

It is probable that, at Arcueil, Berthollet and Laplace were trying to recreate a stimulating atmosphere such as had existed at Lavoisier's home at the Arsenal. Whether this is true or not, the magnitude of Lavoisier's chemical legacy is not in doubt, and his influence is evident in much of the work done in the early decades of the nineteenth century. Phlogiston was overthrown, and with a new working definition of an element it was not to be long before new ideas were being formulated about the fundamental particles of matter.

Dalton

6

The Chemical Atom

The idea that all matter is composed of minute atoms had first been suggested in ancient Greece, and Boyle had employed the concept of atomism in his mechanical philosophy. But atomism had as yet had little success in explaining the phenomena of chemistry. It was difficult to see how these minute particles, which were supposed to be the universal building blocks of nature, could provide an explanation for the chemical properties of the huge number of different materials known, a number that was continually increasing.

Lavoisier's concept of an element provided the foundation for the new version of atomism which appeared in the early years of the nineteenth century. The new theory, known as the *chemical atomic theory*, had as its central tenet that different elements have fundamentally different atoms. In consequence, repeated division of a piece of lead would ultimately yield the last atom of lead, and similarly repeated division of a piece of gold would yield the last atom of gold. If lead and gold were genuine elements, then the atoms of lead and the atoms of gold were different. This explained the different properties of lead and gold, and the transmutation so keenly sought by the alchemists became a theoretical impossibility.

Working in the tradition of Black and Cavendish, Lavoisier had emphasised the importance of the use of the balance in chemical investigations. The balance had been employed by assayers and mineral prospectors for hundreds of years, but in Lavoisier's time the precision balance was still a specialised piece of equipment. Black had used an apothecary's balance, but Cavendish and Lavoisier had much more accurate balances constructed to their own specifications. The age of quantitative chemistry had now truly arrived.

QUANTITATIVE ANALYSIS AND THE LAW OF CONSTANT COMPOSITION

The techniques of quantitative analysis were advanced significantly by the German, Martin Klaproth (1743-1817). He devoted much attention to sources of error and their elimination. He published all his experimental data, such as weights of

samples and precipitates, so that others could check for any errors. Frequently in the analysis of minerals he found that the sum of the constituents was less than 100 per cent. Previous workers had tended to ignore such discrepancies, ascribing them to experimental error, but Klaproth realised that in such cases there might be a previously unknown substance present. In 1789 he thus discovered the oxides of the hitherto unknown elements uranium and zirconium, although it was many years before the metals themselves were isolated. Another famous analyst of the period was Louis Nicolas Vauquelin (1763–1829), who discovered chromium in 1798. Around this time, several other metals were discovered by the careful analysis of minerals.

Quantitative analysis was soon employed to verify the law of constant composition. It had for many years been assumed by most chemists that different samples of the same pure compound would have identical compositions. In 1799, the Frenchman Joseph Proust (1754–1826) analysed basic copper carbonate of natural occurrence (malachite) and the same compound prepared in the laboratory. Both samples gave the same analytical results. He demonstrated a similar constancy of composition in many other compounds, and he showed that several metals form more than one oxide and sulphide, each of definite composition.

Proust's conclusions were immediately challenged by Berthollet, who maintained that many compounds could have a variable composition. Berthollet quoted the example of the metal copper, which appeared to form a wide range of oxides. Proust pointed out that this was due to the formation of different mixtures of two oxides, each of definite composition. Berthollet's concept of continuously variable composition would have been hard to reconcile with the chemical atomic theory, but by about 1808 Proust's views were generally accepted. However, many years later it was discovered that some compounds, such as the oxides and sulphides of iron, could indeed have a variable composition. In the case of iron(II) sulphide, a compound corresponding to the formula FeS is rarely encountered, and samples are usually deficient in iron to a variable extent. This is due to some of the lattice sites of iron(II) ions being vacant, while others are occupied by iron(III) ions to maintain electrical neutrality. These non-stoichiometric compounds are sometimes called *Berthollide compounds*.

Quantitative results of a different kind were obtained by Jeremias Richter (1762–1807). He was obsessed with obtaining mathematical relationships in chemistry, and he helped to establish the concept of equivalent or combining weight. His work was summarised in 1802 by Ernst Fischer (1754–1831), who produced a table of equivalent weights of acids and bases related to sulphuric acid having a value of 1000. On this scale, muriatic acid (HCl) had a value of 712, and soda and potash had values of 859 and 1605 respectively. This meant that 859 parts of soda or 1605 parts of potash were required to neutralise 1000 parts of sulphuric acid or 712 parts of muriatic acid.

To the modern mind, ideas such as definite proportions and equivalent weight seem to cry out for an explanation in terms of a chemical atomic theory. However, we must remember that today everyone is taught to think in terms of atoms and molecules very early in their study of chemistry. Such explanations were certainly not obvious at the beginning of the nineteenth century, and indeed John Dalton

(1766–1844), who propounded the chemical atomic theory, started to think about atoms as a result of a study of phenomena which were physical rather than chemical.

Dalton (Figure 6.1) was born in Eaglesfield, near the English Lake District. His father was a hand loom weaver, and, since the family were Quakers, Dalton was educated at the local Quaker schools. At the age of twelve he opened his own Quaker school, but he had little authority over some of his rougher pupils, and he soon relinquished his post to work as a farm-hand. At the age of fifteen he moved to Kendal to assist at a Quaker boarding school where his brother Jonathan was already teaching, and four years later the brothers were in charge of the school.

At Kendal, Dalton was befriended by John Gough. Dalton learned much from this remarkable man, who although blind was an expert in Latin, Greek, mathematics and science. It was Gough who encouraged Dalton to start keeping a meteorological journal. His records commenced on 24 March 1787, and were made every day until the day before he died 57 years later.

For a time Dalton considered entering the medical profession. However, his reputation as a teacher was growing, and he was giving lectures on scientific subjects to the general public in Kendal. Consequently he was invited in 1793 to teach at the New College in Manchester, a Dissenting Academy similar to the one in nearby Warrington which had employed Priestley. Soon after his arrival in Manchester, Dalton published his first book, entitled *Meteorological Observations and Essays*. This was written in Kendal, and reveals Dalton's lack of a formal scientific education and his lack of contact with fellow scientists. Nevertheless, the book contains Dalton's first speculations concerning the atmosphere and the water vapour it contains, and it was as a result of such speculations that the chemical atomic theory was born.

Dalton's move to Manchester ended his isolation, for he immediately joined the Literary and Philosophical Society, which had been founded in 1781. The first paper he read before the Society was concerned with the colour blindness from which he suffered, and was the first description of this syndrome, which is still occasionally called *Daltonism*. Membership of the Society introduced Dalton to a circle of friends with whom he was able to discuss the ideas that had been forming in his mind concerning the atmosphere. Particularly important was his friendship with William Henry (1774–1836), who had worked on the solubility of gases in water.

After the publication of his atomic theory, Dalton remained in Manchester, defending the theory and seeking further experimental evidence for it. In spite of the international reputation he eventually acquired, he continued to work as a teacher. In 1800 he had resigned from New College and he concentrated on giving private tuition in mathematics, experimental philosophy and chemistry. He also gave courses of public lectures in Manchester and other cities. When he died he was widely regarded as Manchester's leading citizen.

DALTON'S THEORIES ON GASEOUS MIXTURES

Initially, Dalton employed a model for a gas very similar to that used by Newton. It is important to realise that Newton's (and Dalton's) picture of a gas was

essentially a static one, and quite different from the dynamic model provided by the kinetic theory of gases, which was not developed until the middle of the nineteenth century. Newton imagined a gas to be a three-dimensional array of mutually repulsive particles. He showed that, if the repulsive force is inversely proportional to the distance between the particles, then the pressure of a fixed quantity of gas doubles when the volume is halved, in accordance with Boyle's law.

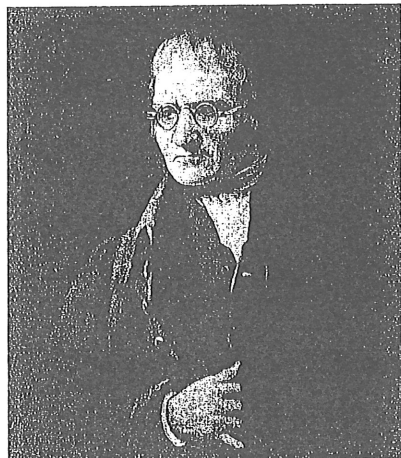


Figure 6.1 John Dalton (1766–1844)

Newton had imagined all air particles to be identical, but by Dalton's time it had been shown that air contains both oxygen and nitrogen, with variable amounts of water vapour. In 1801 Dalton rejected the current idea that air was a loose chemical compound between these constituents, but was then confronted with the problem that a physical mixture should separate into layers, with the most dense substance (oxygen) forming the bottom layer. In an attempt to explain the homogeneity of air, Dalton hit upon the idea that each particle could only repel others of its own kind, and that dissimilar particles exerted no forces on each other. From this he deduced that, in a mixture of gases, each constituent should exert the same pressure as it would if it alone occupied that volume. This conclusion, although based on an incorrect model, is valid, and is now known as Dalton's law of partial pressures.

Dalton soon became dissatisfied with this model for gaseous mixtures, for it was difficult to imagine how particles could repel only those of their own kind. Dalton considered the gaseous particles to consist of hard centres surrounded by an atmosphere of heat (caloric). The atmosphere of heat was supposed to be the cause of the repulsive power, so on this basis there should be repulsion between dissimilar particles. Dalton's next idea was that different types of particle had

different sizes, and that in consequence no equilibrium could be established between particles of different sizes exerting different forces. Therefore, the constituents of a gaseous mixture would not separate into layers. If the particles of different gases had different sizes, they would also presumably have different weights.

