

# LIVES IN CHEMISTRY

John Scales Avery

November 12, 2019

# INTRODUCTION<sup>1</sup>

## Human history as cultural history

At present, history is taught as though power struggles were its most important aspect. Furthermore, the present teaching of history is an indoctrination in nationalism. We need to reform our teaching of history so that the emphasis will be placed on the gradual growth of human culture and knowledge, a growth to which all nations and ethnic groups have contributed.

This book is part of a series on cultural history. Here is a list of the other books in the series that have, until now, been completed:

- Lives in Medicine
- Lives in Ecology
- Lives in Physics
- Lives in Economics
- Lives in the Peace Movement

The pdf files of these books may be freely downloaded and circulated from the following web address:

<http://eacpe.org/about-john-scales-avery/>

## Culture, education, solidarity and sustainability

Cultural and educational activities have a small ecological footprint, and therefore are more sustainable than pollution-producing, fossil-fuel-using jobs in industry. Furthermore, since culture and knowledge are shared among all nations, work in culture and education leads societies naturally towards internationalism and peace.

Economies based on a high level of consumption of material goods are unsustainable and will have to be abandoned by a future world that renounces the use of fossil fuels in order to avoid catastrophic climate change, a world where non-renewable resources such as metals will become increasingly rare and expensive. How then can full employment be maintained?

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<sup>1</sup>This book makes some use of my previously published book chapters and articles, but most of the material is new.

The creation of renewable energy infrastructure will provide work for a large number of people; but in addition, sustainable economies of the future will need to shift many workers from jobs in industry to jobs in the service sector. Within the service sector, jobs in culture and education are particularly valuable because they will help to avoid the disastrous wars that are currently producing enormous human suffering and millions of refugees, wars that threaten to escalate into an all-destroying global thermonuclear war.<sup>2</sup>

Nor is a truly sustainable economic system utopian or impossible. To achieve it, we should begin by shifting jobs to the creation of renewable energy infrastructure, and to the fields of culture and education. By so doing we will support human solidarity and avoid the twin disasters of catastrophic war and climate change.

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<sup>2</sup><http://www.fredsakademiet.dk/library/need.pdf>  
<http://eruditio.worldacademy.org/issue-5/article/urgent-need-renewable-energy>



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# Chapter 1

## THE INVENTION OF METALLURGY

### 1.1 The first use of fire

#### The first chemical reaction controlled by humans

The control of fire marks an extremely important step in human cultural evolution. It allowed prehuman species such as *Homo erectus* to extend their range to colder climates, and it later led to the discovery of pottery and metallurgy. Chemical reactions that do not take place at room temperatures, often do so at higher temperatures, and thus fire was the key that unlocked all of chemistry.

The first use of fire is believed to have taken place roughly a million years ago. However, the invention of pottery was much more recent. The first known pottery artifacts are the Gravettian figurines that are believed to be from 29,000 to 25,000 BC. Metallurgy probably evolved from the use of minerals containing oxides of copper to decorate pottery, as is discussed below.

#### *Homo erectus*

The first fossil remains of *H. erectus* were discovered in Sumatra in 1857 by the young Dutch physician, Eugène Dubois. Most paleoanthropologists believe that *H. erectus* evolved in Africa, and was the first hominin to leave that continent, during a period when the climates of Africa and the Middle East were more favorable to migration than they later became. However, there is a minority school of thought that maintains that *H. erectus* evolved in Asia. In any case the species survived in Asia until only 143,000 years before the present, and was able to use fire.



Figure 1.1: Fire is was the first chemical reaction that humans were able to use. The first use of fire by species related to humans occurred roughly a million years ago, but the chemistry of combustion was not properly understood until the time of Lavoisier. Neolithic human use of fire led to the inventions of pottery and metallurgy.



Figure 1.2: A diorama showing *Homo erectus*, the earliest human species that is known to have controlled fire.

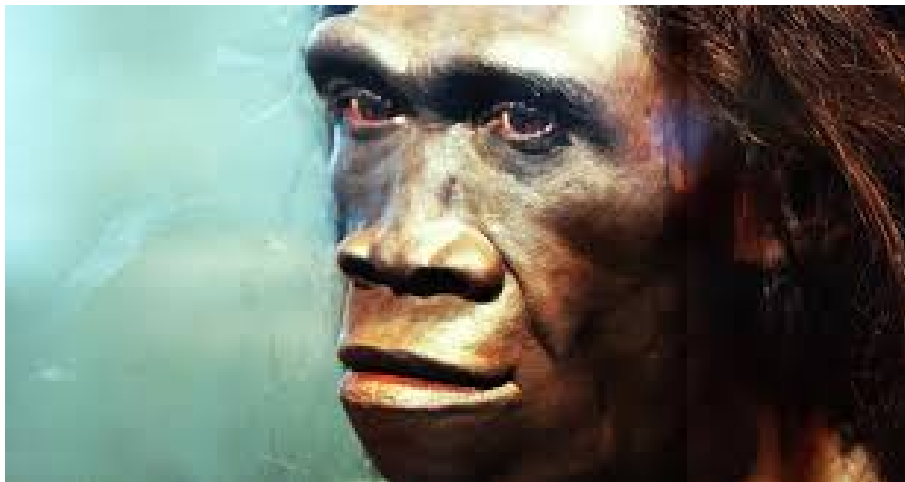


Figure 1.3: *Homo erectus* left Africa, and spread throughout Eurasia, as far as Georgia, Armenia, India, Sri Lanka, China and Indonesia.



Figure 1.4: **Homo erectus** using fire.

## 1.2 Pottery

Pottery was invented during the neolithic period, with the first known artifacts dating from 29,000-25,000 BC. Early pottery was fired at low temperatures ( $600^{\circ}\text{C}$ ). Vessels produced at these low firing temperatures were porous, and therefore not suitable for the storage of liquids. Later, higher temperatures were achieved, and glazes made ceramics impervious to liquids. Stoneware is fired at  $1,100\text{-}1,200^{\circ}\text{C}$ , and it is very hard and impervious to liquids.

### Chinese porcelain

In China, techniques were developed for achieving very high kiln temperatures. Porcelain is fired at  $1,200\text{-}1,400^{\circ}\text{C}$ , and kaolin is included in the mixture being fired. This produces the vitrification and semi-transparency that are characteristic of porcelain ceramics.

For many years, China retained a monopoly on the lucrative production and trade of high-quality porcelain objects. However, both Japan and Europe later discovered the secrets of porcelain manufacture, and their products began to compete with imports from China.



Figure 1.5: Earliest known ceramics are the Gravettian figurines that date to 29,000 to 25,000 BC.



Figure 1.6: Xianrendong cave pottery fragments, radiocarbon dated to circa 20,000 BP. China.



Figure 1.7: A black pottery cooking cauldron from the Hemudu culture (c. 5000 - c. 3000 BC), China.



Figure 1.8: Greek red-figure vase in the krater shape, between 470 and 460 BC, by the Altamura Painter



Figure 1.9: A Ming Dynasty blue and white porcelain dish.

## 1.3 Early metallurgy in Asia Minor

Whatever the ancient civilizations of the Near East knew about chemistry and metallurgy, they probably learned as “spin-off” from their pottery industry. In the Paleolithic and neolithic phases of their culture, like people everywhere in the world, they found lumps of native gold, native copper and meteoric iron, which they hammered into necklaces, bracelets, rings, implements and weapons. In the course of time, however, after settled communities had been established in the Near East for several thousand years, it became much more rare to find a nugget of gold or metallic copper.

Although the exact date and place are uncertain, it is likely that the first true metallurgy, the production of metallic copper from copper oxide and copper carbonate ores, began about 3,500 B.C. in a region of eastern Anatolia rich in deposits of these ores. It is very probable that the discovery was made because colored stones were sometimes used to decorate pottery. When stones consisting of copper oxide or copper carbonate are heated to the very high temperatures of a stone-ware pottery kiln in a reducing atmosphere, metallic copper is produced.

