# THE BIOGRAPHICAL DICTIONARY OF SCIENTISTS

General Editor: David Abbott, PhD

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# Acknowledgements

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# Historical introduction

Chemistry seems to have originated in the countries of Egypt and Mesopotamia several thousand years before Christ. Certainly by about 3000 BC the Egyptians had produced the copper–tin alloy known as bronze, by heating the ores of copper and tin together, and this new material was soon common enough to be made into tools, ornaments, armour and weapons. The Ancient Egyptians were also skilled at extracting juices and infusions from plants, and pigments from minerals, which they used in the embalming and preserving of their dead. By 600 BC the Greeks were also becoming a settled and prosperous people with leisure time in which to think. They began to turn their attention to the nature of the Universe and to the structure of its materials. They were thus the first to study the subject we now call chemical theory. Aristotle (384–322 BC) proposed that there were four elements – earth, air, fire and water – and that everything was a combination of these four. They were thought to possess the following properties: earth was cold and dry, air was hot and moist, fire was hot and dry, and water was cold and moist. The idea of the four elements persisted for 2,000 years. The Greeks also worked out, at least hypothetically, that matter ultimately consisted of small indivisible particles, *atomos* – the origin of our word atom.

From the Egyptians and the Greeks comes *khemeia*, alchemy and eventually chemistry as we know it today. The source of the word *khemeia* is debatable, but it is certainly the origin of the word chemistry. It may derive from the Egyptians' word for their country (*Khem*, meaning the black land). It may come from the Greek word *khumos* (the juice of a plant), so that *khemeia* is "the art of extracting juices"; or from the Greek *cheo* (I pour or cast), which refers to the activities of the metal workers. Whatever its origin, the art of *khemeia* soon became akin to magic and was feared by the ordinary people. One of the greatest aims of the subject involved the attempts to transform base metals such as lead and copper into silver or gold. From the four-element theory, it seemed that it should be possible to perform any such change, if only the proper technique could be found.

## The Arabs and alchemy

With the decline of the Greek empire *khemeia* was not pursued and little new was added to the subject until it was embraced by the increasingly powerful Arabs in the seventh century AD. Then for five centuries *al-kimiya*, or alchemy, was in their hands. The Arabs drew many ideas from the *khemeia* of the Greeks, but they were also in contact with the Chinese – for example, the idea that gold possessed healing powers came from China. They believed that "medicine" had to be added to base metals to produce gold, and it was this medicine that was to become the philosopher's stone of the later European alchemists. The idea that not only could the philosopher's stone heal "sick" or base metals, but that it could also act as the elixir of life, was also originally Chinese. The Arab alchemists discovered new classes of chemicals such as the caustic alkalis (from the Arabic *al-qaliy*) and they improved technical procedures such as distillation.

Western Europe had its first contact with the Islamic world as a result of the Crusades. Gradually the works of the Arabs – handed down from the Greeks – were translated into Latin and made available to European scholars in the twelfth and thirteenth centuries. Many men spent their lives trying in vain to change base metals into gold; and many alchemists lost their heads for failing to supply the promised gold. Throughout the fifteenth to seventeenth centuries their symbolism became more and more complex. In 1689 the preparation of silver chloride, by dissolving metallic silver in nitric acid and then adding hydrochloric acid, was described like this:

Recipe ☽, in Ω ☉ solve, cum Ω ⊖ precipitata, filtra. ☽ = Moon = silver (the same symbols were used for the metals and their associated planets), ☉ = nitre, ⊖ = mineral acid, and Ω = spirit.

A new era in chemistry began with the researches of Robert Boyle (1627–1691), who carried out many experiments on air. These experiments were the beginning of a long struggle to find out what air had to do with burning and breathing. From Boyle's time onwards, alchemy became chemistry and it was realized that there was more to the subject than the search for the philosopher's stone.

## Chemistry as an experimental science

During the 1700s the phlogiston theory gained popularity. It went back to the alchemists' idea that combustible bodies lost something when they burned. Metals were thought to be composed of a calx (different for each) combined with phlogiston, which was the same in all metals. When a candle burned in air, phlogiston was given off. It was believed that combustible objects were rich in phlogiston and what was left after combustion possessed no phlogiston and would therefore not burn. Thus wood possessed phlogiston but ash did not; when metals rusted, it was considered that the metals contained phlogiston but that its rust or calx did not. By 1780 this theory was almost universally accepted by chemists. Joseph Priestley (1733–1804) was a supporter of the theory and in 1774 he had succeeded in obtaining from mercuric oxide a new gas which was five or six times purer than ordinary air. It was, of course, oxygen but Priestley called it "dephlogisticated air" because a smouldering splint of wood thrust into an atmosphere of this new gas burst into flames much more readily than it did in an ordinary atmosphere. He took this to mean that the gas must be without the usual content of phlogiston, and was therefore eager to accept a new supply.

It was Antoine Lavoisier (1743–1794) who put an end to the phlogiston theory by working out what was really happening in combustion. He repeated Priestley's experiments in 1775 and named the dephlogisticated air oxygen. He realized that air was not a single substance but a mixture of gases, made up of two different gases in the proportion of 1 to 4. He deduced that one-fifth of the air was Priestley's dephlogisticated air (oxygen), and that it was this part only that combined with rusting or burning materials and was essential to life. Oxygen means "acid-producer" and Lavoisier thought, erroneously, that oxygen was an essential part of all acids. He was a careful experimenter and user of the balance, and from his time onwards experimental chemistry was concerned only with materials that could be weighed or otherwise measured. All the "mystery" disappeared and Lavoisier went on to work out a logical system of chemical nomenclature, much of which has survived to the present day.

Early in the nineteenth century many well-known chemists were active. Claude Berthollet (1748–1822) worked on chemical change and composition, and Joseph Gay-Lussac (1778–1850) studied the volumes of gases that take part in chemical reactions. Others included Berzelius, Cannizzaro, Avogadro, Davy, Dumas, Kolbe, Wöhler and Kekulé. The era of modern chemistry was beginning.