Dalton first announced his theory concerning the sizes and weights of particles of different gases in a paper concerned with the solubility of gases in water. This paper was read to the Manchester Literary and Philosophical Society in 1803 and published in 1805. Dalton had performed experiments of his own on the subject, and he also used the results obtained by his friend William Henry, who had discovered that the mass of gas absorbed by a liquid is proportional to the pressure. Dalton argued that, when a gas dissolves in a liquid, the process is simply one of mechanical mixing of the gaseous particles with those of the liquid, and is not a chemical combination. He then admitted that the greatest weakness of the mechanical hypothesis is that a liquid like water should dissolve all gases to the same extent, but stated that this difficulty is overcome if the ultimate particles of different gases have different sizes and weights. He continued:

'An enquiry into the relative weights of the ultimate particles of bodies is a subject, as far as I know, entirely new: I have lately been prosecuting this enquiry with remarkable success. The principle cannot be entered upon in this paper; but I shall just subjoin the results, as far as they appear to be ascertained by my experiments'.

There then follows the first table of atomic weights ever published (Table 6.1). Dalton does not reveal here how his atomic weights were calculated, and tantalisingly he does not elaborate his theory any further. Throughout this paper Dalton talks about *ultimate particles* rather than atoms.

ATOMIC WEIGHTS AND MULTIPLE PROPORTIONS

The first full account of the chemical atomic theory was given in 1807 by Thomas Thomson (1773–1852) in the third edition of his *System of Chemistry*. Thomson had visited Dalton in 1804, and had been converted to Dalton's views on that occasion. Indeed, there is some evidence to suggest that Thomson had been on the verge of a similar theory himself. Dalton published his own account in his book *A New System of Chemical Philosophy*, which appeared in 1808.

By now Dalton was using the term *atom* for the ultimate particles of all substances; elements were composed of simple atoms, and compounds of compound atoms. In order to assign atomic weights, it was necessary to make assumptions concerning the composition of compound atoms. Dalton adopted what he called the *Principle of Simplicity*, in which he stated that, where two elements A and B form only one compound, its compound atom contains one atom of A and one of B. If a second compound exists, its atoms will contain two of A and one of B, and a third will be composed of one of A and two of B, etc. On this basis Dalton proposed that the water atom was composed of one atom of hydrogen joined to one atom of oxygen. The rather poor analytical data available in 1808

indicated that hydrogen and oxygen combined in a weight ratio of 1:7 (rather than 1:8), and thus oxygen was now given a relative weight value of 7 on the basis of hydrogen having a value of 1. Although Dalton's formula for water was wrong, he did suggest the correct atomic composition of many simple compounds, such as carbon monoxide, carbon dioxide, nitrous oxide, nitric oxide and nitrogen dioxide.

Dalton's theory provided a ready explanation for the law of definite proportions. It also predicted that when two elements form more than one compound, the various weights of one element which combine with a fixed weight of the other should be in simple numerical ratio. This prediction, now known as the law of multiple proportions, was found by Dalton to be obeyed by the oxides of nitrogen and by olefiant gas and marsh gas (ethene and methane).

Table 6.1 Dalton's first set of atomic weight values (1805)

Hydrogen	1
Azot	4.2
Carbone	4.3
Ammonia	5.2
Oxygen	5.5
Water	6.5
Phosphorus	7.2
Phosphuretted hydrogen	8.2
Nitrous gas	9.3
Ether	9.6
Gaseous oxide of carbone	9.8
Nitrous oxide	13.7
Sulphur	14.4
Nitric acid	15.2
Sulphuretted hydrogen	15.4
Carbonic acid	15.3
Alcohol	15.1
Sulphureous acid	19.9
Sulphuric acid	25.4
Carburetted hydrogen from stagnant water	6.3
Olefiant gas	5.3

Part and parcel of Dalton's theory was the atomic symbolism that he invented. Earlier chemists and alchemists had used various symbols, but these were little more than a kind of shorthand, although for the alchemists a symbol might have suggested a mystic connection, for example between a metal and a planet. A good example of early chemical symbolism is found in Geoffroy's table of affinities of 1718 (see Figure 4.1). Dalton introduced symbols that had a quantitative as well as a qualitative significance (Figure 6.2). The symbols were circles with a distinctive pattern or letter inside them; each circle represented one atom of that particular element. Compound atoms were represented by touching circles. The arrangement of elementary atoms in the compound atoms was to some extent arbitrary, but Dalton suggested that atoms of the same kind would repel each other.

He thereby arrived at the correct arrangements for carbon dioxide (linear) and sulphur trioxide (triangular).

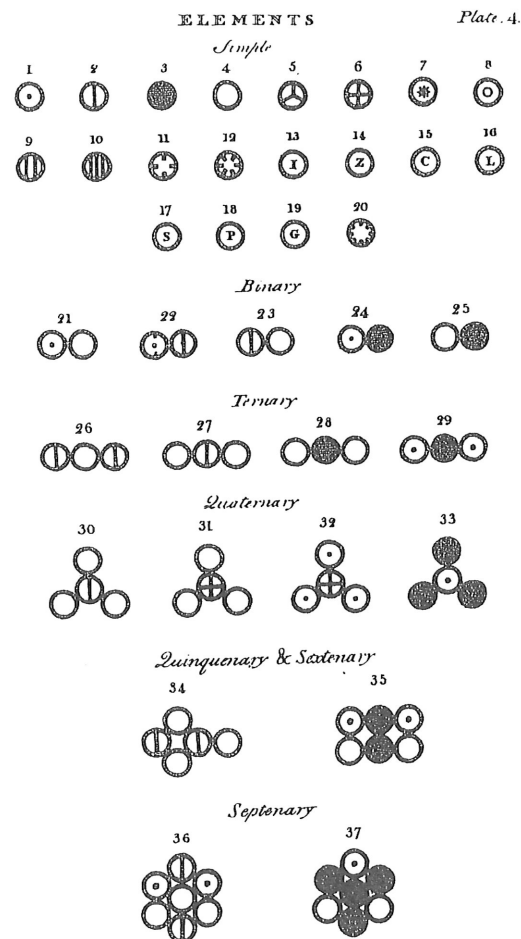


Figure 6.2 Dalton's atomic symbols. Number 28 is a compound atom of carbonic acid (carbon dioxide), and number 31 is a compound atom of sulphuric acid (sulphur trioxide)

As we have seen, it was Thomas Thomson who gave the first published account of Dalton's theory. Thomson also helped to advance it in an important paper read to the Royal Society in January 1808, shortly before Dalton's *New System* was published. Thomson showed that oxalic acid (ethanedioic acid) forms two sets of salts (the normal and the acid salts) and that the quantities of acid that react with a given quantity of base to form the two salts are in the ratio 1:2. This provided another verification of the principle of multiple proportions predicted by Dalton, although this time the combining particles were compound atoms rather than elementary atoms. In the same paper Thomson showed for the first time how the empirical formula of a compound could be calculated from its percentage composition by mass. Using Lavoisier's figures for the composition of sugar (64 per cent oxygen, 28 per cent carbon, 8 per cent hydrogen), Thomson divided them by his own values for atomic weights (oxygen 6, carbon 4.5, hydrogen 1) to obtain figures in the approximate ratio 5:3:4. Thomson represented the sugar particle as $5w + 3c + 4h$, where w , c and h represented one relative weight unit of oxygen, carbon, and hydrogen respectively.

Later, in 1808, William Hyde Wollaston (1766–1828) published a paper in which he announced that he had managed to prepare three salts by reacting oxalic acid with a base, the quantities of acid reacting with a given quantity of base being in the ratio 1:2:4. The last type of salt is now known as a tetroxalate (e.g. potassium tetroxalate, $\text{KH}_3(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$). Wollaston was unable to prepare a salt in which acid and base reacted in a 3:1 ratio, and he speculated that such a combination of acid and base atoms might result in an unstable arrangement. Wollaston continued to think in structural terms and in 1812 he expanded on an idea that Dalton had advanced in the *New System* in which the geometry of crystals was explained in terms of the regular packing of spherical particles (Figure 6.3). This was as far as the structural aspects of Dalton's theory were explored for the time being. Although Dalton's diagrams of compound atoms had also conveyed structural information, Dalton's atomic symbols were soon replaced by a system of letters devised by Berzelius. It was to be another half-century before the spatial arrangement of atoms was to receive further consideration.

CONTROVERSY OVER THE CHEMICAL ATOMIC THEORY

A serious objection to Dalton's theory concerned the principle of simplicity. If Dalton's hypothesis that a compound atom of water was composed of just one atom of hydrogen and one atom of oxygen was wrong, then the atomic weight of oxygen would not simply be the weight of it found experimentally to combine with unit weight of hydrogen. The apparent impossibility of there ever being any way to determine the composition of compound atoms persuaded some chemists that the atomic theory would never have much practical application. By 1814 Wollaston had lost some of his earlier enthusiasm for Dalton's theory, and he proposed that equivalent (or combining) weights be used in place of atomic weights. Richter had calculated equivalents for acids and bases, and Wollaston extended the concept to include salts and individual elements. Wollaston's equivalents were quoted on a

Atomic Structure, Radiochemistry and Chemical Bonding

In previous chapters we have seen how Dalton's atomic theory encountered difficulties, especially during the first half of the nineteenth century. After 1860 the chemical atom became so useful, especially to organic chemists, that only a few dissenting voices were heard in this branch of the science. However, to many physicists the atomic concept seemed unnecessary, and some of the great advances in nineteenth century physics had been made without reference to atomism. Then, in a series of discoveries which were made in rapid succession around the turn of the century, the existence of atoms was established to the satisfaction of everyone. All atoms were shown to contain identical subatomic particles, which were called *electrons*. Furthermore, certain atoms were shown to be undergoing spontaneous and continuous transmutation into others. The atomic concept may have been vindicated, but at the cost of disproving Dalton's tenets of the indivisibility and immutability of atoms. Further advances placed the periodic table on a firm theoretical basis, and provided an explanation of the forces involved in chemical bonding.