Imagine a potter who has made this discovery - who has found that he can produce a very rare and valuable metal from an abundant colored stone: He will abandon pottery and go into full-scale production as a metallurgist. He will try all sorts of other colored stones to see what he can make from them. He will also try to keep his methods secret, exaggerating their miraculous character, and he will try to keep a monopoly on the process. Such was probably the beginning of metallurgy!

However, it is impossible to keep a good thing secret for long. Knowledge of smelting and refining copper spread eastward along the mountain chain to Khorassan and Bukhara, and from there southward to Baluchistan, whose mines supplied copper to the peoples of the Indus valley. Also, from Bukhara, metallurgy spread northeast through the Kizil Kum desert to the ancestors of the Shang tribe inhabiting the Yellow River valley in China.

By 3,000 B.C., Sumer, Egypt and Cyprus also had adopted metallurgy and had even discovered secret methods of their own. Egypt obtained its copper ores from mines in Sinai, while Sumer imported ore from Oman. The use of the Oman copper ores was fortunate for the Sumerians, because these ores contain as much as fourteen percent tin and two percent nickel, so that the metal produced by reducing them is natural bronze, whose properties are much more desirable than those of copper. The demand for bronze continued even after the Oman ores were exhausted, and eventually it was discovered that bronze could be produced artificially by adding tin and nickel to copper.



Figure 1.10: Gui bronze vessel from ancient China.

## 1.4 Iron

Meteoric iron was used to make daggers by the ancient Egyptians. However, the discovery that iron could be made from ores by heating iron ores in a reducing atmosphere came later, and ushered in the era that has come to be known as the Iron Age. It is thought that the first refinement of metallic iron from ores was achieved in South Asia and in the ancient Near East in about 1200 BC. Later, the technique spread to the Aegean region (1190 BC), the Balkans (1100 BC), Central Europe and Britain (800 BC), and Northern Europe (500 BC).

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## Chapter 2

# LEUCIPPIUS, DEMOCRATES AND EPICURIUS

### 2.1 The atomists

In the 5th century B.C. there was a great deal of discussion among the Greek philosophers about whether there is anything permanent in the universe. Heraclitus (540 B.C. - 475 B.C.) maintained that *everything* is in a state of flux. Parmenides (540 B.C. - c. 470 B.C.) maintained that on the contrary *nothing* changes - that all change is illusory. Leucippus (490 B.C. - c. 420 B.C.) and his student Democritus (470 B.C. - c. 380 B.C.), by a lucky chance, hit on what a modern scientist would regard as very nearly the correct answer.

According to Democritus, if we cut an apple in half, and then cut the half into parts, and keep on in this way for long enough, we will eventually come down to pieces which cannot be further subdivided. Democritus called these ultimate building blocks of matter “atoms”, which means “indivisible”. He visualized the spaces between the atoms as being empty, and he thought that when a knife cuts an apple, the sharp edge of the blade fits into the empty spaces between the atoms and forces them apart.

Democritus believed that each atom is unchanged in the processes which we observe with our senses, where matter seems to change its form. However, he believed that the atoms are in a state of constant motion, and that they can combine with each other in various ways, thus producing the physical and chemical changes which we observe in nature. In other words, each atom is in itself eternal, but the way in which the atoms combine with each other is in a state of constant flux because of the motion of the atoms.

This is very nearly the same answer which we would give today to the question of which things in the universe are permanent and which change. Of course, the objects which we call “atoms” *can* be further subdivided, but if Democritus were living today he would say that we have merely made the mistake of calling the wrong things “atoms”. We should really apply the word to fundamental particles such as quarks, which cannot be further subdivided.

In discussing which things in the universe are permanent and which change, we would

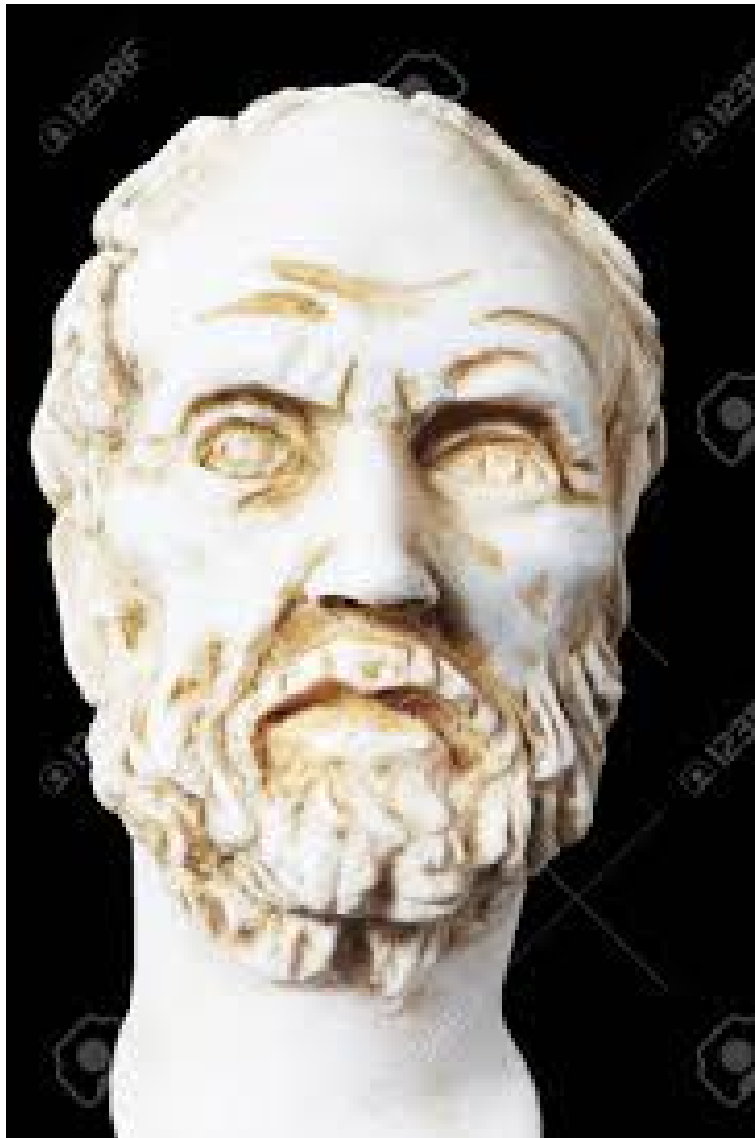


Figure 2.1: **Democratus** (c. 460-370 BC).