## Atomic theory and new elements

An English chemist, John Dalton (1766–1844), founded the atomic theory in 1803 and in so doing finally crushed the belief that the transmutation to gold was possible. He realized that the same two elements can combine with each other in more than one set of proportions, and that the variation in combining proportions gives rise to different compounds with different properties. For example, he determined that one part (by weight) of hydrogen combined with eight parts of oxygen to form water, and if it was assumed (incorrectly) that a molecule of water consisted of one atom of hydrogen and one atom of oxygen, then it was possible to set the mass of the hydrogen atom arbitrarily at 1 and call the mass of oxygen 8 (on the same scale). In this way Dalton set up the first table of atomic weights (now called relative atomic masses), and although this was probably his most important achievement, it contained many incorrect assumptions. These errors and anomalies were researched by Jöns Berzelius (1779–1848), who found that for many elements the atomic weights were not simple multiples of that of hydrogen. For many years, oxygen was made the standard and set at 16.000 until the mid-twentieth century, when carbon ($=12.000$) was adopted. Berzelius suggested representing each element by a symbol consisting of the first one or two letters of the name of the element (sometimes in Latin) and these became the chemical symbols of the elements as still used today.

At about the same time, in 1808, Humphry Davy (1778–1829) was using an electric current to obtain from their oxides elements that had proved to be unisolatable by chemical means: potassium, sodium, magnesium, barium and calcium. His assistant, Michael Faraday (1791–1867), was to become even better known in connection with this technique, electrolysis. By 1830, more than 50 elements had been isolated; chemistry had moved a long way from the four elements of the Ancient Greeks, but their properties seemed to be random. In 1829 the German chemist Johann Döbereiner (1780–1849) thought that he had observed some slight degree of order. He wondered if it was just coincidence that the properties of the element bromine seemed to lie between those of chlorine and iodine, but he went on to notice a similar gradation of properties in the triplets calcium, strontium and barium and with sulphur, selenium and tellurium. In all of these examples, the atomic weight of the element in the middle of the set was about half way between the atomic weights of the other two

elements. He called these groups "triads", but because he was unable to find any other such groups, most chemists remained unimpressed by his discovery. Then in 1864 John Newlands (1837–1898) arranged the elements in order of their increasing atomic weights and found that if he wrote them in horizontal rows, and started a new row with every eighth element, similar elements tended to fall in the same vertical columns. Döbereiner's three sets of triads were among them. Newlands called this his "Law of Octaves" by analogy with the repeating octaves in music. Unfortunately there were many places in his chart where obviously dissimilar elements fell together and so it was generally felt that Newland's similarities were not significant but probably only coincidental. He did not have his work published.

In 1862 a German chemist, Julius Lothar Meyer (1830–1895), looked at the volumes of certain fixed weights of elements, and talked of atomic volumes. He plotted the values of these for each element against its atomic weight, and found that there were sharp peaks in the graph at the alkali metals – sodium, potassium, rubidium and caesium. Each part of the graph between the peaks corresponded to a "period" or horizontal row in the table of the elements, and it became obvious where Newlands had gone wrong. He had assumed that each period contained only seven elements; in fact the later periods had to be longer than the earlier ones. By the time Meyer published his findings, he had been anticipated by the Russian chemist Dmitri Mendeleyev (1834–1907), who in 1869 published his version of the Periodic Table, which was more or less as we have it today. He had the insight to leave gaps in his table for three elements which he postulated had not yet been discovered, and was even able to predict what their properties would be. Chemists were sceptical, but within 15 years all three of the "missing" elements had been discovered and their properties were found to agree with Mendeleyev's predictions.

### The beginnings of physical chemistry

Until the beginning of the nineteenth century, the areas covered by the subjects of chemistry and physics seemed well-defined and quite distinct. Chemistry studied changes where the molecular bonding structure of a substance was altered, and physics studied phenomena in which no such change occurred. Then in 1840 physics and chemistry merged in the work of Germain Hess (1802–1850). It had been realized that heat – a physical phenomenon – was produced by chemical reactions such as the burning of wood, coal and oil, and it was gradually becoming clear that all chemical reactions involved some sort of heat transfer.

Hess showed that the quantity of heat produced or absorbed when one substance was changed into another was the same no matter by which chemical route the change occurred, and it seemed likely that the law of conservation of energy was equally applicable to chemistry and physics. Thermochemistry had been founded and work was able to begin on thermodynamics. Most of this research was done in Germany and it was Wilhelm Ostwald (1853–1932), towards the end of the nineteenth century, who was responsible for physical chemistry developing into a discipline in its own right. He worked on chemical kinetics and catalysis in particular, but was the last important scientist to refuse to accept that atoms were real – there was at that time still no direct evidence to prove that they existed. Other contemporary chemists working in the new field of physical chemistry included Jacobus van't Hoff (1852–1911) and Svante Arrhenius (1859–1927). Van't Hoff studied solutions and showed that molecules of dissolved substances behaved according to rules analogous to those that describe the behaviour of gases. Arrhenius carried on the work which had been begun by Davy and Faraday on solutions that could carry an electric current. Faraday had called the current-carrying particles "ions", but nobody had worked out what they were. Arrhenius suggested that they were atoms or groups of atoms which bore either a positive or a negative electric charge. His theory of ionic dissociation was used to explain many of the phenomena in electrochemistry.

Towards the end of the nineteenth century, mainly as a result of the increasing interest in the physical side of chemistry, gases came under fresh scrutiny and some errors were found in the law that had been proposed three centuries earlier by Robert Boyle. Henri Regnault (1810–1878), James Clerk Maxwell (1831–1879) and Ludwig Boltzmann (1844–1906) had all worked on the behaviour of gases, and the kinetic theory of gases had been derived. Taking all their findings into account, Johannes van der Waals (1837–1923) arrived at an equation that related pressure, volume and temperature of gases and made due allowance for the sizes of the different gas molecules and the attractions between them. By the end of the century William Ramsay (1852–1916) had begun to discover a special group of gases – the inert or rare gases – which have a valency (oxidation state) of zero and which fit neatly into the Periodic Table between the halogens and the alkali metals.