CATHODE RAYS

The early ideas on atomic structure followed from studies on the passage of electricity through rarefied gases. As early as 1821, Davy had observed a luminosity accompanying the passage of a spark, and he noticed that the colour depended on the residual gas in the tube. In the middle of the century Heinrich Geissler (1814–1879) devised the mercury vapour pump, and with its aid was able to manufacture tubes in which the gaseous pressure was much lower than anything previously available. Using Geissler tubes, Julius Plücker (1801–1868) noticed that the phosphorescent spot which appeared on the glass when the tube was in operation could be moved by a magnet, thus suggesting that the beam emanating from the cathode was electrically charged. Eugen Goldstein (1850–1930) observed that objects placed in the beam cast a shadow on the glass wall of the tube. He coined the term *cathode rays* to describe the radiation.

These experiments were repeated and extended in 1879 by William Crookes, the discoverer of thallium (Chapter 9). Crookes demonstrated that the luminous effects observed by Davy and others were distinct from the phenomena observed in very highly evacuated tubes, when the luminosity diminishes but the phosphorescence of the glass increases. Crookes believed that in the very highly evacuated tubes in a state of discharge there appeared a fourth state of matter, which he termed *radiant matter*. He demonstrated that the beam of radiant matter was deflected by a magnet in a direction indicating a negative charge, and he showed that a small paddle wheel placed in the beam was made to rotate (Figure 11.1). He interpreted this as being evidence that radiant matter is particulate in nature, and he called the particles *negatively electrified molecules*. Concluding his account of his work, Crookes said: '... here, it seems to me, lie Ultimate Realities, subtle, far reaching, wonderful!'

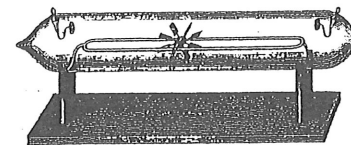


Figure 11.1 Crookes's paddle wheel apparatus. Crookes thought that the rotation of the paddle wheel was due to the impact of particles. It is now known that the rotation is caused by one side of a vane becoming warmer as a result of electron bombardment, and the molecules of the residual gas in the tube recoiling with greater energy when they collide with the heated surface.

THE ELECTRON

Towards the end of the nineteenth century there were two distinct theories concerning the nature of cathode rays. One school of thought, to which most German physicists subscribed, was that cathode rays were waves moving through the *ether*. This theory likened cathode rays to light, which was thought to be propagated in this way. The other view was the negative-particle theory of Crookes. In 1897 Joseph John Thomson (1856–1940) published the results of some experiments which he had conducted to test the particle theory.

Supporters of the wave theory had argued that the negative particles ejected from the cathode were distinct from the rays which caused the phosphorescence on the glass. Thomson built a tube containing a collecting cylinder connected to an electrometer. When the phosphorescent spot was deflected by a magnet into the cylinder, the electrometer detected a charge in the cylinder.

Having established that the electrical and phosphorescent effects of cathode rays could not be separated, Thomson proceeded to demolish another objection to the charged-particle theory. This was that no deflection of the cathode ray beam had been observed when it was passed between two plates maintained at a small potential difference. Thomson argued that the passage of the rays rendered the

residual gas in the tube conducting, thus annulling the charge on the plates. Thomson showed that a deflection did in fact occur under conditions of very high vacuum, but that there was no deflection when the vacuum was not so good. Thomson remarked:

'... I can see no escape from the conclusion that they [the cathode rays] are charges of negative electricity carried by matter. The question arises, What are these particles? Are they atoms, or molecules, or matter in a still finer state of subdivision? To throw some light on this point I have made a series of measurements of the ratio of the mass of these particles to the charge carried ...'.

Thomson (Figure 11.2) was born at Manchester where his father was a bookseller. His ambition was to become an engineer, but the death of his father meant that his family could not afford the extra fees which were charged to students of this subject. Instead, he concentrated on the study of mathematics, physics and chemistry, and won a scholarship to Trinity College, Cambridge. As a result of an outstanding examination performance he became a fellow of Trinity in 1880, and he remained at the college until his death 60 years later. His early research was theoretical, and many were surprised when in 1884 he was elected to the Cavendish Professorship in Experimental Physics. He proved to have a genius for devising experiments, although he was not a particularly skilful laboratory worker. He became Master of Trinity College in 1918, when he relinquished the Cavendish Professorship. He is remembered not only because his work was of the greatest significance, but also because under his leadership the Cavendish Laboratory in Cambridge became a world famous centre for research in atomic physics.

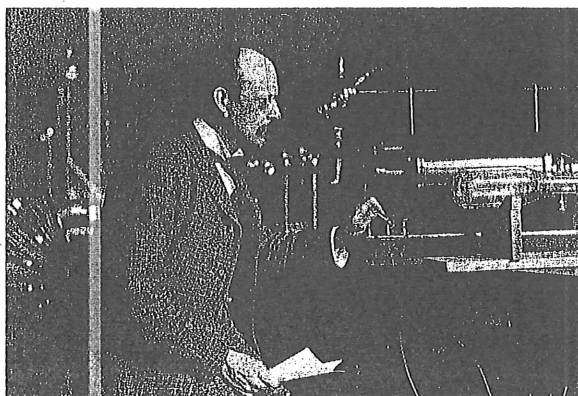


Figure 11.2 Joseph John Thomson (1856–1940)

Thomson measured the extent of the deflection produced in the beam by a given electric field, and he then found the strength of the magnetic field necessary to produce the identical deflection (Figure 11.3). The value Thomson calculated for the mass-to-charge ratio (m/e) was approximately one-thousandth of that for the hydrogen ion, and was independent of the residual gas in the tube. Thomson devised some ingenious experiments to measure the value of the charge carried by the new particle, and found that it was of the same order of magnitude as that of the hydrogen ion. This indicated that the particle, which was given the name *electron*, possessed a very small mass.

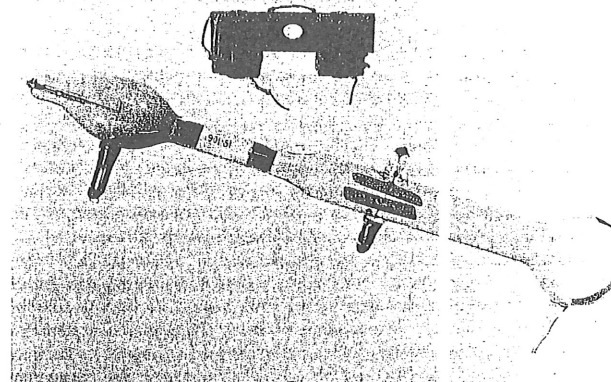


Figure 11.3 The apparatus used by Thomson to measure the mass-to-charge ratio of the electron

Between 1908 and 1917 the American physicist Robert Andrews Millikan (1868–1953) performed an elegant series of experiments to obtain an accurate value of the charge carried by the electron (e). Millikan measured the rate of rise of a small charged oil droplet of known mass in an electric field, and was thereby able to calculate the charge on the droplet. In all cases this was found to be an integral multiple of a constant value, which therefore represented the magnitude of a unit charge. Millikan's value was very close to the currently accepted figure of 1.602×10^{-19} C. The values obtained by Thomson and Millikan, in conjunction with Thomson's mass/charge determinations, pointed to a very small mass for the electron. Current estimates accord the electron a mass of $1/1837$ on the relative atomic mass scale.

Not surprisingly, Thomson's suggestion of the existence of subatomic particles common to all atoms was received with some scepticism, but in 1904 he proposed a model for the structure of the atom to fit the available evidence. He suggested that the atom was a sphere of uniform positive charge within which rings of

electrons may rotate. The mass of the atom was almost entirely accounted for by the mass of the electrons, and on this basis the hydrogen atom would contain a very large number of electrons.

RADIOACTIVITY

In 1895 Wilhelm Konrad Röntgen had discovered that the fluorescent spot on a discharge tube emitted a very penetrating radiation, which he called X-radiation. X-rays themselves induced fluorescence in suitable materials and fogged a photographic plate. In 1896 Henri Becquerel (1852–1908) conducted experiments to see if there was a relationship between X-radiation and fluorescence. He placed crystals of salts which fluoresce in ultraviolet light on well wrapped photographic plates and left them exposed to sunlight. With a crystal of potassium uranyl sulphate he observed a silhouette on the developed photographic plate, suggesting that the salt may indeed have emitted X-radiation as it fluoresced. Becquerel prepared to repeat the experiment, but owing to cloudy weather he placed the wrapped plates with the crystals in place in a dark drawer. After three days the weather still had not improved, so he developed some of the plates, expecting to find only a very feeble image. To his amazement, much bolder silhouettes appeared on this occasion. Becquerel found that the new radiation was also emitted by non-fluorescent uranium salts, and that uranium metal emitted a more intense radiation than any of its salts.

Becquerel discovered that the radiation emitted by uranium and its salts had the property of rendering air a conductor of electricity, an effect which Rutherford subsequently explained as being due to the ionisation of the air. It was therefore possible to use an electrometer to measure the intensity of the radiation. Using this technique Marie Curie (1867–1934) embarked in 1898 on a systematic investigation of the new phenomenon.

Curie examined all the known elements and found that, apart from uranium, only thorium appeared to emit ionising radiation. All compounds of these elements were active, and changing the temperature had no effect on the activity. The new property, which Curie named *radioactivity*, appeared to be an atomic phenomenon, because the intensity of the radiation emitted by a uranium compound was found to be proportional to the percentage of uranium it contained.