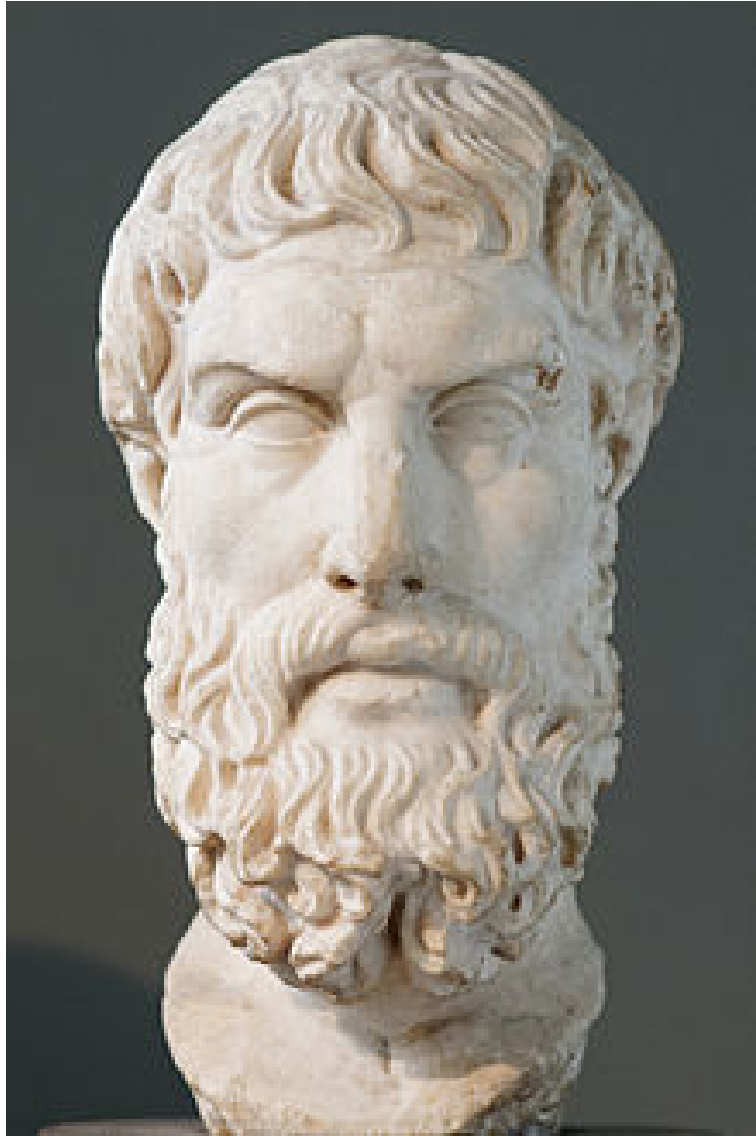


Figure 2.2: Epicurius (341-270 BC) made the atomic ideas of Democratus the cornerstone of his philosophy.

also add, from our modern point of view, that the fundamental laws of the universe are permanent. In following these unchanging laws, matter and energy constantly alter their configuration, but the basic laws of nature remain invariant. For example, the configuration of the planets changes constantly, but these constant changes are governed by Newton's laws of motion, which are eternal.

Of the various ancient philosophers, Democritus is the one who comes closest to our modern viewpoint. However, the ideas of Democritus, like those of Anaxagoras, were too advanced for his contemporaries. Although Democritus was not actually thrown into prison for his beliefs, they aroused considerable hostility. According to Diogenes Laertius, Plato dislike the ideas of Democritus so much that he wished that all of his books could be burned. (Plato had his wish! None of the seventy-two books of Democritus has survived.) Aristotle also argued against atomism, and because of the enormous authority which was attached to Aristotle's opinions, atomism almost disappeared from western thought until the time of John Dalton (1766 - 1844)

## 2.2 De Natura Rerum

That the ideas of Democritus did not disappear entirely was due to the influence of Epicurus (341 B.C. - 270 B.C.), who made mechanism and atomism the cornerstones of his philosophy. The Roman poet Lucretius (95 B.C. - 55 B.C.) expounded the philosophy of Epicurus in a long poem called *De Natura Rerum* (On the Nature of Things). During the middle ages, this poem disappeared completely, but in 1417, a single surviving manuscript was discovered. The poem was then published, using Gutenberg's newly-invented printing press, and it became extremely popular. Thus, the idea of atoms was not entirely lost, and after being revived by John Dalton, it became one of the cornerstones of modern science.

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# Chapter 3

## PAPER AND PRINTING

### The importance of paper and printing

The key inventions of ink, paper and printing are of great importance in the history of human cultural development. Although first invented in China, printing with movable type had a decisive impact, not on China, but on Europe, where printing enabled the rapid and wide diffusion of knowledge needed for the Scientific Revolution, of which the Chemical Revolution was a part.

### 3.1 Civilizations of the east

After the fall of Rome in the 5th century A.D., Europe became a culturally backward area. However, the great civilizations of Asia and the Middle East continued to flourish, and it was through contact with these civilizations that science was reborn in the west.

During the dark ages of Europe, a particularly high level of civilization existed in China. The art of working in bronze was developed in China during the Shang dynasty (1,500 B.C. - 1,100 B.C.) and it reached a high pitch of excellence in the Chou dynasty (1,100 B.C. - 250 B.C.).

In the Chou period, many of the cultural characteristics which we recognize as particularly Chinese were developed. During this period, the Chinese evolved a code of behavior based on politeness and ethics. Much of this code of behavior is derived from the teachings of K'ung Fu-tzu (Confucius), a philosopher and government official who lived between 551 B.C. and 479 B.C.. In his writings about ethics and politics, K'ung Fu-tzu advocated respect for tradition and authority, and the effect of his teaching was to strengthen the conservative tendencies in Chinese civilization. He was not a religious leader, but a moral and political philosopher, like the philosophers of ancient Greece. He is traditionally given credit for the compilation of the Five Classics of Chinese Literature, which include books of history, philosophy and poetry, together with rules for religious ceremonies.

The rational teachings of K'ung Fu-tzu were complemented by the more mystical and intuitive doctrines of Lao-tzu and his followers. Lao-tzu lived at about the same time as



Figure 3.1: A painting of K'ung Fu-tzu (551 B.C.- 479 B.C.).

K'ung Fu-tzu, and he founded the Taoist religion. The Taoists believed that unity with nature could be achieved by passively blending oneself with the forces of nature.

On the whole, politicians and scholars followed the practical teachings of K'ung Fu-tzu, while poets and artists became Taoists. The intuitive sensitivity to nature inspired by Taoist beliefs allowed these artists and poets to achieve literature and art of unusual vividness and force with great economy of means. The Taoist religion has much in common with Buddhism, and its existence in China paved the way for the spread of Buddhism from India to China and Japan.

From 800 B.C. onwards, the central authority of the Chou dynasty weakened, and China was ruled by local landlords. This period of disunity was ended in 246 B.C. by Shih Huang Ti, a chieftain from the small northern state of Ch'in, who became the first real emperor of China. (In fact, China derives its name from the state of Ch'in).

Shih Huang Ti was an effective but ruthless ruler. It was during his reign (246 B.C. -210 B.C.) that the great wall of China was built. This wall, built to protect China from the savage attacks of the mounted Mongolian hordes, is one of the wonders of the world. It runs 1,400 miles, over all kinds of terrain, marking a rainfall boundary between the rich agricultural land to the south and the arid steppes to the north.

In most places, the great wall is 25 feet high and 15 feet thick. To complete this fantastic building project, Shih Huang Ti carried absolutism to great extremes, uprooting thousands of families and transporting them to the comfortless north to work on the wall. He burned all the copies of the Confucian classics which he could find, since his opponents quoted these classics to show that his absolutism had exceeded proper bounds.

Soon after the death of Shih Huang Ti, there was a popular reaction to the harshness of his government, and Shih's heirs were overthrown. However, Shih Huang Ti's unification of China endured, although the Ch'in dynasty (250 B.C. - 202 B.C.) was replaced by the Han dynasty (202 B.C. -220 A.D.). The Han emperors extended the boundaries of China to the west into Turkistan, and thus a trade route was opened, through which China exported silk to Persia and Rome.

During the Han period, China was quite receptive to foreign ideas, and was much influenced by the civilization of India. For example, the Chinese pagoda was inspired by the Buddhist shrines of India. The Han emperors adopted Confucianism as the official philosophy of China, and they had the Confucian classics recopied in large numbers. The invention of paper at the end of the first century A.D. facilitated this project, and it greatly stimulated scholarship and literature.

The Han emperors honored scholarship and, in accordance with the political ideas of K'ung Fu-tzu, they made scholarship a means of access to high governmental positions. During the Han dynasty, the imperial government carried through many large-scale irrigation and flood-control projects. These projects were very successful. They increased the food production of China, and gave much prestige to the imperial government.

Like the Roman Empire, the Han dynasty was ended by attacks of barbarians from the north. However, the Huns who overran northern China in 220 A.D. were quicker to adopt civilization than were the tribes which conquered Rome. Also, in the south, the Chinese remained independent; and therefore the dark ages of China were shorter than the

European dark ages.