### Organic chemistry becomes a separate discipline

Meanwhile the separate branches of chemistry were emerging and organic substances were being

distinguished from inorganic ones. In 1807 Berzelius had proposed that substances such as olive oil and sugar, which were products of living organisms, should be called organic, whereas sulphuric acid and salt should be termed inorganic. Chemists at that time had realized that organic substances were easily converted into inorganic substances by heating or in other ways, but it was thought to be impossible to reverse the process and convert inorganic substances into organic ones. They believed in Vitalism – that somehow life did not obey the same laws as did inanimate objects and that some special influence, a "vital force", was needed to convert inorganic substances into organic ones. Then in 1828 Friedrich Wöhler (1800–1882) succeeded in converting ammonium cyanate (an inorganic compound) into urea. In 1845 Adolf Kolbe (1818–1884) synthesized acetic acid, squashing the Vitalism theory for ever. By the middle of the nineteenth century organic compounds were being synthesized in profusion; a new definition of organic compounds was clearly needed, and most organic chemists were working by trial and error. Nevertheless there was a teenage assistant of August von Hofmann (1818–1892), called William Perkin (1838–1907), who was able to retire at the age of only 35 because of a brilliant chance discovery. In 1856 he treated aniline with potassium chromate, added alcohol, and obtained a beautiful purple colour, which he suspected might be a dye (later called aniline purple or mauve). He left school and founded what became the synthetic dyestuffs industry.

Then in 1861 the German chemist Friedrich Kekulé (1829–1886) defined organic chemistry as the chemistry of carbon compounds and this definition has remained, although there are a few carbon compounds (such as carbonates) which are considered to be part of inorganic chemistry. Kekulé suggested that carbon had a valency of four, and proceeded to work out the structures of simple organic compounds on this basis. These representations of the structural formulae showed how organic molecules were generally larger and more complex than inorganic molecules. There was still the problem of the structure of the simple hydrocarbon benzene, $C_6H_6$, until 1865 when Kekulé suggested that rings of carbon atoms might be just as possible as straight chains. The idea that molecules might be three-dimensional came in 1874 when Van't Hoff suggested that the four bonds of the carbon atom were arranged tetrahedrally. If these four bonds are connected to four different types of groups, the carbon atom is said to be asymmetric and the compound shows optical activity – its crystals or solutions rotate the plane of polarized light.

Viktor Meyer (1848–1897) proposed that certain types of optical isomerism could be explained by bonds of nitrogen atoms. Alfred Werner (1866–1919) went on to demonstrate that this principle also applied to metals such as cobalt, chromium and rhodium, and succeeded in working out the necessary theory of molecular structure, known as co-ordination theory. This new approach allowed there to be structural relationships within certain fairly complex inorganic molecules, which were not restricted to bonds involving ordinary valencies. It was to be another 50 years before enough was known about valency for both Kekulé's theory and Werner's to be fully understood, but by 1900 the idea was universally accepted that molecular structure could be represented satisfactorily in three dimensions.

Kekulé's work gave the organic chemist scope to alter a structural formula stage by stage, to convert one molecule into another, and modern synthetic organic chemistry began. Richard Willstätter (1872–1942) was able to work out the structure of chlorophyll and Heinrich Wieland (1877–1957) determined the structures of steroids. Paul Karrer (1889–1971) elucidated the structures of the carotenoids and other vitamins and Robert Robinson (1886–1975) tackled the alkaloids – he worked out the structures of morphine and strychnine. The alkaloids have found medical use as drugs, as have many other organic compounds. The treatment of disease by the use of specific chemicals is known as chemotherapy and was founded by the bacteriologist Paul Ehrlich (1854–1915). The need for drugs to combat disease and infection during World War II spurred on research, and by 1945 the antibiotic penicillin, first isolated by Howard Florey (1898–    ) and Ernst Chain (1906–    ), was being produced in quantity. Other antibiotics such as streptomycin and the tetracyclines soon followed.

Some organic molecules contain thousands of atoms; some, such as rubber, are polymers and others, such as haemoglobin, are proteins. Synthetic polymers have been made which closely resemble natural rubber; the leader in this field was Wallace Carothers (1896–1937), who also invented Nylon. Karl Ziegler (1898–1973) and Giulio Natta (1903–    ) worked out how to prevent branching during polymerization, so that plastics, films and fibres can now be made more or less to order. Work on the make-up of proteins had to wait for the development of chemical techniques such as chromatography (by Mikhail Tswett (1872–1919) and by Archer Martin (1910–    ) and Richard Synge (1914–    )) and electrophoresis (Arne Tiselius (1902–1971)). In the forefront of molecular biological research are Frederick Sanger (1918–    ), John Kendrew

(1917–    ) and Max Perutz (1914–    ). One technique that has been essential for their work is X-ray diffraction, and for the background to this development we have to return to the area of research between chemistry and physics at the beginning of the present century.

## Modern atomic theory

Ever since Faraday had proposed his laws of electrolysis, it had seemed likely that electricity might be carried by particles. The physicist Ernest Rutherford (1871–1937) decided that the unit of positive charge was a particle quite different from the electron, which was the unit of negative charge, and in 1920 he suggested that this fundamental positive particle be called the proton. In 1895 Wilhelm Röntgen (1845–1923) discovered X-rays, but other radiation components – alpha and beta rays – were found to be made up of protons and electrons. In about 1902 it was proved, contrary to all previous ideas, that radioactive elements changed into other elements, and by 1912 the complicated series of changes of these elements had been worked out. In the course of this research, Frederick Soddy (1877–1956) realized that there could be several atoms differing in mass but having the same properties. They were called isotopes and we now know that they differ in the number of neutrons which they possess, although the neutron was not to be discovered until 1932, by the physicist James Chadwick (1891–1974).

