles. Rutherford did not expect any positive results from this experiment, but two days later Geiger reported in great excitement that some of the alpha particles actually recoiled back. According to Rutherford this was the most astonishing event
The building blocks of the atom

![Diagram of Rutherford's experiment](image)

**Figure 1.3**

The apparatus used in Rutherford’s experiment. Alpha particles from the source R, pass through the metal foil (F), and cause scintillations on the fluorescent screen (S). These scintillations are observed by the microscope (M) which can be rotated around TF. (From *Philosophical Magazine*, 25, 604 (1913).)

of his entire life. In his words: ‘It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you.’

Why was Rutherford so astonished? According to Thomson’s model, the density of matter should be practically uniform throughout its volume, because matter was composed of closely packed spherical atoms which were themselves uniform in density. If most of the alpha particles sliced through the gold foil like a knife through soft butter, with only small deviations from their original paths, how could a few of them (about 1 in 8000) recoil like rubber balls from a stone wall?

Calculation showed that the passage of an alpha particle through a single Thomson atom would cause only a small deviation. Passage through many atoms would have a cumulative effect, but it could not be expected that all the deviations would be in the same direction and would add up in the end to a large angle of deviation, just as it would not be expected that in a thousand tosses of a coin it would always land on the same side. There was only one explanation for the surprising phenomenon – the density of matter was not uniform! It was very dense in certain spots, and very rarefied in others.
1.1 The beginnings of atomic research

![Diagram of an atom with an alpha particle beam and a nucleus with an attached gold atom. The alpha particles are deflected.]  

Figure 1.4  
The paths of the alpha particles in Rutherford's experiment. Only particles passing close to the nucleus can be deflected through large angles.

After a series of calculations Rutherford reached the conclusion that most of the mass of the atom was concentrated in a minute nucleus which had a positive charge and a diameter only $1/100\,000$ of that of the atom as a whole. The negative electrons, Rutherford thought, apparently circled the nucleus like planets round the sun, and the size of their orbits was what determined the diameter of the atom. The path of the heavy alpha particles was hardly influenced at all by the light electrons but only by the heavy nucleus, which exerted an electrically repulsive force. Since the gold leaf was extremely thin, each alpha particle passed through only a relatively small number of atoms. In most cases they did not approach the minute nucleus closely and were therefore deflected only slightly, but a few of the alpha particles passed near enough to a nucleus to feel a strong repulsive force and be deflected through a wide angle (see Fig. 1.4).

Rutherford went on to develop a mathematical expression for the relative number of particles deflected through a given angle. It turned out that if his model was correct then this number should depend in a very specific way on the angle of scattering, on the charge of the scattering nucleus and on the speed of the alpha particles. The experimental set-up was improved and in a series of elegant measurements Geiger and Marsden proved that these conclusions were obeyed exactly (see Fig. 1.5).

Rutherford’s experiment is a classic example of how some great discoveries are made. The recipe is as follows. When experimental results do not agree with an existing model or theory, exert your brain and think up a different, more suitable one. To verify your model, draw numerical conclusions from it and test them by experiment. To this recipe one may add spice: sometimes try to test things which at first sight seem unlikely to happen.

The principles of Rutherford’s model (published in 1911) of a small, heavy nucleus of radius $10^{-14}$ to $10^{-15}$ metres surrounded...
The building blocks of the atom

Figure 1.5

The results of Rutherford’s experiment. The dots represent the measured values and the unbroken line represents Rutherford’s theoretical expression for the scattering of alpha particles. The agreement between experiment and theory is obviously quite good. The broken line represents the predictions according to Thomson’s model of the atom. Note that most of the alpha particles experienced small deflections (only a few were deflected by an angle larger than 90°, while about a million particles were deflected by less than 10°). Nevertheless, the number of large-angle deflections was much larger than what was expected according to Thomson’s model.

by light electrons are still valid today, although the perception of the electron orbits have changed more than once through the years, as we shall see later.