In 581 A.D., China was reunited under the Sui dynasty, whose emperors expelled most of the Huns, built a system of roads and canals, and constructed huge granaries for the prevention of famine. These were worthwhile projects, but in order to accomplish them, the Sui emperors used very harsh methods. The result was that their dynasty was soon overthrown and replaced by the T'ang dynasty (618 A.D. - 906 A.D.).

The T'ang period was a brilliant one for China. Just as Europe was sinking further and further into a mire of superstition, ignorance and bloodshed, China entered a period of peace, creativity and culture. During this period, China included Turkistan, northern Indochina and Korea. The T'ang emperors re-established and strengthened the system of civil-service examinations which had been initiated during the Han dynasty.

## 3.2 Ink, paper and printing

It was during the T'ang period that the Chinese made an invention of immense importance to the cultural evolution of mankind. This was the invention of printing. Together with writing, printing is one of the key inventions which form the basis of human cultural evolution.

Printing was invented in China in the 8th or 9th century A.D., probably by Buddhist monks who were interested in producing many copies of the sacred texts which they had translated from Sanskrit. The act of reproducing prayers was also considered to be meritorious by the Buddhists.

The Chinese had for a long time followed the custom of brushing engraved official seals with ink and using them to stamp documents. The type of ink which they used was made from lamp-black, water and binder. In fact, it was what we now call "India ink". However, in spite of its name, India ink is a Chinese invention, which later spread to India, and from there to Europe.

We mentioned that paper of the type which we now use was invented in China in the first century A.D.. Thus, the Buddhist monks of China had all the elements which they needed to make printing practical: They had good ink, cheap, smooth paper, and the tradition of stamping documents with ink-covered engraved seals. The first block prints which they produced date from the 8th century A.D.. They were made by carving a block of wood the size of a printed page so that raised characters remained, brushing ink onto the block, and pressing this onto a sheet of paper.

The oldest known printed book, the "Diamond Sutra", is dated 868 A.D., and it consists of only six printed pages. It was discovered in 1907 by an English scholar who obtained permission from Buddhist monks in Chinese Turkistan to open some walled-up monastery rooms, which were said to have been sealed for 900 years. The rooms were found to contain a library of about 15,000 manuscripts, among which was the Diamond Sutra.

Block printing spread quickly throughout China, and also reached Japan, where wood-block printing ultimately reached great heights in the work of such artists as Hiroshige

and Hokusai. The Chinese made some early experiments with movable type, but movable type never became popular in China, because the Chinese written language contains 10,000 characters. However, printing with movable type was highly successful in Korea as early as the 15th century A.D..

The unsuitability of the Chinese written language for the use of movable type was the greatest tragedy of the Chinese civilization. Writing had been developed at a very early stage in Chinese history, but the system remained a pictographic system, with a different character for each word. A phonetic system of writing was never developed.

The failure to develop a phonetic system of writing had its roots in the Chinese imperial system of government. The Chinese empire formed a vast area in which many different languages were spoken. It was necessary to have a universal language of some kind in order to govern such an empire. The Chinese written language solved this problem admirably.

Suppose that the emperor sent identical letters to two officials in different districts. Reading the letters aloud, the officials might use entirely different words, although the characters in the letters were the same. Thus the Chinese written language was a sort of “Esperanto” which allowed communication between various language groups, and its usefulness as such prevented its replacement by a phonetic system.

The disadvantages of the Chinese system of writing were twofold: First, it was difficult to learn to read and write; and therefore literacy was confined to a small social class whose members could afford a prolonged education. The system of civil-service examinations made participation in the government dependant on a high degree of literacy; and hence the old, established scholar-gentry families maintained a long-term monopoly on power, wealth and education. Social mobility was possible in theory, since the civil service examinations were open to all, but in practice, it was nearly unattainable.

The second great disadvantage of the Chinese system of writing was that it was unsuitable for printing with movable type. An “information explosion” occurred in the west following the introduction of printing with movable type, but this never occurred in China. It is ironical that although both paper and printing were invented by the Chinese, the full effect of these immensely important inventions bypassed China and instead revolutionized the west.

The invention of block printing during the T’ang dynasty had an enormously stimulating effect on literature, and the T’ang period is regarded as the golden age of Chinese lyric poetry. A collection of T’ang poetry, compiled in the 18th century, contains 48,900 poems by more than 2,000 poets.

The technique of producing fine ceramics from porcelain was invented during the T’ang dynasty; and the art of making porcelain reached its highest point in the Sung dynasty (960-1279), which followed the T’ang period. During the Sung dynasty, Chinese landscape painting also reached a high degree of perfection. In this period, the Chinese began to use the magnetic compass for navigation.

The first Chinese text clearly describing the magnetic compass dates from 1088 A.D.. However, the compass is thought to have been invented in China at a very much earlier date. The original Chinese compass was a spoon carved from lodestone, which revolved on a smooth diviner’s board. The historian Joseph Needham believes that sometime between

the 1st and 6th centuries A.D. it was discovered in China that the directive property of the lodestone could be transferred to small iron needles. These could be placed on bits of wood and floated in water. It is thought that by the beginning of the Sung dynasty, the Chinese were also aware of the deviation of the magnetic north from the true geographical north. By 1190 A.D., knowledge of the compass had spread to the west, where it revolutionized navigation and led to the great voyages of discovery which characterized the 15th century.

The Sung dynasty was followed by a period during which China was ruled by the Mongols (1279-1328). Among the Mongol emperors was the famous Kublai Khan, grandson of Genghis Khan. He was an intelligent and capable ruler who appreciated Chinese civilization and sponsored many cultural projects. It was during the Mongol period that Chinese drama and fiction were perfected. During this period, the Mongols ruled not only China, but also southern Russia and Siberia, central Asia and Persia. They were friendly towards Europeans, and their control of the entire route across Asia opened direct contacts between China and the west.

Among the first Europeans to take advantage of this newly-opened route were a family of Venetian merchants called Polo. After spending four years crossing central Asia and the terrible Gobi desert, they reached China in 1279. They were warmly welcomed by Kublai Khan, who invited them to his summer palace at Shangtu ("Xanadu"). The Great Khan took special interest in Marco Polo, a young man of the family who had accompanied his uncles Nicolo and Maffeo on the journey. Marco remained in China for seventeen years as a trusted diplomat in the service of Kublai Khan.

Later, after returning to Italy, Marco Polo took part in a war between Venice and Genoa. He was captured by the Genoese, and while in prison he dictated the story of his adventures to a fellow prisoner who happened to be a skilful author of romances. The result was a colorful and readable book which helped to reawaken the west after the middle ages. The era of exploration which followed the middle ages was partly inspired by Marco Polo's book. (Columbus owned a copy and made enthusiastic notes in the margins!) In his book, Marco Polo describes the fabulous wealth of China, as well as Chinese use of paper money, coal and asbestos.

Other Chinese inventions which were transmitted to the west include metallurgical blowing engines operated by water power, the rotary fan and rotary winnowing machine, the piston bellows, the draw-loom, the wheel-barrow, efficient harnesses for draught animals, the cross bow, the kite, the technique of deep drilling, cast iron, the iron-chain suspension bridge, canal lock-gates, the stern-post rudder and gunpowder. Like paper, printing and the magnetic compass, gunpowder and its use in warfare were destined to have an enormous social and political impact.



Figure 3.2: A painting of Marco Polo dressed as a Tartar.

## India

Evidence of a very early river-valley civilization in India has been found at a site called Mohenjo-Daro. However, in about 2,500 B.C., this early civilization was destroyed by some great disaster, perhaps a series of floods; and for the next thousand years, little is known about the history of India. During this dark period between 2,500 B.C. and 1,500 B.C., India was invaded by the Indo-Aryans, who spoke Sanskrit, a language related to Greek. The Indo-Aryans partly drove out and partly enslaved the smaller and darker native Dravidians. However, there was much intermarriage between the groups, and to prevent further intermarriage, the Indo-Aryans introduced a caste system sanctioned by religion.