Rutherford evolved the theory of the nuclear atom, which suggested that sub-atomic particles made up the atom, which had until that time been considered to be indivisible. The question now was, how did the nuclear atom of one element differ from that of another? In 1909 Max von Laue (1879–1960) began a series of brilliant experiments. He established that crystals consist of atoms arranged in a geometric structure of regularly repeating layers, and that these layers scatter X-rays in a set pattern. In so doing, he had set the scene for X-ray crystallography to be used to help to work out the structures of large molecules for which chemists had not been able to determine formulae.

In 1913 the young scientist Henry Moseley (1887–1915) found that there were characteristic X-rays for each element and that there was an inverse relationship between the wavelength of the X-ray and the atomic weight of the element. This relationship depended on the size of the positive charge on the nucleus of the atom, and the size of this nuclear charge is called the atomic number. Mendeleyev had arranged his Periodic Table, by considering the valencies of the elements, in sequence of their atomic weights, but

the proper periodic classification is by atomic numbers. It was now possible to predict exactly how many elements were still to be discovered. Since the proton is the only positively charged particle in the nucleus, the atomic number is equal to the number of protons; the neutrons contribute to the mass but not to the charge. For example, a sodium atom, with an atomic number of 11 and an atomic weight (relative atomic mass) of 23, has 11 protons and 12 neutrons in its nucleus.

## Isotopes and biochemistry

The new electronic atom was also of great interest to organic chemists. It enabled theoreticians such as Christopher Ingold (1893–1970) to try to interpret organic reactions in terms of the movements of electrons from one point to another within a molecule. Physical chemical methods were being used in organic chemistry, founding physical organic chemistry as a separate discipline. Linus Pauling (1911–    ), a chemist who was to suggest in the 1950s that proteins and nucleic acids possessed a helical shape, worked on the wave properties of electrons, and established the theory of resonance. This idea was very useful in establishing that the structure of the benzene molecule possessed "smeared out" electrons and was a resonance hybrid of the two alternating double bond/single bond structures. The concept of atomic number was clarified by Francis Aston (1877–1945) with the mass spectrograph. This instrument used electric and magnetic fields to deflect ions of identical charge by an extent that depended on their mass – the greater the mass of the ion, the less it was deflected. He found for instance that there were two kinds of neon atoms, one of mass 20 and one of mass 22. The neon-20 was ten times as common as the neon-22, and so it seemed reasonable that the atomic weight of the element was 20.2 – a weighted average of the individual atoms and not necessarily a whole number. In some cases, the weighted average (atomic weight) of a particular atom may be larger than that for an atom of higher atomic number. This explains the relative positions of iodine and tellurium in the Periodic Table, which Mendeleyev had placed correctly without knowing why.

In 1931 Harold Urey (1893–1981) discovered that hydrogen was made up of a pair of isotopes, and he named hydrogen-2 deuterium. In 1934 it occurred to the physicist Enrico Fermi (1901–1954) to bombard uranium (element number 92, the highest atomic number known at that time) in order to see whether he could produce any elements of higher atomic numbers. This approach was pursued by Glenn Seaborg

(1912– ) and the transuranium elements were discovered, going up from element 94 to 104 but becoming increasingly difficult to form and decomposing again more rapidly with increasing atomic number.

The area between physics and chemistry has been replaced by a common ground where atoms and molecules are studied together with the forces that influence them. The boundary between chemistry and biology has also become less well defined and is now a scene of intense activity, with the techniques of chemistry being applied successfully to biological problems. Electron diffraction, chromatography and radioactive tracers have all been used to help to discover what living matter is composed of, although it is possible that these investigations in biology are only now at the stage that atomic physics was at the beginning of this century. It was Lavoisier who said that life is a chemical function, and perhaps the most important advance of all is towards understanding the chemistry of the cell.

# A

**Alder, Kurt** (*1902–1958*), was a German organic chemist who with Otto Diels (1876–1954) developed the diene synthesis, a fundamental process that has become known as the Diels–Alder reaction. It is used on organic chemistry to synthesize cyclic (ring) compounds, including many that can be made into plastics and others – which normally occur only in small quantities in plants and other natural sources – that are the starting materials for various drugs and dyes. This outstanding achievement was recognized by the award of the 1950 Nobel Prize in Chemistry jointly to Alder and Diels.

Alder was born on 10 July 1902 in the industrial town of Königshütte (Krolewska Huta) in Upper Silesia, which was then part of Germany (it is now in Poland). He was the son of a schoolteacher and began his education in his home town. When the region became part of Poland at the end of World War I, the Alder family moved to Berlin. There Kurt Alder finished his schooling and went on to study chemistry, first at the University of Berlin and later at Kiel, where he worked under Otto Diels. Alder became a chemistry reader at Kiel in 1930 and a professor in 1934, but two years later he began a four-year period in industry as Research Director of I. G. Farben at Leverkusen on the northern outskirts of Cologne. He returned to academic life in 1940 as Professor and Director of the Chemical Institute at the University of Cologne, where he remained for the rest of his life. He died in Cologne on 20 June 1958.

The first report of the diene synthesis, stemming from work in Diels' laboratory at Kiel, was made in 1928. The Diels–Alder reaction involves the adding of an organic compound that has two double bonds separated by a single bond (called a conjugated diene) to a compound with only one, activated double bond (termed a dienophile). A common example of a conjugated diene is butadiene (but-1,2:3,4-diene) and of a dienophile is maleic anhydride (*cis*-butenedioic anhydride). These two substances react readily to form the bicyclic compound tetrahydrophthalic anhydride (cyclohexene-1:2-dicarboxylic anhydride) – one of the reactions originally reported by Diels and Alder in 1928:



diene
(butadiene)

dienophile
(maleic anhydride)