Curie measured the intensity of the radiation from the mineral pitchblende. The principal metal in pitchblende is uranium, but smaller quantities of many other metals are present as well. Curie found that the radioactivity of pitchblende was considerably greater than could be explained on the basis of its uranium content, and she concluded that there was an unknown and highly radioactive element present. She dissolved some pitchblende in acid and precipitated each metal in turn and checked with the electrometer to see if the radioactivity had come out of solution. She found that a high radioactivity was associated with the bismuth fraction, and named the new element which was clearly present *polonium* in honour of her native country. However, the spectrum of the precipitate contained no new lines, so it appeared that polonium must be present in extremely small quantity.

Curie also found that the barium fraction was radioactive, and on careful crystallisation of the chloride she found that the least soluble portion was 900 times more radioactive than uranium. The salt still contained large quantities of barium chloride, but it glowed in the dark, and Curie christened the new element present *radium*. The spectroscopist Eugène Demarçay observed new lines in the spectrum of the salt, thus confirming the existence of a new element. It was clear that a huge quantity of pitchblende would be required to obtain a sensible quantity of radium or one of its compounds. Curie obtained one ton of pitchblende residues (from which the uranium had been extracted) as a gift from the Austrian government. After four years of hard work, Curie and her husband Pierre succeeded in isolating 0.1 g of pure radium chloride.

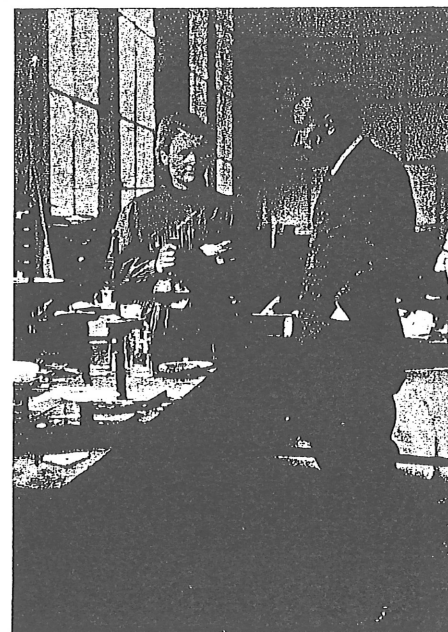


Figure 11.4 Marie Curie (1867–1934) and her husband Pierre in their laboratory

A third new radioactive element was discovered in the pitchblende residues by André Debierne (1874–1949), who was working with the Curies. It was precipitated with the rare-earth elements, but like polonium it was present in such minute quantity that neither the element nor any of its compounds could be isolated in a pure form. This element was named *actinium*.

Marie Curie (Figure 11.4) was born Marya Sklodovska, the daughter of a physics teacher in Warsaw. Her family could not at first afford to send her to university, so between the ages of 18 and 24 she worked as a governess. She then studied physics and mathematics at the Sorbonne in Paris, and shortly after graduating she married the physicist Pierre Curie. Her work on radioactivity was performed for her doctorate, and her thesis has been described as one of the most important ever submitted for such a degree. When the significance of Marie's work became apparent, Pierre abandoned his own research and thereafter they worked together. Their laboratory was an abandoned shed, and their isolation of a minute quantity of pure radium chloride from a huge amount of pitchblende represents one of the most heroic struggles in the history of science. In 1903 the Curies and Becquerel were awarded the Nobel Prize for Physics. In 1904 Pierre became professor of physics at the Sorbonne. He was killed in 1906 by a wagon as he crossed the street, and Marie then succeeded to his professorship. In 1911 she was awarded the Nobel Prize for Chemistry, thus becoming the first person to win two Nobel prizes. During World War I she organised an X-ray service to locate bullets and shrapnel in injured soldiers. After the war she travelled to the United States, where she was presented with one gram of pure radium and a sum of money to enable her to continue her research. She died of leukaemia, contracted as a result of prolonged exposure to radiation.

ALPHA, BETA AND GAMMA RADIATIONS

While the Curies were investigating new radioactive elements, others were studying the emissions from radioactive substances. Foremost in this field was Ernest Rutherford (1871–1937). Working at the Cavendish Laboratory in Cambridge in 1898, he demonstrated that there were two kinds of radiation, which he called *alpha* and *beta* rays. The beta rays were about as penetrating as X-rays, but most alpha rays were stopped by thin sheets of metal foil. In 1899 Becquerel showed that the beta rays could be deflected in a magnetic field in a direction showing that they carried a negative charge. It seemed likely that beta rays were in fact electrons, and using a method similar to Thomson's, Becquerel measured their mass/charge ratio and obtained a value similar to that which Thomson had found for the electron.

In 1903 Crookes devised his *spinthariscopes* in which alpha rays fell on a zinc sulphide screen. Tiny flashes of light were observed, thus showing that the alpha ray was a stream of particles. Alpha rays were only deflected very slightly by a magnetic field in a direction which indicated a positive charge. In 1903 Rutherford succeeded in measuring this deflection and used it to calculate the mass/charge ratio. His first value was roughly similar to that of the hydrogen ion, but a more accurate determination in 1906 yielded a value of approximately double that of the hydrogen ion. Once the particulate nature of alpha and beta radiations had been demonstrated, the names alpha and beta *particle* slowly came into use.

A third radiation was observed in 1903 by P. Villard. Since it was highly penetrating and undeflected by a magnetic field, Rutherford suggested that it was

electromagnetic radiation of shorter wavelength than X-rays, and he named the emission *gamma radiation*.

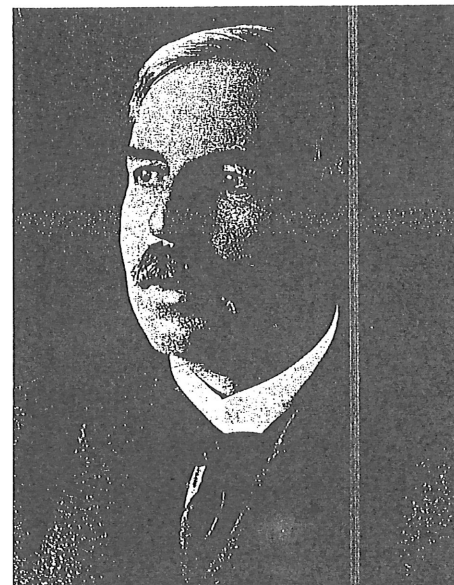


Figure 11.5 Ernest Rutherford (1871–1937)

Rutherford realised that his result for mass/charge for the alpha particle was consistent with it being a doubly positively charged helium ion. Terrestrial helium had recently been obtained by Ramsay (Chapter 9) by heating the uranium mineral cleveite, and it was soon found that other uranium minerals produced the gas. Direct experimental proof of the nature of the alpha particle was obtained in 1909 by Rutherford and Royds, who allowed alpha particles from *emanation*, a radioactive gas emitted by radium, to pass through a glass tube whose walls were only 0.01 mm thick. The alpha particles were collected in a thicker outer glass tube, and after six days the contents of this tube were compressed and the spectrum recorded. The lines of helium were clearly visible. Rutherford and Royds ended their paper with the words: 'We can conclude with certainty from these experiments that the alpha particle after losing its charge is a helium atom'.

Rutherford (Figure 11.5) was born on a small farm near Nelson in New Zealand. He won first class honours at Canterbury College in Christchurch, and then commenced research on electromagnetism. In 1895 he won a scholarship to travel to the Cavendish Laboratory in Cambridge to work with J. J. Thomson. He continued his work on electromagnetism for a further year, and then he and Thomson investigated the conductivity induced in air by the X-radiation recently discovered by Röntgen. Rutherford realised that the conductivity was due to the ionisation of the air, and he soon showed that radioactive emissions produced a similar effect. In 1898 he moved to McGill University in Montreal, where he formed his productive partnership with Soddy. He returned to England in 1907 to become professor at Manchester. During World War I he served on the War Research Committee. One day in 1917 he arrived late for a meeting and by way of explanation he said: 'I have been engaged on experiments which suggest that the atom can be artificially disintegrated. If it is true, it is of far greater importance than a war'. In 1919 he succeeded Thomson as professor at the Cavendish in Cambridge, where he more than maintained the pre-eminent position of that laboratory in the realm of atomic physics. His great genius lay in devising crucial experiments whose results were of the utmost significance but which employed relatively simple apparatus. He continued to head the Cavendish until his death.

THE MECHANISM OF THE RADIOACTIVE PROCESS

Evidence had also been accumulating which enabled a theory to be advanced concerning the mechanism of the radioactive process. An important experiment was performed by Crookes in 1900. He found that he was able to obtain a radioactive precipitate from a solution of a uranium salt. The uranium, which remained in solution, had become almost totally inactive. This was a remarkable finding, as the recent work of the Curies had indicated that the activity was a property of the uranium atom. Crookes called the active substance in the precipitate *uranium X*. After a year he re-examined the uranium X and found that it was now inactive, while the original uranium had regained its activity. In retrospect, it is fortunate that Crookes used a photographic method to measure the activity. The alpha particles, which uranium continues to emit, would not penetrate the wrapping of the photographic plate and were not detected.

Becquerel obtained similar results with a uranium solution using a different precipitating reagent, and in 1902 Rutherford, working with Frederick Soddy (1877–1956) (Figure 11.6), precipitated radioactive *thorium X* from a solution of a thorium salt. Over a period of a month thorium X became inactive while the original thorium in solution regained its activity. In 1900 Friedrich Ernst Dorn had observed that a radioactive gas was given off by radium, and in the same year Owens and Rutherford found that a similar gas was produced by thorium. Both these *emanations* were alpha emitters; the radioactivity of the gas from thorium lasted for only a few minutes, but that from radium lasted for a few days. Surfaces which had been in contact with these emanations were found to be contaminated with radioactive deposits. Ramsay and Whytlaw-Gray measured the atomic weight

of radium emanation and found it to be 222, approximately 4 units less than that of radium.