According to Hindu religious belief, the soul of a person who has died is reborn in another body. If, throughout his life, the person has faithfully performed the duties of his caste, then his or her soul may be reborn into a higher caste. Finally, after existing as a Brahman, the soul may be so purified that it can be released from the cycle of death and rebirth.

In the 6th century B.C., Gautama Buddha founded a new religion in India. Gautama Buddha was convinced that all the troubles of humankind spring from attachment to earthly things. He felt that the only escape from sorrow is through the renunciation of earthly desires. He also urged his disciples to follow a high ethical code, the Eightfold Way. Among the sayings of Buddha are the following:

“Hatred does not cease by hatred at any time; hatred ceases by love.”

“Let a man overcome anger by love; let him overcome evil by good.”

“All men tremble at punishment. All men love life. Remember that you are like them, and do not cause slaughter.”

One of the early converts to Buddhism was the emperor Asoka Maura, who reigned in India between 273 B.C. and 232 B.C.. During one of his wars of conquest, Asoka Maura became so sickened by the slaughter that he resolved never again to use war as an instrument of policy. He became one of the most humane rulers in history, and he also did much to promote the spread of Buddhism throughout Asia.

Under the Mauryan dynasty (322 B.C. - 184 B.C.), the Gupta dynasty (320 B.C. - 500 A.D.) and also under the rajah Harsha (606 A.D. - 647 A.D.), India had periods of unity, peace and prosperity. At other times, the country was divided and upset by internal wars. The Gupta period especially is regarded as the golden age of India's classical past. During this period, India led the world in such fields as medicine and mathematics.

The Guptas established both universities and hospitals. According to the Chinese Buddhist pilgrim, Fa-Hsien, who visited India in 405 A.D., “The nobles and householders have founded hospitals within the city to which the poor of all countries, the destitute, crippled and diseased may go. They receive every kind of help without payment.”

Indian doctors were trained in cleansing wounds, in using ointments and in surgery. They also developed antidotes for poisons and for snakebite, and they knew some techniques for the prevention of disease through vaccination.

When they had completed their training, medical students in India took an oath, which resembled the Hippocratic oath: “Not for yourself, not for the fulfillment of any earthly

desire or gain, but solely for the good of suffering humanity should you treat your patients.”

In Indian mathematics, algebra and trigonometry were especially highly developed. For example, the astronomer Brahmagupta (598 A.D. - 660 A.D.) applied algebraic methods to astronomical problems. The notation for zero and the decimal system were invented in India, probably during the 8th or 9th century A.D.. These mathematical techniques were later transmitted to Europe by the Arabs.

Many Indian techniques of manufacture were also transmitted to the west by the Arabs. Textile manufacture in particular was highly developed in India, and the Arabs, who were the middlemen in the trade with the west, learned to duplicate some of the most famous kinds of cloth. One kind of textile which they copied was called “quttan” by the Arabs, a word which in English has become “cotton”. Other Indian textiles included cashmere (Kashmir), chintz and calico (from Calcutta, which was once called Calicut). Muslin derives its name from Mosul, an Arab city where it was manufactured, while damask was made in Damascus.

Indian mining and metallurgy were also highly developed. The Europeans of the middle ages prized fine laminated steel from Damascus; but it was not in Damascus that the technique of making steel originated. The Arabs learned steel-making from the Persians, and Persia learned it from India.

After the burning of the great library at Alexandria and the destruction of Hellenistic civilization, most of the books of the classical Greek and Hellenistic philosophers were lost. However, a few of these books survived and were translated from Greek, first into Syriac, then into Arabic and finally from Arabic into Latin. By this roundabout route, fragments from the wreck of the classical Greek and Hellenistic civilizations drifted back into the consciousness of the west.

We mentioned that the Roman empire was ended in the 5th century A.D. by attacks of barbaric Germanic tribes from northern Europe. However, by that time, the Roman empire had split into two halves. The eastern half, with its capital at Byzantium (Constantinople), survived until 1453, when the last emperor was killed vainly defending the walls of his city against the Turks.

The Byzantine empire included many Syriac-speaking subjects; and in fact, beginning in the 3rd century A.D., Syriac replaced Greek as the major language of western Asia. In the 5th century A.D., there was a split in the Christian church of Byzantium; and the Nestorian church, separated from the official Byzantine church. The Nestorians were bitterly persecuted by the Byzantines, and therefore they migrated, first to Mesopotamia, and later to south-west Persia. (Some Nestorians migrated as far as China.)

During the early part of the middle ages, the Nestorian capital at Gondisapur was a great center of intellectual activity. The works of Plato, Aristotle, Hippocrates, Euclid, Archimedes, Ptolemy, Hero and Galen were translated into Syriac by Nestorian scholars, who had brought these books with them from Byzantium.

Among the most distinguished of the Nestorian translators were the members of a family called Bukht-Yishu (meaning “Jesus hath delivered”), which produced seven generations of outstanding scholars. Members of this family were fluent not only in Greek and Syriac, but also in Arabic and Persian.

In the 7th century A.D., the Islamic religion suddenly emerged as a conquering and proselytizing force. Inspired by the teachings of Mohammad (570 A.D. - 632 A.D.), the Arabs and their converts rapidly conquered western Asia, northern Africa, and Spain. During the initial stages of the conquest, the Islamic religion inspired a fanaticism in its followers which was often hostile to learning. However, this initial fanaticism quickly changed to an appreciation of the ancient cultures of the conquered territories; and during the middle ages, the Islamic world reached a very high level of culture and civilization.

Thus, while the century from 750 to 850 was primarily a period of translation from Greek to Syriac, the century from 850 to 950 was a period of translation from Syriac to Arabic. It was during this latter century that Yuhanna Ibn Masawiah (a member of the Bukht-Yishu family, and medical advisor to Caliph Harun al-Rashid) produced many important translations into Arabic.

The skill of the physicians of the Bukht-Yishu family convinced the Caliphs of the value of Greek learning; and in this way the family played an extremely important role in the preservation of the western cultural heritage. Caliph al-Mamun, the son of Harun al-Rashid, established at Baghdad a library and a school for translation, and soon Baghdad replaced Gondisapur as a center of learning.

The English word "chemistry" is derived from the Arabic words "*al-chimia*", which mean "the changing". The earliest alchemical writer in Arabic was Jabir (760-815), a friend of Harun al-Rashid. Much of his writing deals with the occult, but mixed with this is a certain amount of real chemical knowledge. For example, in his *Book of Properties*, Jabir gives the following recipe for making what we now call lead hydroxycarbonate (white lead), which is used in painting and pottery glazes:

"Take a pound of litharge, powder it well and heat it gently with four pounds of vinegar until the latter is reduced to half its original volume. Then take a pound of soda and heat it with four pounds of fresh water until the volume of the latter is halved. Filter the two solutions until they are quite clear, and then gradually add the solution of soda to that of the litharge. A white substance is formed, which settles to the bottom. Pour off the supernatant water, and leave the residue to dry. It will become a salt as white as snow."

Another important alchemical writer was Rhazes (c. 860 - c. 950). He was born in the ancient city of Ray, near Teheran, and his name means "the man from Ray". Rhazes studied medicine in Baghdad, and he became chief physician at the hospital there. He wrote the first accurate descriptions of smallpox and measles, and his medical writings include methods for setting broken bones with casts made from plaster of Paris. Rhazes was the first person to classify substances into vegetable, animal and mineral. The word "*al-kali*", which appears in his writings, means "the calcined" in Arabic. It is the source of our word "alkali", as well as of the symbol K for potassium.

The greatest physician of the middle ages, Avicenna, (Abu-Ali al Hussain Ibn Abdullah Ibn Sina, 980-1037), was also a Persian, like Rhazes. More than a hundred books are attributed to him. They were translated into Latin in the 12th century, and they were among the most important medical books used in Europe until the time of Harvey. Avicenna also wrote on alchemy, and he is important for having denied the possibility of transmutation of elements.