Diels-Alder adduct
(tetrahydrophthalic anhydride)
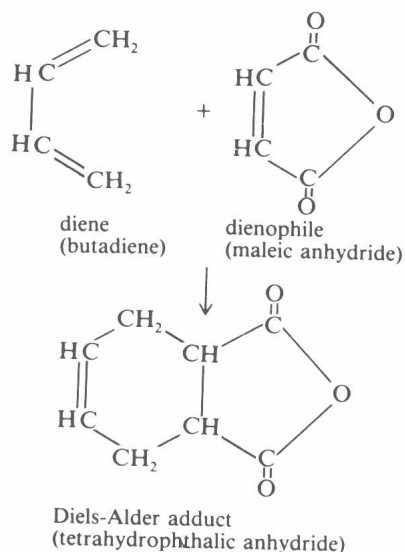
Azo-diesters, general formula $RCO_2.N{:}N.CO_2R$, also act as dienophiles in the reaction, as can other unsaturated acids and their esters. With a cyclodiene, the synthesis yields a bridged cyclic compound:



cyclopentadiene

azo-diester

adduct
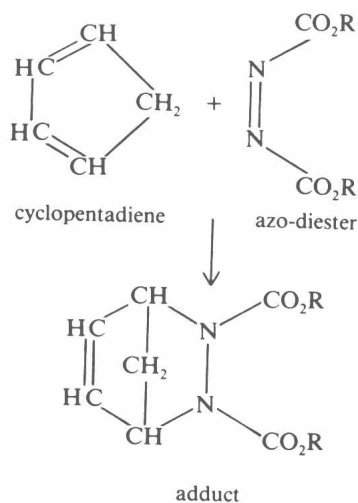
One or two reactions of this type had been reported in the early 1900s, but Diels and Alder were the first to recognize its widespread and general nature. They also demonstrated the ease with which it takes place and the high yield of the product – two vitally important factors for successful organic synthesis. In association with

Diels, and later with his own students, Alder continued to study the general conditions of the diene synthesis and the overall scope of the method for synthetic purposes. In his Nobel Prize address, Alder listed more than a dozen different dienes of widely differing structure that participate in the reaction. He also showed that the reaction is equally general with respect to dienophiles, provided that their double bonds are activated by a nearby group such as carboxyl, carbonyl, cyano, nitro or ester. Many of the compounds studied were prepared for the first time in Alder's laboratory.

Alder was a particularly able stereochemist, and he showed that the diene addition takes place at double bonds with a *cis* configuration – i.e., where the two groups substituting the double bond are both on the same side of it, as opposed to the *trans* isomer, with the groups on opposite sides:

$$HCO_2 \diagdown \qquad \diagup CO_2H$$
$$C = C$$
$$H \diagup \qquad \diagdown H$$

*cis* configuration
(maleic acid)

$$HCO_2 \diagdown \qquad \diagup H$$
$$C = C$$
$$H \diagup \qquad \diagdown CO_2H$$

*trans* configuration
(fumaric acid)
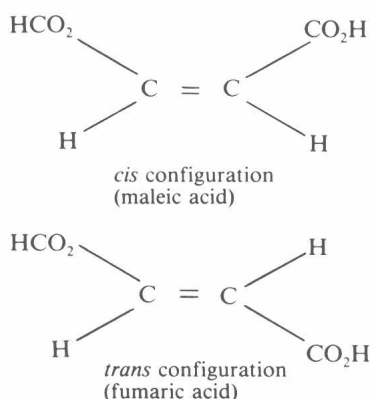
That is why maleic acid (*cis*-butenedicarboxylic acid) reacts whereas its isomer fumaric acid (*trans*-butenedicarboxylic acid) does not. The stereospecific nature of the Diels–Alder reaction has thus become useful in structural studies for the detection of conjugated double bonds.

The bridged ring, or bicyclic, compounds formed by using cyclic dienes (such as cyclopentadiene, above) are closely related to many naturally occuring organic compounds such as camphor and pinene, which belong to the group known as terpenes. The diene synthesis stimulated and made easier the understanding of this important group of natural products by providing a means of synthesizing them. Indeed, the ease with which the reaction takes place suggests that it may be the natural biosynthetic pathway. It has been found to be relevant in connection with quinone (vitamin K) – whose synthetic analogues are used to stimulate blood clotting – and anthraquinone type dyes now used universally. Many other commercial products have been made possible by Alder's work, including drugs, insecticides, lubricating oils, synthetic rubber and plastics. He made a great contribution to synthetic organic chemistry at a time when it was effecting a great transition in industry and science.

**Andrews, Thomas** (*1813–1885*), was an Irish physical chemist, best known for postulating the idea of critical temperature and pressure from his experimental work on the liquefaction of gases, which demonstrated the continuity of the liquid and gaseous states. He also studied heats of chemical combination and was the first to establish the composition of ozone, proving it to be an allotrope of oxygen.

Andrews was born in Belfast on 19 December 1813, the son of a linen merchant. He attended five universities (acting on the advice of a physician friend of his father), beginning at the age of 15 at the University of Glasgow; after only a year there he published two scientific papers. Then in 1830 he went to Paris where, like his contemporary Louis Pasteur (1822–1895), he studied under the French organic chemist Jean Baptiste Dumas. He also became acquainted with several famous scientists of that time, including Joseph Gay-Lussac and Henri Becquerel. He returned to Ireland, but to Trinity College Dublin, and went from there via Belfast to Edinburgh. In 1835 he graduated from Edinburgh as a qualified doctor and surgeon, with a thesis on the circulation and properties of blood.

Even while following his medical studies, Andrews continued to experiment in chemistry, although he declined professorships in that subject at both the Richmond School of Medicine and at the Park Street School of Medicine, Dublin, preferring to devote his time to the private medical practice he had established in Belfast. He did, however, lecture on chemistry for a few hours each week at the Royal Belfast Academical Institution. It was during this time that he began work on a study of the heats of chemical combination, and in 1844 his paper on the thermal changes that accompany the neutralization of acids by bases won him the Medal of the Royal Society (of which he became a Fellow five years later). By this time he was one of the leading scientific figures in the British Isles. In 1845 he was appointed Vice-President designate of the projected Queen's College, Belfast, in order that he might contribute to its foundation and philosophy, and in 1849 he became its Professor of Chemistry. He held both posts until 1879, when ill-health forced his retirement. He died in Belfast six years later, on 26 November 1885.