Figure 11.6 Frederick Soddy (1877–1956)

On the basis of this evidence, Rutherford and Soddy in 1902 put forward their disintegration hypothesis. They proposed that radioactive elements were undergoing spontaneous transformation into new elements, and therefore the atoms of radioactive elements were breaking down into new atoms. Within the space of five years the Daltonian concept of the chemical atom had undergone a radical change. Not only had the existence of subatomic particles (electrons) been demonstrated, but also transmutation was shown to be a natural phenomenon. In their paper of 1902 Rutherford and Soddy also demonstrated that the decay of a radioactive substance followed an exponential law.

Once it became clear that radioactive elements were decaying to new elements, which were themselves radioactive, a great deal of effort was expended in working out the decay sequences. In most cases the new elements were at first obtained in quantities too small to be weighed and were distinguished from each other only by the type of decay they exhibited and the rate at which the decay occurred. Three *decay series* were elucidated: the uranium series proceeded through radium and terminated with the stable radium G; the thorium series ended in the stable thorium D; and the actinium series ended in actinium D. Between them, these series contained around 25 new radioelements.

ISOTOPES

Although these new elements were obtained in quantities which were far too small to enable their atomic weights to be determined, attempts were made to assign them to positions in the periodic table on the basis of their chemical properties.

These investigations uncovered the problem that some of the new elements were so similar to familiar elements that once mixed with them they could not be separated again. Thus in 1906 Bertram Borden Boltwood (1870–1927) of Yale University was unable to separate ionium (the immediate precursor of radium in the uranium series) from thorium. Similarly, Geörgy Hevesy (1885–1966) was unsuccessful in his attempts to separate radium D from lead.

The solution to these problems was proposed simultaneously and independently by Kasimir Fajans (1887–1975) and Frederick Soddy in 1913. Their conclusions, now known as the *group displacement laws*, were that when an alpha particle is emitted the new element occupies a position two places to the left in the periodic table, whereas the loss of a beta particle produces an element one place to the right of the parent. Following from this was the revolutionary proposal that the elements between lead and uranium in the periodic table could exist as more than one kind of atom, differing in mass but displaying identical chemical properties. The problems encountered by Boltwood in his attempts to separate ionium from thorium were now explained on the grounds that ionium *was* thorium. Fajans called a group of chemically identical atoms with differing atomic weights a *pleiad*, but Soddy's term *isotopes* has been generally adopted. It was therefore proposed that most of the new radioelements were isotopes of existing elements. The gaseous emanations were shown to be isotopes of the same new rare-gas element, now known as *radon*.

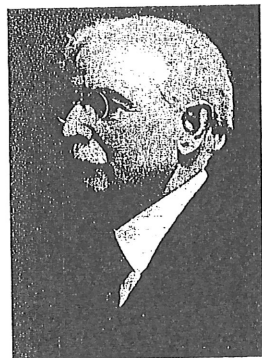


Figure 11.7 Theodore William Richards (1868–1928)

The group displacement laws predicted that the end-products of the three decay series were stable isotopes of lead with differing atomic weights. It therefore followed that samples of lead of different mineral origin should have different isotopic compositions and hence different atomic weights. The acknowledged expert of the day on atomic weight determination was Theodore William Richards (1868–1928) (Figure 11.7) of Harvard University. He had brought new standards

of accuracy to the traditional gravimetric methods. Fajans sent Max Lambert (1891–1925) from Karlsruhe to Harvard to learn Richards's techniques and to determine the atomic weight of lead from different sources. Richards and Lambert published their results in 1914, and, as they themselves remarked, the outcome was striking. Common lead was found to have an atomic weight of 207.15, whereas that from North Carolina uraninite gave a value of 206.40. The differences between these values was many times the experimental error for the technique. Other workers measured the atomic weight of lead from other sources, and the highest value (207.90) was obtained by Hönigschmid for lead from a thorite mineral.

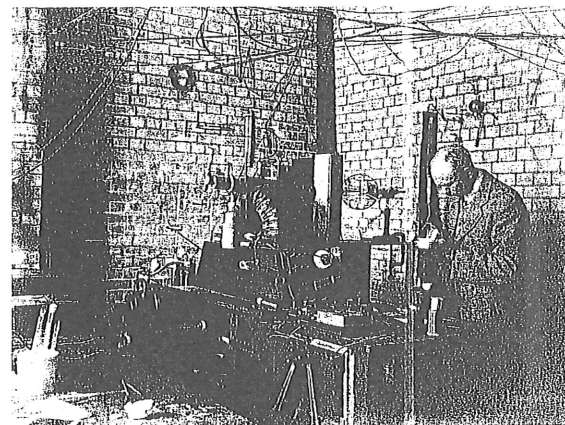


Figure 11.8 Francis William Aston (1877–1945) with his mass spectrograph

At the time that Soddy and Fajans were postulating that heavy elements exist as isotopes, Thomson was obtaining evidence which was to point to a similar conclusion for neon. Thomson had conducted a long series of experiments on the *positive rays* which pass through a perforated cathode in a discharge tube. It became clear that these were composed of positive ions derived from the residual gas in the tube. By deflecting the rays with electric and magnetic fields arranged at right-angles, ions with similar mass/charge values fell on a parabola at the end of the tube, which acted as a fluorescent screen. By 1913 Thomson's apparatus was sufficiently refined for him to estimate the masses of the positive ions (assuming they carried unit positive charge). He found that neon gave two parabolas, corresponding to atomic weights of 20 and 22. Thomson initially thought that the heavier ion might be derived from the compound NeH , formed between neon and traces of hydrogen in the tube. His assistant, Francis William Aston (1877–1945), suspected that the explanation might reside in the existence of two different types of neon atom, and he attempted to separate them by repeated diffusion through an apparatus made of pipe-clay, but was unsuccessful.

This work was halted by World War I, but in 1919 Aston resumed his investigations. He recorded the positive ions in the discharge tube by arranging for them to fall on a photographic plate, and he called his instrument the *mass spectrograph* (Figure 11.8). He demonstrated conclusively that both the lines Thomson had observed were due to neon alone, and he also showed that there was a third isotope of neon of very low abundance with atomic weight 21. Aston developed the apparatus still further and soon demonstrated that many other elements occur as isotopes. Aston measured his atomic masses on the scale $^{16}\text{O} = 16.0000$, and in his *whole-number rule* stated that isotopic masses were integral on this scale. Fractional atomic weights were due to a mixture of isotopes present in the natural element.

Mass spectrographs were also built in the United States by A. J. Dempster and K. T. Bainbridge. The mass spectrograph has been succeeded by the *mass spectrometer*, in which the intensity of the separated ion beams are measured electrically. These instruments are now widely used in the determination of molecular structure (Chapter 13). The term *relative atomic mass* is now used in place of atomic weight, and isotopic masses are measured on the $^{12}\text{C} = 12.0000$ scale. Aston himself soon discovered that small deviations from the whole-number rule are the norm.

THE NUCLEAR ATOM

Soon after Thomson published his theory that the atom was a sphere of uniform positive charge containing rotating rings of electrons, experimental evidence started to accumulate which was inconsistent with it. When tracks of alpha particles were photographed by means of the cloud chamber, it was observed that they sometimes made an abrupt turn. In 1906 Rutherford observed that a beam of alpha particles would penetrate very thin metal foil, but a photographic plate placed behind the foil registered a diffuse spot, indicating that some of the particles had been deflected. The phenomenon was studied carefully by Hans Geiger (1882–1945) and Ernest Marsden, who found that, although most particles experienced either no deflection or a very small one, a small minority were sharply deflected, some through angles greater than 90° . As Rutherford later remarked: 'It was about as credible as if you had fired a 15 inch shell at a piece of tissue paper and it had come back and hit you'.

On the basis of these results, Rutherford in 1911 postulated that the atom consists of a tiny central positively charged region, which he subsequently termed the *nucleus*. The nuclear positive charge was balanced by electrons revolving round the nucleus at a considerable distance. The results of the alpha particle scattering experiments were thereby explained; the positive alpha particle would experience little or no deviation unless it happened to approach very close to the positively charged nucleus.

NUCLEAR CHARGE AND ATOMIC NUMBER

Attention was then directed to the question of the magnitude of the nuclear positive charge. In 1913 Geiger and Marsden re-examined the scattering of alpha particles by gold foil and concluded that 'the number of elementary charges composing the centre of the atom is equal to half the atomic weight'. A similar conclusion had been reached two years earlier by Charles Barkla (1877–1944) for light elements up to atomic weight 32 by studying the energies of X-rays scattered by those elements.

In 1913 the Dutchman Antonius Johannes van den Broek (1870–1926) proposed that since the average difference in atomic weight between successive elements in the periodic table was about two units, the number of nuclear charges would differ by one unit between adjacent elements. He suggested that the nuclear charge number defined an element's position in the periodic table. However, he thought that the charge on the uranium nucleus was 118, and on this basis concluded that many elements remained undiscovered.

Direct experimental evidence on the magnitude of nuclear charge was provided in 1913 by Henry Moseley (1887–1915) (Figure 11.9) as a result of studies of the X-ray spectra of elements. Since the discovery of X-rays by Roentgen in 1895, there had been a controversy as to their nature. They were not deflected by magnetic fields and were therefore not charged particles, but neither were they diffracted by the most closely ruled gratings, as would have been expected if they were short-wavelength radiation. In 1912 Max von Laue (1879–1950) proposed that X-rays were composed of radiation of such short wavelength that successive atomic layers in crystals might form an effective diffraction grating. The theory was tested by W. Friedrich and P. Knipping, who directed a narrow beam of X-rays at a large crystal of copper sulphate and obtained a crude diffraction pattern on a photographic plate (Figure 11.10). This crucial experiment led to the development of X-ray crystallography, which was to become such an important technique in the determination of molecular structure (Chapter 13). However, the immediate importance of X-ray diffraction was that demonstrated by W. H. and W. L. Bragg, in that it provided a method of measuring the wavelength of X-rays.