Figure 3.3: In mathematics, one of the most outstanding Arabic writers was al-Khwarizmi (c.780 - c.850), commemorated here on a Russian stamp.

In mathematics, one of the most outstanding Arabic writers was al-Khwarizmi (c. 780 - c. 850). The title of his book, *Ilm al-jabr wa'd muqabalah*, is the source of the English word "algebra". In Arabic *al-jabr* means "the equating". Al-Khwarizmi's name has also become an English word, "algorism", the old word for arithmetic. Al-Khwarizmi drew from both Greek and Hindu sources, and through his writings the decimal system and the use of zero were transmitted to the west.

One of the outstanding Arabic physicists was al-Hazen (965-1038). He made the mistake of claiming to be able to construct a machine which could regulate the flooding of the Nile. This claim won him a position in the service of the Egyptian Caliph, al-Hakim. However, as al-Hazen observed Caliph al-Hakim in action, he began to realize that if he did not construct his machine *immediately*, he was likely to pay with his life! This led al-Hazen to the rather desperate measure of pretending to be insane, a ruse which he kept up for many years. Meanwhile he did excellent work in optics, and in this field he went far beyond anything done by the Greeks.

Al-Hazen studied the reflection of light by the atmosphere, an effect which makes the stars appear displaced from their true positions when they are near the horizon; and he calculated the height of the atmospheric layer above the earth to be about ten miles. He also studied the rainbow, the halo, and the reflection of light from spherical and parabolic mirrors. In his book, *On the Burning Sphere*, he shows a deep understanding of the properties of convex lenses. Al-Hazen also used a dark room with a pin-hole opening to study the image of the sun during an eclipse. This is the first mention of the *camera obscura*, and it is perhaps correct to attribute the invention of the *camera obscura* to al-Hazen.

Another Islamic philosopher who had great influence on western thought was Averröes, who lived in Spain from 1126 to 1198. His writings took the form of thoughtful commentaries on the works of Aristotle. He shocked both his Moslem and his Christian readers by maintaining that the world was not created at a definite instant, but that it instead evolved over a long period of time, and is still evolving.

Like Aristotle, Averröes seems to have been groping towards the ideas of evolution which were later developed in geology by Steno, Hutton and Lyell and in biology by Darwin and Wallace. Much of the scholastic philosophy which developed at the University of Paris during the 13th century was aimed at refuting the doctrines of Averröes; but nevertheless, his ideas survived and helped to shape the modern picture of the world.



Figure 3.4: **Paper is a Chinese invention**



Figure 3.5: Italian paper-mill, probably from the 16th century.



Figure 3.6: The Diamond Sutra, 868 A.D., is the first known printed book.

### 3.3 Islamic civilization and printing

#### Some Islamic contributions to civilization

In the 5th century A.D., there was a split in the Christian church of Byzantium; and the Nestorian church, separated from the official Byzantine church. The Nestorians were bitterly persecuted by the Byzantines, and therefore they migrated, first to Mesopotamia, and later to south-west Persia. (Some Nestorians migrated as far as China.)

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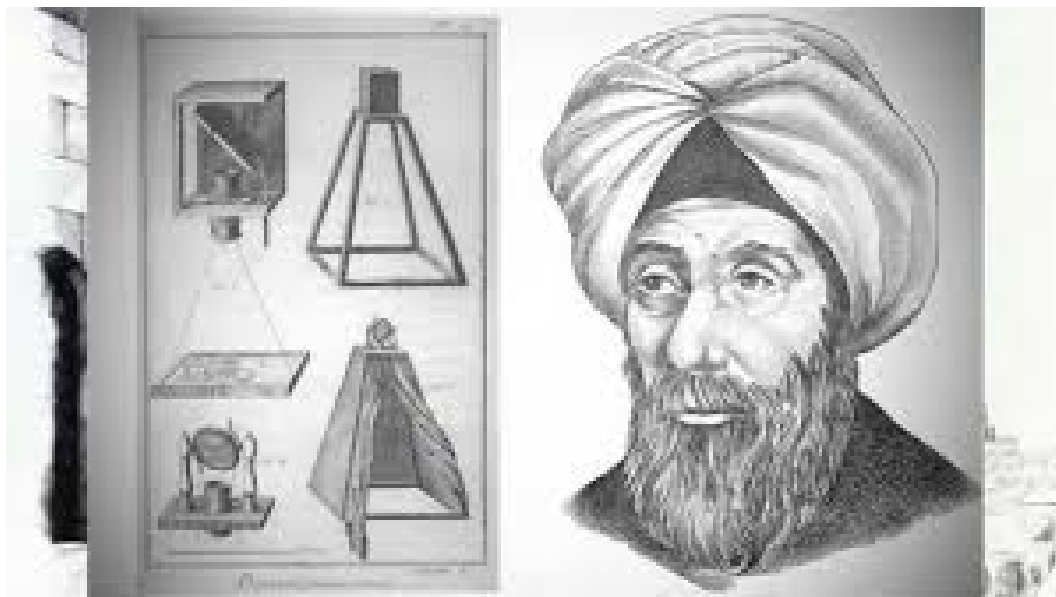


Figure 3.7: **Al-Hazen invented the camera-obscura during the years 1012-1021. It was a forerunner of the modern camera.**

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Muslims in Egypt and probably elsewhere were using printing to mass-produce texts as early as the 10th century. Dozens of examples of their output are preserved in museums and libraries, but have, until recently, been overlooked and neglected by scholars. This phenomenon is yet another example of the 1000-year missing history of science and technology.

It is, however, true that Muslims did not use printing to produce books, nor extended texts in any form, until the 18th century. This challenge was taken up by Europeans from the 15th century onwards, and it would not have been possible there, without the availability of another gift from the Muslims, paper, which had earlier reached Europe from the Muslim world, via Spain and Italy.



Figure 3.8: A handwritten Islamic manuscript: Qazwini, 'Ajaib al-makhlukat, MS probably from Mosul, ca.1305. British Library.

### 3.4 Gutenberg

Johannes Gensfleisch zur Laden zum Gutenberg (c.1400-1468) was born in the German city of Mainz. He was the youngest son of an upper-class merchant, Friele Gensfleisch zur Laden, whose long-established family traced its roots back to the 13th century.

Johannes Gutenberg was educated as a goldsmith and blacksmith, and may also have attended the University of Erfurt. In 1440, while he was living in Strassburg, he is said to have perfected and unveiled his system of printing with movable type.

By 1448, he was back in Mainz, where he took a loan from his brother-on-law to meet the expenses of setting up a printing press. In 1450, the press was in operation, and Gutenberg took a further loan, 800 guilders, from the moneylender Johann Fust. Peter Schöffer, who became Fust's son-in-law also joined the enterprise, and is believed to have designed the type faces.

Among the many technical innovations introduced by Gutenberg are the invention of a process for mass-producing movable type; the use of oil-based ink for printing books; adjustable molds; mechanical movable type; and the use of a wooden printing press similar to the agricultural screw presses of the period. The alloy which he used was a mixture of lead, tin, and antimony that melted at a relatively low temperature for faster and more economical casting, cast well, and created a durable type. The combination of all these elements made the mass production of books both practical and economically feasible.

Gutenberg's greatest artistic achievement was his printed Bible, but this project also cost so much that it left him with debts of more than 20,000 guilders. A court order gave Fust control of the Bible printing project, and half of the printed Bibles.

Although he had suffered bankruptcy, the aging Gutenberg's greatness was acknowledged in 1465. He was given the title "Hofmann" (Gentleman of the Court) and awarded a yearly stipend, as well as 2,180 liters of grain and 2,000 liters of wine tax-free. He died in 1468, having enjoyed this official recognition for only three years.