Andrews' research was concentrated into three

main channels: the heat of chemical combination, ozone, and changes in physical state. He was only one of many mid-nineteenth century investigators of thermochemistry: his Russian contemporary Germain Hess was carrying out similar experiments at St Petersburg. Andrews' chief contribution was the direct determination of heats of neutralization and of formation of halides (chlorides, bromides and iodides), but the law of constant heat summation was finally worked out by and is now named after Hess.

Before Andrews began to study ozone, it was postulated that the gas was either a "compound" of oxygen or that it was an oxide of hydrogen that contained a larger proportion of oxygen than does water. Andrews proved conclusively that ozone is an allotrope of oxygen, that from whatever source it is "one and the same body, having identical properties and the same constitution, and is not a compound body but oxygen in an altered or allotropic condition". Ozone is triatomic, with molecules represented by the formula $O_3$.

Many other scientists had tried to explain the relationship between gases and liquids, but none had really come to grips with the fundamentals. It is for his meticulous experimental work in this area that Andrews is best remembered. He constructed elaborate equipment in which he initially investigated the liquefaction of carbon dioxide, exploring the state of the substance (gas or liquid) over a wide range of temperatures and pressures. By 1869 he had concluded that if carbon dioxide is maintained at any temperature above 30.9°C, it cannot be condensed into a liquid by any pressure no matter how great. This discovery of a
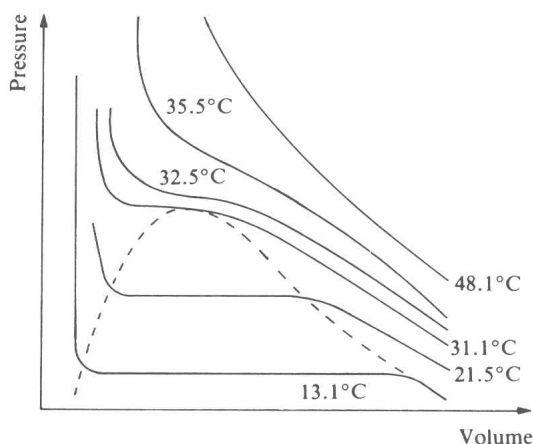


*Pressure-volume isotherms for carbon dioxide. The critical temperature is 30·9°C and the critical pressure 72·8 atmospheres. At temperatures and pressure corresponding to the region under the dotted curve, carbon dioxide is a liquid (the isotherm is a horizontal line).*

critical temperature (or critical point) soon enabled other workers – such as Raoul Pictet (1846–1929) in Geneva and Louis Cailletet (1832–1913) in France, both of whom independently in 1877 liquefied oxygen – to liquefy gases that had previously been thought to be "non-condensible", the so-called permanent gases. Hydrogen, nitrogen and air were also liquefied by applying pressure to the gases once they had been cooled to below their critical temperatures. Andrews also worked out sets of pressure-volume isotherms at temperatures above and below the critical temperature, and brought a sense of order to what had previously been a chaotic branch of physical chemistry.

**Arrhenius, Svante August** (*1859–1927*), was a Swedish physical chemist who first explained that in an electrolyte (a solution of a chemical dissolved in water) the dissolved substance is dissociated into electrically charged ions. The electrolyte conducts electricity because the ions migrate through the solution. Although later modified, Arrhenius' theory of conductivity in solutions has stood the test of time. It was a major contribution to physical chemistry, ultimately acknowledged by the award to Arrhenius of the 1903 Nobel Prize in Chemistry.

Arrhenius was born in Uppsala on 19 February 1859, the son of a surveyor and estate manager who was also a supervisor at the local university. He was a brilliant student, entering Uppsala University at the age of 17 to study chemistry, physics and mathematics. After graduating in 1878, he stayed to write his doctorial thesis, but became dissatisfied with the teaching at Uppsala and went to Stockholm to study solutions and electrolytes under Erik Edlund (1819–1888).

In 1884 he submitted his thesis, which contained the basis of the dissociation theory of electrolytes (although he did not at that time use the term dissociation), together with many other novel theories which aroused only suspicion and doubt in his superiors. The largely theoretical document was not welcomed by the academics, who were devoted experimentalists; Arrhenius later boasted that he had never performed an exact experiment in his life and preferred to take a general view of relationships from the results of many approximate experiments. The thesis (written in French) was awarded only a fourth class, the lowest possible pass, but Arrhenius sent copies of it to several eminent chemists, including Friedrich Wilhelm Ostwald (at Riga), Rudolf Clausius (Bonn), Lothar Meyer (Tübingen) and Jacobus Van't Hoff (Amsterdam). Ostwald's offer to Arrhenius of an academic appointment moderated the scepticism of the Uppsala authorities,

who finally offered him a position and, later, a travelling fellowship. This enabled him to spend some time with other scientists working in the same field, such as Friedrich Kohlrausch and Hermann Nernst at Würzburg, Ludwig Boltzmann at Graz and Jacobus van't Hoff, whose solution theories paralleled that of Arrhenius.

In 1891 Arrhenius was offered a professorship at Giessen in Germany as successor to Justus von Liebig, but he declined in preference for an appointment at the Royal Institute of Technology in Stockholm. Four years later he became professor of physics at a time when his work was attracting the attention of scientists throughout Europe, if not in his native Sweden – his election to the Swedish Academy of Sciences had to wait another six years until 1901 (the same year in which Van't Hoff was awarded the first Nobel Prize in Chemistry). He again declined a German professorship, in Berlin, in 1905 and took instead the specially created post of Director of the Nobel Institute of Physical Chemistry (Stockholm), where he remained until shortly before his death on 2 October 1927.

The Arrhenius theory of electrolytes (1887) is concerned with the formation, number and speed of ions in solution. The key to the theory is the behaviour of the dissolved substance (solute) and the liquid (solvent), both of which are capable of dissociating into ions. It postulates that there is an equilibrium between undissociated solute molecules and its ions, whose movement or migration can conduct an electric current through the solution. Its chief points may be summarized as follows:

(a) An electrolytic solution contains free ions (i.e., dissociation takes place even if no current is passed through the solution).