Moseley devised an apparatus which enabled the X-rays generated by firing electrons at a metallic target in a cathode ray tube to be diffracted by a crystal of potassium ferrocyanide and the resulting spectral lines to be recorded photographically. Moseley found that each element produced its own characteristic set of X-ray lines, and he commented that the method 'makes the analysis of X-rays as simple as any other branch of spectroscopy'. In his first paper Moseley measured the frequencies of one of the characteristic lines in the X-ray spectra of the elements from calcium to zinc (with the exception of scandium). He found that the frequency of the lines was proportional to Q , where Q increased by a constant amount between consecutive elements when ordered according to the periodic table. Moseley continued:

'Except in the case of nickel and cobalt this is also the order of atomic weights. While, however, Q increases uniformly the atomic weights vary in an apparently arbitrary manner, so that an exception in their order does not come as a surprise. We have here

a proof that there is in the atom a fundamental quantity which increases by regular steps as we pass from one element to the next. This quantity can only be the charge on the central positive nucleus, the existence of which we already have definite proof.

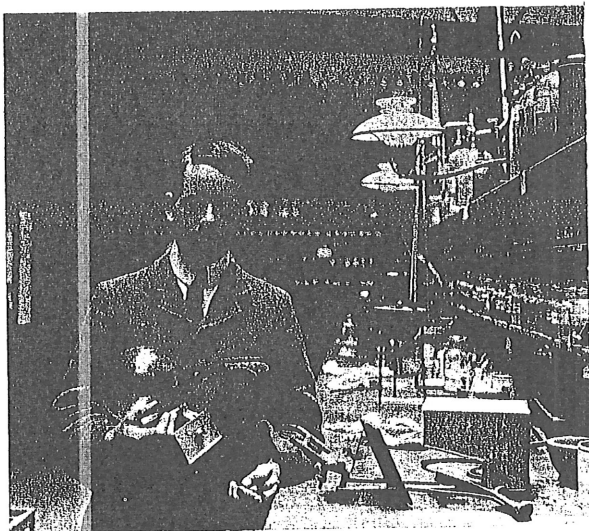


Figure 11.9 Henry Gwyn Jeffreys Moseley (1887–1915)

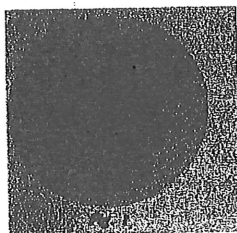


Figure 11.10 The first X-ray diffraction photograph obtained by Friedrich and Knipping in 1912 using a crystal of copper sulphate

Moseley introduced the term *atomic number*, N , for the fundamental quantity to which he referred. He showed that N was related to Q , and that ' N is the same as the number of the place occupied by the element in the periodic system'.

The following year Moseley reported on the X-ray spectra of 30 further elements lying between aluminium and gold. He confirmed that gold has an atomic number of 79, and that elements with atomic numbers 43, 61, 72 and 75 remained

undiscovered. Moseley's work not only indicated how many new elements were to be expected, but also confirmed the validity of placing argon before potassium, cobalt before nickel, and tellurium before iodine, in inverse order of atomic weight. In 1915 Moseley was killed in action in the battle of Suvla Bay. The investigation he had pursued so successfully was completed in 1916 by Siegbahn and Friman, who determined the X-ray spectra of all the available metals from gold to uranium, and thereby demonstrated that the latter has an atomic number of 92.

NUCLEAR PARTICLES

After Rutherford had established that the tiny atomic nucleus contained all the positive charge and most of the mass of the atom, there was much speculation that all nuclei might be composed of positive hydrogen nuclei along with a certain number of electrons. Thus the helium nucleus would be composed of four hydrogen nuclei and two electrons, and its net positive charge of two units would be balanced by two extranuclear electrons.

In 1917 Rutherford achieved the artificial disintegration of a nucleus. His apparatus (Figure 11.11) consisted of an evacuated chamber containing the alpha emitter radium C (^{214}Bi). Alpha particles passed through a hole covered by a very thin silver plate and were detected by a zinc sulphide screen. When nitrogen gas was admitted to the chamber, the number of scintillations recorded on the screen increased. Rutherford suggested that hydrogen nuclei were being ejected from the nitrogen atoms as a result of collisions with the alpha particles. In 1920 Rutherford named the hydrogen nucleus the *proton*.

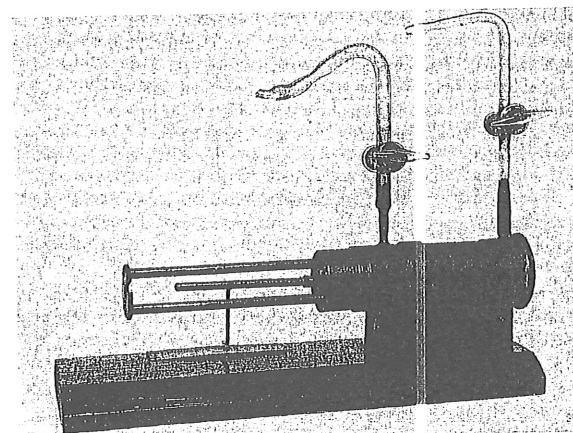


Figure 11.11 The apparatus that Rutherford used to show that nitrogen atoms were being disintegrated by alpha particles

Until 1932 it was generally accepted that the nucleus consisted of protons and electrons, but in that year the attention of James Chadwick (1891–1974) was captured by a recent experiment of Irène Joliot–Curie (1897–1956) and her husband Frédéric Joliot (1900–1958). They had found that light elements such as beryllium when bombarded with fast alpha particles from polonium emitted a very penetrating radiation. This radiation could not be deflected by a magnetic field, but when passed into paraffin wax caused protons to be ejected which had a remarkably high velocity. The Joliot–Curies were unable to provide a satisfactory explanation for the high energy and penetrating power of the radiation, but Chadwick demonstrated that it consisted of a neutral particle with approximately the same mass as the proton. Chadwick termed the new particle the *neutron*, although for a while he regarded it simply as a composite of a proton and an electron. Subsequent work showed that the neutron should be regarded as an elementary particle in its own right.

ELECTRONIC STRUCTURE

Rutherford's theory that the extranuclear electrons were circling the nucleus suffered from the objection that, according to classical theory, orbiting electrons should lose their energy and spiral inwards. The solution to the problem was suggested in 1913 by Niels Bohr (1885–1962), who introduced the concepts of the quantum theory to the motion of the extranuclear electrons. It was Max Planck (1858–1947) who in 1900 had introduced the revolutionary idea that energy is not emitted or absorbed by bodies on a continuous basis but in certain discrete units called *quanta*. The theory encountered considerable opposition, but successfully explained experimental observations on blackbody radiation. Bohr proposed that electrons moved in certain orbits around the nucleus, orbits nearer the nucleus being able to accommodate fewer electrons than those further away. An electron orbit corresponded to an *energy level*. An electron remained in the same orbit unless promoted to a higher one by absorption of the appropriate amount of energy, and an excited electron could 'fall back' to a vacancy in a lower orbit with the emission of a quantum of electromagnetic radiation.



Figure 11.12 Niels Henrik David Bohr (1885–1962)

Bohr (Figure 11.12) was born in Copenhagen, where his father was professor of physiology at the University. He obtained his doctorate at Copenhagen in 1911 with a dissertation on the electron theory of metals. While at Copenhagen he became convinced of the inability of classical electrodynamics to account for atomic phenomena. He went to Cambridge in 1911 to work with Thomson, and then moved to Manchester to collaborate with Rutherford. Bohr was one of the first to see that the chemical properties of the atom were explicable in terms of the extranuclear electrons, whereas the radioactive properties were due to the nucleus itself. Bohr arrived at the group displacement laws and the concept of isotopes before Soddy and Fajans, but Rutherford thought that the evidence did not justify the conclusions and dissuaded him from publishing. Bohr returned to Copenhagen in 1916, and two years later became the first Director of the Institute for Theoretical Physics. Under Bohr's leadership the Institute attracted many leading physicists from all over the world. After the discovery of nuclear fission, Bohr worked on the mechanics of the process and showed that the fissile isotope of uranium was ^{235}U and that ^{238}U would usually absorb slow neutrons without fission. After the outbreak of World War II he stayed in Denmark but in 1943, fearing imprisonment by the occupying Germans, he escaped to Sweden in a fishing boat. He was flown to England in the bomb bay of an unarmed plane, and was amazed to learn of the progress which had been made in the Manhattan atomic bomb project. As well as making some contributions to the project himself, Bohr was one of the first to advocate the international control of atomic weapons once the war was over. He returned to Denmark after the war and played a leading part in the foundation of CERN (European Centre for Nuclear Research).

Bohr's theory was received with a certain amount of scepticism by Rutherford, but it did have the advantage of explaining various features of atomic spectra. There had been numerous attempts to rationalise the lines observed in atomic emission spectra since the invention of the spectroscope by Bunsen and Kirchhoff in 1859 (Chapter 9). Little progress was made until 1885 when Johann Jacob Balmer (1825–1898), a Swiss school teacher, showed that the wavelengths of the four lines then known in the hydrogen spectrum could be expressed in terms of a simple equation. In 1890 Balmer's formula was rearranged by Johannes Robert Rydberg (1854–1919) to the form

$$1/\lambda = R(1/2^2 - 1/n^2)$$

Rydberg expressed the wavelengths in centimetres; thus $1/\lambda$ was the wavenumber value of the radiation, or the number of waves per centimetre. R , the Rydberg constant, had the value $109\,720\text{ cm}^{-1}$. The wavelengths of the four lines corresponded to values of n ranging from 3 to 6. Until 1908 the hydrogen spectrum had been found to contain only this series of lines in the visible region (the *Balmer series*), but over the next two decades a series was found in the ultraviolet by Lyman, and three more were found in the infrared by Paschen, Brackett and Pfund. The wavenumber values of the lines in these new series corresponded with the substitution of the integer values of 1, 3, 4 and 5, respectively, in place of 2 in the Rydberg formula.