Printing quickly affected both religion and science in Europe. By 1517, when Martin Luther posted his Ninety-Five Theses on the door of All Saint's Church in Wittenburg, many cities had printing presses. The theses were quickly reprinted and translated, and they spread throughout Europe. This initiated a pamphlet war, in which both sides used printing to spread their views. The impact of Luther's German translation of the Bible was greatly increased by the fact that inexpensive printed copies were widely available.

Science was similarly revolutionized. Nicolaus Copernicus (1473-1543) had a far greater impact on the history of science than his near contemporary Leonardo da Vinci (1452-1519) because of printing. Leonardo's thousands of pages of notes and his innovations in virtually all the fields of human knowledge have only recently become available in printed form. By contrast, the publication Copernicus' great book, *De revolutionibus orbium coelestium* (On the Revolutions of the Celestial Spheres) initiated a sequence of discoveries by Tycho Brahe, Galileo, Johannes Kepler and Isaac Newton, discoveries upon which the modern world is built.



Figure 3.9: Gutenberg is credited with introducing printing with movable type into Europe, with many improvements of technique. His inventions were a turning point in European history, and ushered in the modern era, the Reformation, the Age of Reason and the Industrial Revolution.



Figure 3.10: Gutenberg's printing press



Figure 3.11: Gutenberg's bible

## Suggestions for further reading

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# Chapter 4

## ALCHEMISTS

### 4.1 Searching for the Philosopher's Stone

Alchemy originated in Hellenistic Egypt during the first few centuries AD, and later spread to many parts of the world, including both Asia and Europe. Just as astrology preceded true astronomy and astrophysics, so alchemy preceded true chemistry. It combined mysticism, secrecy and superstition with a number of genuine chemical discoveries and methods.

One of the aims of alchemists was the transmutation of base metals into silver or gold. Like the ancient Greeks, they believed earth, water, air and fire to be elements, and they thought that transmutation of one metal into another could be achieved by combining these four elements in the proper way.

Other aims of the alchemists were to find an elixir that could confer immortality, to find a medicine that could cure all diseases, and to discover a universal solvent. In Europe, the alchemists of the Middle Ages thought that these aims could be achieved if they could only find the Philosopher's Stone.

Besides isolating substances that are now known to be true elements, such as sulfur and mercury, alchemists produced medicines that were of value to patients. Alchemy developed differently depending on the region. In both India and China, alchemy led to the discovery of gunpowder. In England, Roger Bacon (1219-1292) was the first to record the composition of gunpowder. Bacon worked as an alchemist as well as in other fields. Bacon's greatest work, the *Opus Magnus* was intended to reform the curricula of universities. Besides alchemy, it also discusses mathematics, optics and astronomy, and advocates the use of the experimental method.

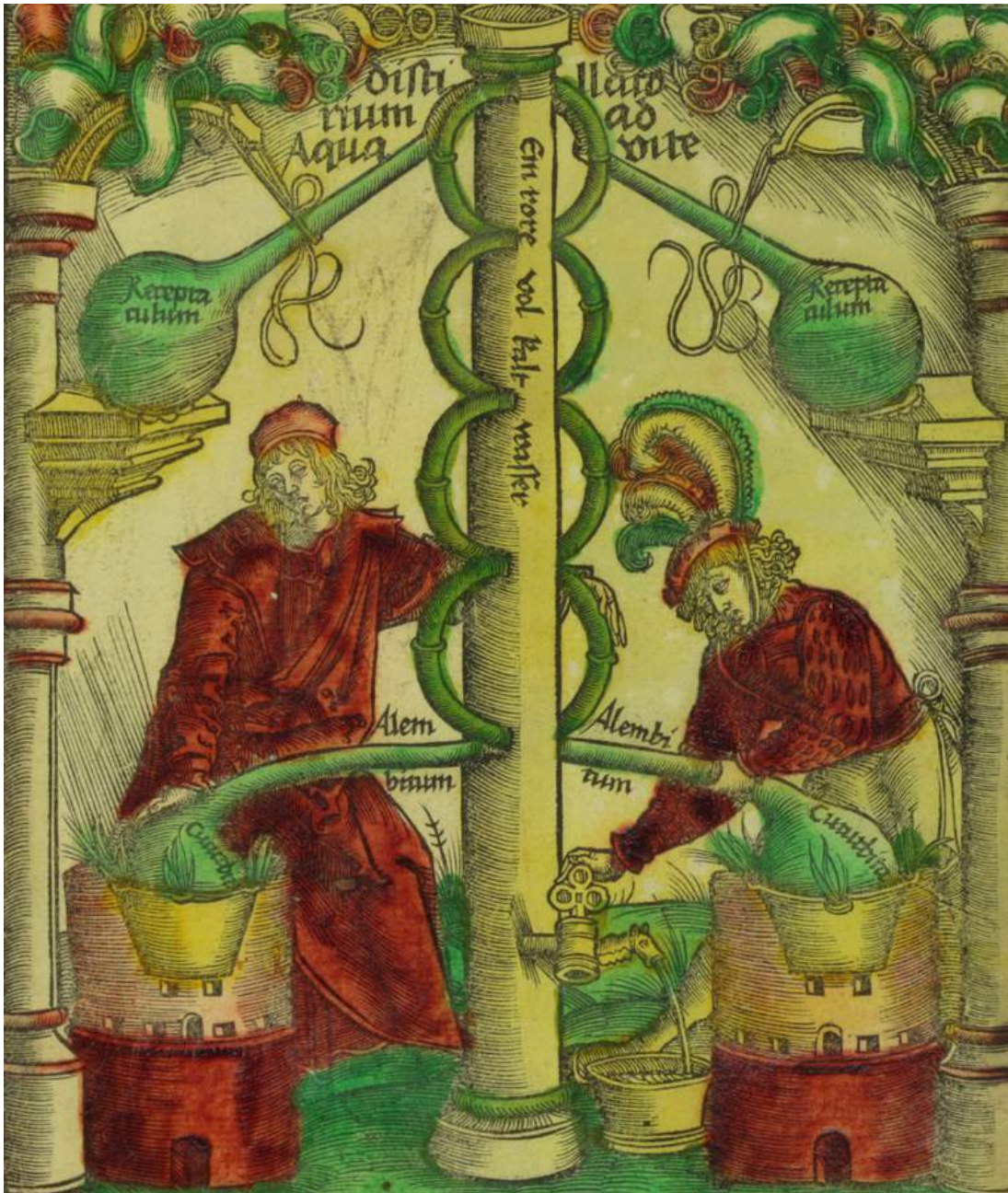


Figure 4.1: The alchemy of the Middle Ages in Europe contained strong elements of secrecy and mysticism.



Figure 4.2: *Kimiya-yi sa'adal* (The Alchemy of Happiness), a text on Islamic philosophy and alchemy by the Persian philosopher and mystic Al-Ghazali (11th century).