(b) Conduction of an electric current through such a solution depends on the number and speed of migration of the ions present.

(c) In a weak electrolyte, the degree of ionization (dissociation) increases with increasing dilution.

(d) In a weak electrolyte at infinite dilution, ionization is complete.

(e) In a strong electrolyte, ionization is always incomplete because the ions impede each other's migration; this interference is less in dilute solutions of strong electrolytes.

Apart from (e), regarding strong electrolytes (a difficulty not resolved until the work of Peter Debye and Erich Hückel in the 1920s), Arrhenius' theory is still largely accepted.

In another notable achievement, Arrhenius adapted Van't Hoff's work on the colligative properties of non-electrolyte solutions. He found that solutions of salts, acids and bases – electro-lytes – possess greater osmotic pressures, higher vapour pressures and lower freezing points than Van't Hoff's calculated values but explained the discrepancies in terms of ionic dissociation by taking into account the number of solute ions (as opposed to molecules) present. In 1889 Arrhenius suggested that a molecule will take part in a chemical reaction on collision only if it has a higher than average energy – that is, if it is activated. As a result, the rate of a chemical reaction is proportional to the number of activated molecules (not to the total number of molecules, or concentration) and can be related to the activation energy.

After 1905 Arrhenius widened his research activities. For example, he applied the laws of theoretical chemistry to physiological problems (particularly immunology); once again initial criticism was replaced by universal acceptance. With N. Ekholm he published papers on cosmic physics concerning the Northern Lights, the transport of living matter ("spores") through space from one planet to another, and the climatic changes of the Earth over geological time – pointing out the "greenhouse effect" brought about by carbon dioxide in the atmosphere. Arrhenius became more and more respected by the world of science and was much sought after for meetings, lectures and discussions throughout the world. In his latter years he had to rise at 4 am in order to maintain his scientific activities, and this consistent hard work probably contributed to his death at the age of 68.

**Aston, Francis William** (*1877–1945*), was a British chemist and physicist who developed the mass spectrograph, which he used to study atomic masses and to establish the existence of isotopes. For his unique contribution to analytic chemistry and the study of atomic theory he was awarded the 1922 Nobel Prize in Chemistry.

Aston was born on 1 September 1877 at Harbourne, Birmingham, the son of a merchant. He went to school at Malvern College, where he excelled at mathematics and science, and then to Mason College (which later became the University of Birmingham) to study chemistry. There from 1898 to 1900 he studied optical rotation with P. F. Frankland (1858–1946). Aston then left academic life for three years to work with a firm of brewers, although during his spare time he continued to experiment with discharge tubes. He returned to Mason College in 1903 to study gaseous discharges, before moving in 1909 to the Cavendish Laboratory, Cambridge, where J.J. Thomson was also investigating positive rays from discharge tubes. Thomson and Aston examined the effects of electric and magnetic fields on positive rays, showing that the rays were deflected

– one of the basic principles of the mass spectrograph.

Aston's researches were interrupted by World War I, during which he worked at the Royal Aircraft Establishment, Farnborough, on the treatment of aeroplane fabrics using dopes (lacquers). He escaped injury in 1914 after crashing in an experimental aircraft. After the war he returned to Cambridge and improved his earlier equipment, and the mass spectrograph was born. He went on to refine the instrument and apply it to a study of atomic masses and isotopes. Aston continued to live and work in Cambridge, where he died on 20 November 1945.

Between 1910 and 1913, Thomson and Aston showed that the amount of deflection of positive rays in electric and magnetic fields depends on their mass. The deflected rays were made to reveal their positions by aiming them at a photographic plate. Thomson was seeking evidence for an earlier theory of William Crookes that the non-integral atomic mass of neon (20.2) was caused by the presence of two very similar but different atoms. Each was expected to have a whole-number atomic mass, but their mixture would result in an "average" non-integral value. The Cambridge scientists found that the two paths of deflected positive rays from a neon discharge tube were consistent with atomic masses of 20 and 22. Aston attempted to fractionate neon and in 1913 made a partial separation by repeatedly diffusing the gas through porous pipeclay.

Aston's first improvement to the apparatus, made in 1919, caused the positive-ray deflections by both electric and magnetic fields to be in the same plane. The image produced on the photo-graphic plate became known as a mass spectrum, and the instrument itself as a mass spectrograph.

Its principle is relatively simple. A beam of positive ions is produced by an electric discharge tube (in which a high voltage is passed between electrodes in a glass tube containing rarefied gas), which has holes in its cathode to let the accelerated ions pass through. The beam passes between a pair of electrically charged plates, whose electric field deflects the moving ions according to their charge-to-mass ratio, $e/m$ (where $e$ is the charge on the ion – usually 1 or 2 – and $m$ is its mass). Lighter ions are deflected most, whereas those of largest mass are deflected least. The now separate ion streams then pass through a magnetic field arranged at right-angles to the electric field, which deflects them still further in the same plane. The streams strike a photographic plate, where they expose a series of lines that constitute the mass spectrum. The position of a line depends on the ion's mass, and its intensity depends on the relative abundance of the ion in the original positive-ion beam.