Bohr assumed that the angular momentum of the electron in an orbit had to be an integral multiple of $h/2\pi$, where h is Planck's constant. He was therefore able to derive an equation for the energy evolved when an electron in a hydrogen atom changes its orbit. The equation was of the same form as the Rydberg equation and contained a constant term made up of known quantities such as Planck's constant and the mass and charge of the electron. When Bohr used the accepted values for these quantities to evaluate the constant in his equation, he obtained a value remarkably close to the Rydberg constant. By making appropriate modifications to his equation, Bohr was able to predict the frequencies of the lines in the spectra of other one-electron species such as He^+ , Li^{2+} , Be^{3+} , etc. These spectra were later observed in electric discharges and the frequencies were found to be very close to Bohr's predictions.

Bohr also attempted to write electronic structures (in terms of orbits) for elements up to chromium. However, the theoretical treatment of multi-electron systems proved to be very complex, and Bohr assigned electronic structures for elements principally on the basis of chemical properties. Thus lithium was assigned a structure of (2,1) but nitrogen was presumed to be (4,3) because of its trivalency. Over the next few years, Bohr, along with Arnold Sommerfeld (1868–1951), William Wilson and Charles Bury, refined electronic structures on the basis of both spectral and chemical behaviour.

The observation of spectral lines under high resolution revealed that many possessed a fine structure, and this led to the concept of electronic *sublevels*. These were named s, p, d and f levels, the letters having their origin in the atomic spectra of the alkali metals in which four series of lines were observed, which were known as *sharp*, *principal*, *diffuse* and *fundamental*. In 1896 some lines had been found to be split in a magnetic field by Pieter Zeeman (1865–1943), and this phenomenon was now explained in terms of electron spin. Each electron was now described in terms of four quantum numbers: principal (n), orbital (l), magnetic (m) and spin (s). In 1925 Wolfgang Pauli (1900–1958) put forward his *exclusion principle*, which stated that no two electrons in a given atom could have all four quantum numbers the same.

QUANTUM MECHANICS

In 1924 Louis de Broglie (1892–1987) introduced ideas which were to revolutionise our concept of the electron and other fundamental particles. The quantum theory had proposed that electromagnetic radiation was particulate in some of its properties, but only a wave theory could explain diffraction. De Broglie proposed that both the wave and particle theories should be accepted. He also suggested that matter should be regarded as not only particulate in nature, but should also be considered to have a wave nature as well. The validity of this viewpoint was demonstrated in 1927 with Davisson and Germer's experimental observation of the diffraction of electrons by crystals.

Shortly after de Broglie's theory appeared, new mathematical treatments, known collectively as *quantum mechanics*, were introduced to describe the behaviour of electrons in atoms. Erwin Schrödinger (1887–1961) developed *wave mechanics*, and Werner Heisenberg (1901–1976) used a different approach called *matrix mechanics*. Heisenberg's treatment led to the *uncertainty principle*, which stated that it is impossible simultaneously to determine precisely both the position and the velocity of the electron. Other workers in the field were Max Born (1882–1970), Pascual Jordan and Paul Dirac (1902–1984). Although the approaches of Schrödinger and Heisenberg seemed very different, it was ultimately realised that there is a fundamental unity between them.

The Schrödinger wave equation is one of the cornerstones of modern theoretical chemistry. From a consideration of a standing wave in three dimensions, Schrödinger derived an expression involving the wavefunction Ψ , the coordinates x , y and z and the total and potential energies E and V (Figure 11.13). Schrödinger suggested that the square of the wavefunction (Ψ^2) represented electron density at a particular point, but Born suggested that it represents the *probability* of finding the electron at that point. Solution of the wave equation for 90 per cent probability yields an envelope within which there is that chance of finding the electron. Such envelopes are known as *orbitals*. Only approximate solutions to the wave equation are possible, but from these have come our models of the various types of orbital. Each type of sublevel (s , p , d , f) consists of a characteristic number of orbitals (one, three, five, seven, respectively), and each orbital can hold two electrons with opposite spins.

$$\frac{\delta^2 \Psi}{\delta x^2} + \frac{\delta^2 \Psi}{\delta y^2} + \frac{\delta^2 \Psi}{\delta z^2} + \frac{8\pi^2 m}{h} (E - V) \Psi = 0$$

Figure 11.13 The Schrödinger wave equation

THE CHEMICAL BOND

The first attempt to explain the chemical bond in terms of electrons was made in 1904 by Thomson in his paper on the structure of the atom. He proposed that transfer of corpuscles (electrons) occurred from one atom to another at the moment of compound formation. He continued:

The electronegative atoms will thus get a charge of negative electricity and the electropositive atoms one of positive, the oppositely charged atoms will attract each other, and a chemical compound of the electropositive and electronegative atoms will be formed.

The application of Thomson's ideas to less polar compounds presented serious difficulties. There was no escape from the conclusion that certain atoms, e.g. carbon, could either accept or donate electrons depending on the nature of the atoms it was joined to. Thus, in methane, the carbon atom was supposed to receive

electrons from the hydrogen atoms; but, in tetrachloromethane, it was carbon which was the provider of electrons. This reasoning led to the conclusion that for certain compounds *electronic isomers* (or *electromers*) might exist (Figure 11.14), but none could be isolated.



Figure 11.14 Proposed electromers of nitrogen trichloride

In 1916, after Moseley had provided evidence of the number of extranuclear electrons in an atom and Bohr had introduced the idea of electrons being arranged in shells, Gilbert Newton Lewis (1875–1946) published an important paper entitled *The Atom and the Molecule*. Lewis was developing some ideas which he had jotted down as early as 1902 (Figure 11.15). He had imagined the electrons to be arranged in concentric cubes, and his sketch implies that he considered that bonding occurred between atoms as a result of the transfer of sufficient electrons to complete a cube. Lewis discussed his ideas with colleagues and students but published nothing on this subject before his paper of 1916.

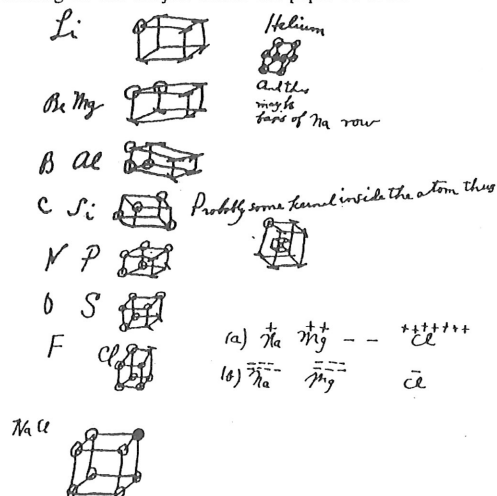


Figure 11.15 Lewis's sketch of 1902

In his 1916 paper Lewis stated clearly that bonding in polar compounds occurred as a result of electron transfer, which yielded oppositely charged ions with complete cubes of electrons. In the same year, Walther Kossel (1888–1956), in

Germany, also realised the importance of eight electrons but imagined the shells to be circles rather than cubes. His picture of bonding in polar compounds was essentially the same as that of Lewis.

Lewis not only considered very polar compounds such as sodium chloride, but also extended his discussion to entities such as hydrogen chloride and iodine. Lewis proposed that in such cases electrons could be shared in pairs between the atoms by the two cubes sharing a side or a face. In the same paper Lewis introduced the familiar symbolism of dots to represent electrons in the outer shells (Figure 11.17). He also suggested that polar molecules resulted from unequal sharing of electron pairs, and that bonding in compounds such as sodium chloride could be regarded as an extreme case of unequal sharing.

Lewis (Figure 11.16) was born in Weymouth, Massachusetts. After gaining his Ph.D. from Harvard in 1899, he travelled to Europe, spending time in Leipzig and Göttingen. Among the great European chemists he worked with were Ostwald and Nernst. After returning to the United States, he was an instructor at Harvard for a brief period, before going to Manila in the Philippines to work for the Bureau of Science. He returned to the United States in 1905 and worked at the Massachusetts Institute of Technology until 1912. In that year he became chairman of the chemistry department at the University of California at Berkeley, where he remained until his death. Lewis is remembered not only for his work on bonding but also for his contributions to thermodynamics. His careful experiments provided experimental justification for the third law of thermodynamics, which states that entropy becomes zero at absolute zero for all perfect crystals. He also widened the definitions of the terms *acid* and *base* (Chapter 13).

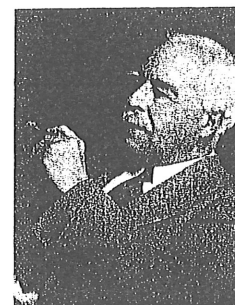


Figure 11.16 Gilbert Newton Lewis (1875–1946)

Lewis's ideas were extended in 1919 by Irving Langmuir (1881–1957), who drew a clearer distinction between the bonding in the two types of compound and introduced the terms *electrovalency*, *covalency* and *octet*. Like Lewis, he also represented covalent compounds by means of joined cubes (Figure 11.18). Other developments soon followed. In 1920 Wendell M. Latimer and Worth H. Rodebush

introduced the concept of the *hydrogen bond* to explain the association between molecules in liquids such as water and acetic acid. The *coordinate bond*, in which both shared electrons originate from the same atom, was proposed in 1927 by Neil Vincent Sidgwick (1873–1952) to explain the bonding between the central metal ion and the ammonia molecules in ammine complexes such as $[\text{Cr}(\text{NH}_3)_6]^{3+}$. This was an extension of another of Lewis's ideas. In his paper of 1916 Lewis had explained the bonding in the ammonium ion as a sharing of the lone pair of electrons of an ammonia molecule with a hydrogen ion.