Elements and isotopes

As more was learnt about the structure of the atom it turned out that the 92 elements occurring in nature could be characterized not only by the mass of their atoms – as was done by the nineteenth-century chemists – but also by the charge on their nuclei. The magnitude of the nuclear charge must be such as to balance the total charge of the electrons orbiting the nucleus. If we denote
1.1 The beginnings of atomic research

![Periodic Table](image)

Figure 1.6 The periodic table of elements. Atomic numbers are given below the symbol for each element.

the number of electrons by \(Z\), their total charge will be \(-Ze\) (where \(-e\) is the charge on a single electron). Thus the nuclear charge will be \(+Ze\). The quantity \(Z\) is known as the ‘atomic number’ of the element and is by definition an integer.

The mathematical expression derived by Rutherford for the scattering of alpha particles made it possible to determine the value of \(Z\) of the scattering atom. At about the same time it was found that \(Z\) could also be determined from the properties of the X-rays emitted by the element\(^*\) (J. J. Thomson in 1906, H. G. Moseley in 1913). It turned out that when the elements are arranged in the order of the periodic table (see Fig. 1.6), their atomic numbers increase in consecutive numbers, i.e. 1 for hydrogen, 2 for helium, 3 for lithium, and so on. This means that the charge on the hydrogen nucleus is \(+e\) and a single electron is orbiting its nucleus, the charge on the helium nucleus is \(+2e\) and two electrons are orbiting round it, and so on.

This was a surprising discovery. The periodic table (or system) of the elements is a diagram in which all the chemical elements are arranged in a certain order (see Fig. 1.6). It was first proposed by the Russian chemist Dmitri Mendeleev, who discovered, in about 1870, that when all the known elements were arranged according to increasing atomic weight, an interesting regularity or periodicity became apparent. This manifests itself in the remarkable similarity between elements occupying the same vertical column in

\* X-rays were discovered by the German physicist W. C. Röntgen in 1895 (in 1901 he won the Nobel prize for this discovery). These rays are generated in a vacuum tube similar in principle to the cathode ray tube (Fig. 1.1) when the fast electrons hit the anode.
The building blocks of the atom

Figure 1.7

Schematic description of a modern mass spectrograph. Atoms from a source (1) are ionized by the bombardment of electrons flowing from a heated cathode (2). The ions travel through an electric (3) and a magnetic (4) field and eventually fall on a photographic plate (5). Ions of different masses produce different lines on the plate.

It took 40 years to go from the identification of a regularity in the properties of chemical elements to the understanding of the structural explanation. The sequence "phenomenology—regularities—structure" is common in the evolution of science. Tycho Brahe's observations, Kepler's regularities and Newton's mechanics provide yet another example.

Note that other chemists, such as the Frenchman B. de Chancourtois in 1862 and the Englishman I. A. R. Newlands (1865) had already noticed the periodicity in the properties of elements. However, many chemical elements had not yet been discovered, and the table. For example, all the elements of the last column are inert gases which tend not to participate in chemical reactions (the noble gases), while the elements of the preceding column are very reactive non-metals (the halogens), and those of the first column are reactive metals (the alkali metals).

The reason for the regularity was not clear until it turned out that the ordinal number of each element in the periodic table is the same as its atomic number \( Z \). This discovery shed new light on the periodic table, implying some connection between chemical properties and the number of electrons in the atom.

The mass of the atom is conveniently expressed in units called 'atomic mass units' (amu, or u)\(^*\) (1 amu = 1.661 \times 10^{-27} \text{ kg}). The mass of the hydrogen atom is about 1.0 amu, and that of the helium atom 4.0 amu. We have already mentioned the fact that during the nineteenth century the atomic masses of the various elements were measured to some accuracy by methods based on chemical reactions. In the twentieth century more accurate measurements were performed by finding the \( e/m \) ratios of ions, using vacuum tubes similar to the one originally applied by Thomson to study the electron properties. (A modern version of this apparatus is called the mass spectrograph. It is shown in Fig. 1.7.) The first measurements of this sort were performed by Thomson himself. In 1913 Thomson measured the ratio \( e/m \) for ions of neon (\( Z = 10 \)) and found that there were two kinds of neon atoms, the more abundant one having a mass of 20.0, and the rarer one having a mass of 22 (these are denoted Ne\(^{20}\) and Ne\(^{22}\)). In earlier measurements, based on chemical methods which did

\(^*\) This unit is defined in such a way that the mass of one atom of the common carbon is exactly 12 amu (a small percentage of carbon atoms found in nature have a mass of 13 amu).