The work with neon established that two spectral lines are produced on the plate, one about nine times darker (on a positive print) than the other. Calculation showed that these correspond to two types of ions of atomic masses 20 and 22. There are nine times as many of the former as of the latter, giving a weighted average atomic mass of about 20.2 (the value originally reported in 1898 by William Ramsay and Morris Travers, the discoverers of neon). Aston stated that there must be two kinds of neon atoms which differ in mass but not in chemical properties, i.e. that naturally occurring neon gas consists of two isotopes.
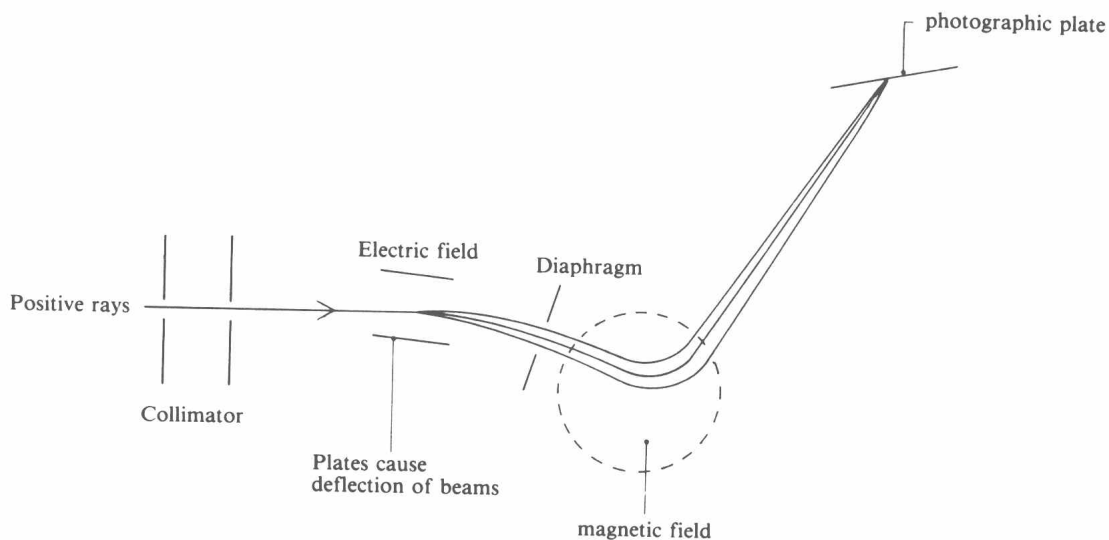


*The principle of Aston's mass spectrograph.*

Over the next few years Aston examined the isotopic composition of more than 50 elements. Most were found to have isotopes – tin has ten – with atomic masses that are whole numbers (integers). In 1920, using the first mass spectrograph, he determined the mass of a hydrogen atom and found it to be 1 per cent greater than a whole number (1.01). (Twelve years later in the United States Harold Urey discovered deuterium, an isotope of hydrogen with mass 2.) With an improved spectrograph, accurate to 1 part in 10,000, Aston confirmed that some other isotopes also show small deviations from the whole-number rule. The slight discrepancy is the packing fraction. (For example, the particles that make up four atoms of hydrogen are the same as those in one atom of helium, but in helium they are "packed" and have 1 per cent less mass. This mass defect is now known to be the source of the thermonuclear energy released during the fusion of hydrogen to form helium.)

Aston's interests also included astronomy, particularly observations of the Sun and its eclipses. His knowledge of photography made him a valuable member of the expeditions that studied eclipses in Sumatra (1925), Canada (1932) and Japan (1936). But Aston will be remembered for his development of the mass spectrograph, which became an essential tool in the study of nuclear physics and later found application in the determination of the structures of organic compounds.

**Avogadro, Amedeo, Conte de Quaregna** (*1776–1856*), was an Italian scientist who shares with his contemporary Claud Berthollet (1748–1822) the honour of being one of the founders of physical chemistry. Although he was a professor of physics, he acknowledged no boundary between physics and chemistry and based most of his findings on a mathematical approach. Principally remembered for the hypothesis subsequently known as Avogadro's Law (which states that, at a given temperature, equal volumes of all gases contain the same number of molecules), he gained no recognition for his achievement during his lifetime. He lived in what was a scientific backwater, with the result that his writings received scant examination or regard from the leading authorities of his day.

Avogadro was born in Turin on 9 June 1776. He began his career in 1796 by obtaining a doctorate in law and for the next three years practised as a lawyer. In 1800 he began to take private lessons in mathematics and physics, made impressive progress and decided to make the natural sciences his vocation. He was appointed as a demonstrator at the Academy of Turin in 1806 and

Professor of Natural Philosophy at the College of Vercelli in 1809, and when in 1820 the first professorship in mathematical physics in Italy was established at Turin, Avogadro was chosen for the post. Because of the political turmoil at that time the position was subsequently abolished, but calmer times permitted its re-establishment in 1832 and two years later Avogadro again held the appointment. He remained at Turin until his retirement in 1850. When he died there on 9 July 1856 his European contemporaries still regarded him as an incorrigibly self-deluding provincial professor of physics.

In 1809 Joseph Gay-Lussac had discovered that all gases, when subjected to an equal rise in temperature, expand by the same amount. Avogadro therefore deduced (and announced in 1811) that at a given temperature all gases must contain the same number of particles per unit volume. He also made it clear that the gas particles need not be individual atoms but might consist of molecules, the term he introduced to describe combinations of atoms. No previous scientists had made this fundamental distinction between the atoms of a substance and its molecules.

Using his hypothesis Avogadro provided the theoretical explanation of Gay-Lussac's law of combining volumes. It had already been observed that the electrolysis of water (to form hydrogen and oxygen) produces twice as much hydrogen (by volume) as oxygen. He reasoned that each molecule of water must contain hydrogen and oxygen atoms in the proportion of 2 to 1. Also, because the oxygen gas collected weighs eight times as much as the hydrogen, oxygen atoms must be 16 times as heavy as hydrogen atoms. It also follows from Avogadro's hypothesis that a molar volume of any substance (i.e., the volume whose mass is one gram molecular weight) contains the same number of molecules. This quantity, now known as Avogadro's number or constant, is equal to $6.02252 \times 10^{23}$.

Leading chemists of the day paid little attention to Avogadro's hypothesis, with the result that the confusion between atoms and molecules and between atomic weights and molecular weights continued for nearly 50 years. In 1858, only two years after Avogadro's death, his fellow Italian Stanislao Cannizzaro showed how the application of Avogadro's hypothesis could solve many of the major problems in chemistry. At the Karlsruhe Chemical Congress of 1860 Avogadro's 1811 paper was read again to a much wider and more receptive audience of distinguished scientists. One of the most impressed was the young German chemist Julius Lothar Meyer. He found this final establishment of order in place of conflicting theories one of the great stimuli that