Figure 11.17 Lewis's 'dot' formulae

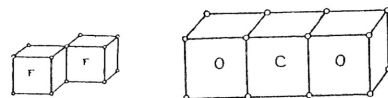
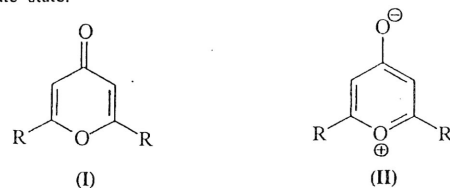


Figure 11.18 Langmuir's diagrams of joined cubes

In the 1920s two British chemists, Robert Robinson (1893–1975) and Christopher Ingold (1893–1970), separately started to develop explanations of the course of organic reactions based upon the Lewis–Langmuir concepts of bonding in covalent compounds. These early ideas on reaction mechanisms produced new insights into the bonding in the organic molecules themselves. In 1922 Robinson introduced the idea of the concerted movement of pairs of electrons in conjugated systems, and showed how one Kekulé formula for benzene could be converted into the other by the movement of electron pairs.

In 1924 F. G. Arndt drew attention to the fact that the reactions of the γ -pyrones were not consistent with their classical formula I (Figure 11.19). Utilising the recently introduced idea of the *zwitterion*, he proposed an alternative structure (II). Arndt's vital contribution was to suggest that neither formula provided an accurate representation of the molecule, but that the true structure was some kind of intermediate state.

Figure 11.19 Two possible formulae for the γ -pyrones

Arndt's concept was elaborated in 1926 by Ingold, who pointed out that dimethylaniline might not only have structure III (Figure 11.20) but that there

might also be a contribution from structure IV. Ingold further proposed that, because of the electron-attracting power of nitrogen, the nitrogen atom in structure III should act as the negative end of the dipole, but that the polarity is reversed in structure IV. Ingold noted that dipole moment measurements should be capable of establishing whether structure IV makes a contribution. When the measurements were made, it was clear that the structure of dimethylaniline is indeed intermediate between forms III and IV. Ingold proposed the term *mesomerism* to describe the intermediate character of the bonding. Until this time many organic chemists had doubted if physical chemistry was capable of yielding any results of value for their discipline, but now *physical organic chemistry* rapidly began to make important contributions, especially in the areas of molecular structure and reaction mechanisms.

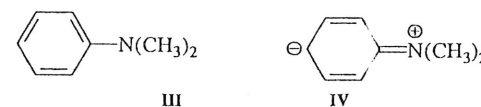


Figure 11.20 Two possible formulae for dimethylaniline

VALENCE BOND AND MOLECULAR ORBITAL THEORIES

The new science of quantum mechanics proved to be capable of providing an explanation of the concept of mesomerism as well as the more familiar aspects of bonding such as directed valency. The two approaches which have been developed are known as the *valence bond theory* and the *molecular orbital theory*.

The valence bond approach uses the wavefunctions of the valence electrons of two approaching atoms to calculate the potential energy of the system as a function of the interatomic distance (Figure 11.21). This method was first applied to the hydrogen molecule by Walter Heitler (*b.* 1904) and Fritz London (1900–1954) in 1927, and subsequent refinements to the calculations have produced remarkably good values for the bond energy and the bond length.

More than anyone else it has been Linus Pauling (*b.* 1901) who has been responsible for the development and application of the valence bond theory. In the early 1930s he deduced from quantum mechanics the tetrahedrally directed valencies of carbon, and he introduced the concept of the hybridisation of atomic orbitals. He introduced the idea of *resonance* as the quantum-mechanical counterpart of mesomerism. The wavefunction for the molecule must contain terms for all possible structures, and the molecule is said to *resonate* between them. In 1933 Pauling described the benzene molecule as a resonance hybrid between the two Kekulé structures and the three possible Dewar structures (Figure 11.22).

Pauling and John C. Slater applied the valence bond theory to coordination compounds, describing the bonding in terms of overlap of an orbital of the ligand containing a lone pair of electrons with a vacant hybridised orbital on the central metal ion. This model gave a satisfactory explanation of both the geometry and

magnetic properties of many complexes, but was unable to explain their spectral behaviour.

Pauling (Figure 11.23) was born in Oregon, and was a student at the Oregon Agricultural College. His father had died when Pauling was nine, and he took a series of jobs to support himself while he studied. He so distinguished himself at chemistry that he was given some teaching duties at the College while still an undergraduate. Pauling then moved to the newly opened California Institute of Technology to study for his Ph.D. He worked on X-ray diffraction, solving the structure of many minerals. In 1925 Pauling went to Europe, where he spent two years with Arnold Sommerfeld, who was working on the new quantum mechanics. On his return to the United States, Pauling performed his famous work on bonding, which resulted in 1939 in the publication of his book *The Nature of the Chemical Bond*. In the 1930s Pauling became interested in biologically important substances, especially proteins. Although it had been known for many years that proteins consisted of amino acids, a number of possible ways had been suggested in which the amino acids might be linked. Pauling argued that the arrangement which best fitted the data available at the time was that the amino acids were joined together in long chains. He studied amino acids and small peptides by X-ray diffraction, and in 1950 he used the data he had acquired to propose the alpha-helical structure for the peptide chain. In the 1940s Pauling studied samples of haemoglobin isolated from normal humans and those suffering from sickle-cell anaemia. He showed that the two haemoglobins moved differently in electrophoresis and therefore had different molecular structures. This was the first example of a *molecular disease*. Pauling is one of the select few who have won two Nobel prizes. He was awarded the Chemistry Prize in 1954 and the Peace Prize in 1962 for his campaigns against the proliferation and testing of nuclear weapons. His views that large doses of vitamin C are effective in combatting the common cold and cancer have been criticised by the medical fraternity. He has remained active in his eighties, and has published papers on high-temperature superconductivity. His work has been characterised throughout by brilliant intuition and insight, and he is undoubtedly one of the greatest chemists of the twentieth century.

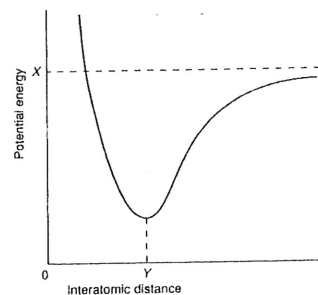


Figure 11.21 Plot of potential energy against interatomic distance for a diatomic molecule

Robert Mulliken (1896–1986) was the chief originator of the molecular orbital approach. This theory rests on the postulate that, when a compound is formed, electrons move in new orbitals which extend over several atomic nuclei. The mathematical approximation used is known as the LCAO (linear combination of atomic orbitals) method. In the molecular orbital theory, a molecule is considered to possess a series of orbitals of increasing energy. Electrons occupy the lower energy *bonding orbitals*, while there will be vacancies in the higher energy *antibonding orbitals*. Just as atomic spectra can be explained in terms of the movement of electrons between atomic orbitals, the absorption spectra of molecules in the ultraviolet and visible regions are best explained in terms of electron movement between molecular orbitals.

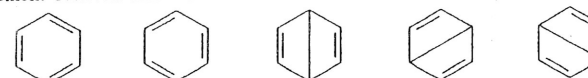


Figure 11.22 The five structures contributing to the normal state of the benzene molecule



Figure 11.23 Linus Carl Pauling (b. 1901)

It was Erich Hückel (1896–1980) who first attempted to apply the molecular orbital theory to organic molecules. He introduced the terms *sigma* (σ) and *pi* (π)

bonding. He applied the molecular orbital theory to aromatic molecules in 1931 when he derived the rule that for a cyclic compound to display aromatic character, it must possess $(4n + 2) \pi$ electrons, where n is an integer.

The spectral behaviour of coordination complexes was first satisfactorily explained in terms of the *crystal field theory*, developed in 1935 by John H. van Vleck from the work of Hans Bethe. On this theory the bonding is regarded as being essentially electrostatic in nature, there being an attraction between the central positive ion and the negative or partially negative ligand. Later, molecular orbital concepts were introduced into the crystal field theory to produce the modern *ligand field theory*.

Both the valence bond and molecular orbital theories continue to be used today, and both involve approximations. Neither approach can claim to be final, and the chemist uses the method most suited to the problem in hand.

12

Inorganic Chemistry

With the rapid development of carbon chemistry after 1860, a considerable number of chemists, especially in Germany, devoted all their attention to this branch of the subject. Chemistry therefore became divided into organic and inorganic specialisms, and towards the end of the century physical chemistry began to emerge as a third discipline. The progress in carbon chemistry outshone that made in other areas until the 1890s, when new discoveries and theories relating to coordination compounds signalled the coming of age of inorganic chemistry.

NEW ELEMENTS

We have seen how the number of known elements continued to grow during the second half of the nineteenth century. Powerful tools in the detection of new elements were the spectroscope, invented in 1860 (Chapter 9), and radioactivity, first exploited by Marie and Pierre Curie in 1898 (Chapter 11). Mendeleev's periodic classification had predicted the existence of gallium, scandium and germanium, but the discovery of the rare gases had come as a surprise (Chapter 9). In contrast, the existence of fluorine had been suspected for many years, but its extreme reactivity resulted in its isolation being delayed until 1886.

The mineral fluorspar had been used as a flux since the middle ages (the name comes from the Latin *fluor* meaning *flow*), and in the *Traité* Lavoisier had included the fluoric radical as a simple substance (element) as yet unknown. Scheele obtained hydrofluoric acid in 1771. In 1813 Ampère pointed out the many similarities between the fluoric and muriatic (chlorine) compounds. He suggested the unknown element be called fluorine, and in the same year Humphry Davy tried to prepare it by the electrolysis of hydrofluoric acid. The corrosive nature of the acid presented insuperable problems, and it was to be another 73 years before the isolation of the element was achieved. During that time the toxic nature of fluorine compounds was to be responsible for the deaths of at least two chemists and was to ruin the health of many more. Success was finally achieved by Henri Moissan (1852–1907), who electrolysed potassium fluoride dissolved in anhydrous hydrofluoric acid using platinum apparatus.