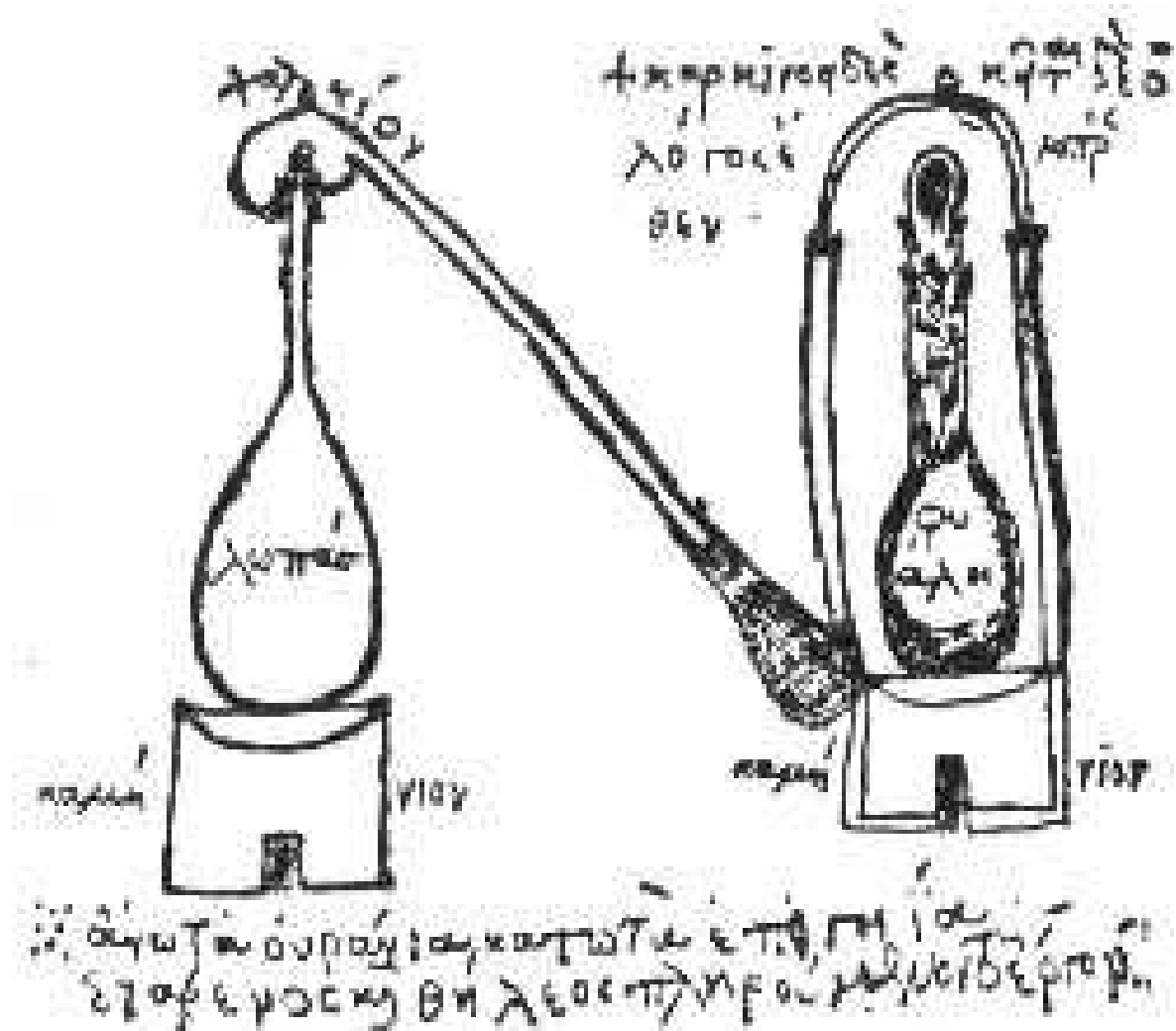


Figure 4.3: Ambix, cucurbit and retort of Zosimos, from Marcelin Berthelot, *Collection des anciens alchimistes grecs* (3 vol., Paris, 1887-1888).



Figure 4.4: A medieval alchemist.

## 4.2 Robert Boyle: The last alchemist or the first modern chemist?

### “Son of the Earl of Cork and father of chemistry”

Robert Boyle (1627-1691) was born in Ireland, the seventh son and fourteenth child of the immensely rich 1st Earl of Cork. As a very young boy, Boyle was privately tutored in Latin, Greek and French. When he was eight years old, following the death of his mother, he was sent to England to be educated at Eton College.

After three years at Eton, Boyle traveled to continental Europe with a French tutor. Galileo Galilei was still alive at that time, and they visited him in Florence. Undoubtedly, Galileo’s insistence on adherence to strictly experimental methods made a strong impression on the youthful Boyle.

In 1644, Robert Boyle, then 17 years old, returned to England with a strong interest in scientific research. With the death of his father, he had inherited substantial estates in Ireland, as well as a mansion in Stalbridge, Dorset, England. He lived at Stalbridge between 1644 and 1652, and performed many of his experiments there. He also became a very active member of the “invisible college”, which later developed into the Royal Society of London. He visited his Irish estates between 1652 and 1654, but found it difficult to do experimental work in Ireland because of the lack of proper equipment.

In 1654 Robert Boyle moved to Oxford, where he was better able to perform his experiments. He rented a large apartment there, and hired Robert Hooke as his scientific

assistant. Together they built an air pump, with which Boyle established the fact that at a constant temperature, the volume of any gas is inversely proportional to the pressure, a relationship that has come to be known as Boyle's Law.

Robert Boyle's last 20 years were spent in the London home of his sister Katherine, with whom he shared all his scientific discussions and ideas. He and his sister worked together on many problems and experiments. Katherine's salon brought Boyle into contact with many important intellectuals of the time, and thus widened his influence.

Although Robert Boyle was an experimentalist, and thus a pioneer of modern chemistry, he was also an alchemist. He believed the transmutation of base metals into silver and gold to be possible. Boyle even helped to achieve the 1689 repeal of a statute forbidding the "multiplication of gold".

### Important scientific publications of Robert Boyle

- 1660 - New Experiments Physico-Mechanical: Touching the Spring of the Air and their Effects
- 1661 - The Sceptical Chymist
- 1662 - Whereunto is Added a Defence of the Authors Explication of the Experiments, Against the Objections of Franciscus Linus and Thomas Hobbes (a book-length addendum to the second edition of New Experiments Physico-Mechanical)
- 1663 - Considerations touching the Usefulness of Experimental Natural Philosophy (followed by a second part in 1671)
- 1664 - Experiments and Considerations Touching Colours, with Observations on a Diamond that Shines in the Dark
- 1665 - New Experiments and Observations upon Cold
- 1666 - Hydrostatical Paradoxes
- 1666 - Origin of Forms and Qualities according to the Corpuscular Philosophy. (A continuation of his work on the spring of air demonstrated that a reduction in ambient pressure could lead to bubble formation in living tissue. This description of a viper in a vacuum was the first recorded description of decompression sickness.)
- 1669 - A Continuation of New Experiments Physico-mechanical, Touching the Spring and Weight of the Air, and Their Effects
- 1670 - Tracts about the Cosmical Qualities of Things, the Temperature of the Subterranean and Submarine Regions, the Bottom of the Sea, etc. with an Introduction to the History of Particular Qualities
- 1672 - Origin and Virtues of Gems
- 1673 - Essays of the Strange Subtilty, Great Efficacy, Determinate Nature of Effluvi-ums
- 1674 - Two volumes of tracts on the Saltiness of the Sea, Suspicions about the Hidden Realities of the Air, Cold, Celestial Magnets
- 1674 - Animadversions upon Mr. Hobbes's Problemata de Vacuo
- 1676 - Experiments and Notes about the Mechanical Origin or Production of Particular Qualities, including some notes on electricity and magnetism

#### 4.2. ROBERT BOYLE: THE LAST ALCHEMIST OR THE FIRST MODERN CHEMIST?57

- 1678 - Observations upon an artificial Substance that Shines without any Preceding Illustration
- 1680 - The Aerial Noctiluca
- 1682 - New Experiments and Observations upon the Icy Noctiluca (a further continuation of his work on the air)
- 1684 - Memoirs for the Natural History of the Human Blood
- 1685 - Short Memoirs for the Natural Experimental History of Mineral Waters
- 1686 - A Free Enquiry into the Vulgarly Received Notion of Nature
- 1690 - Medicina Hydrostatica
- 1691 - Experimenta et Observationes Physicae



Figure 4.5: Robert Boyle (1627-1691).

#### 4.2. ROBERT BOYLE: THE LAST ALCHEMIST OR THE FIRST MODERN CHEMIST?59



Figure 4.6: Robert Hooke (1635-1703). As a young man, he worked as Robert Boyle's assistant during Boyle's stay at Oxford University, helping Boyle to construct his improved air pump. Hooke later made many important contributions to microscopy, physics and astronomy.

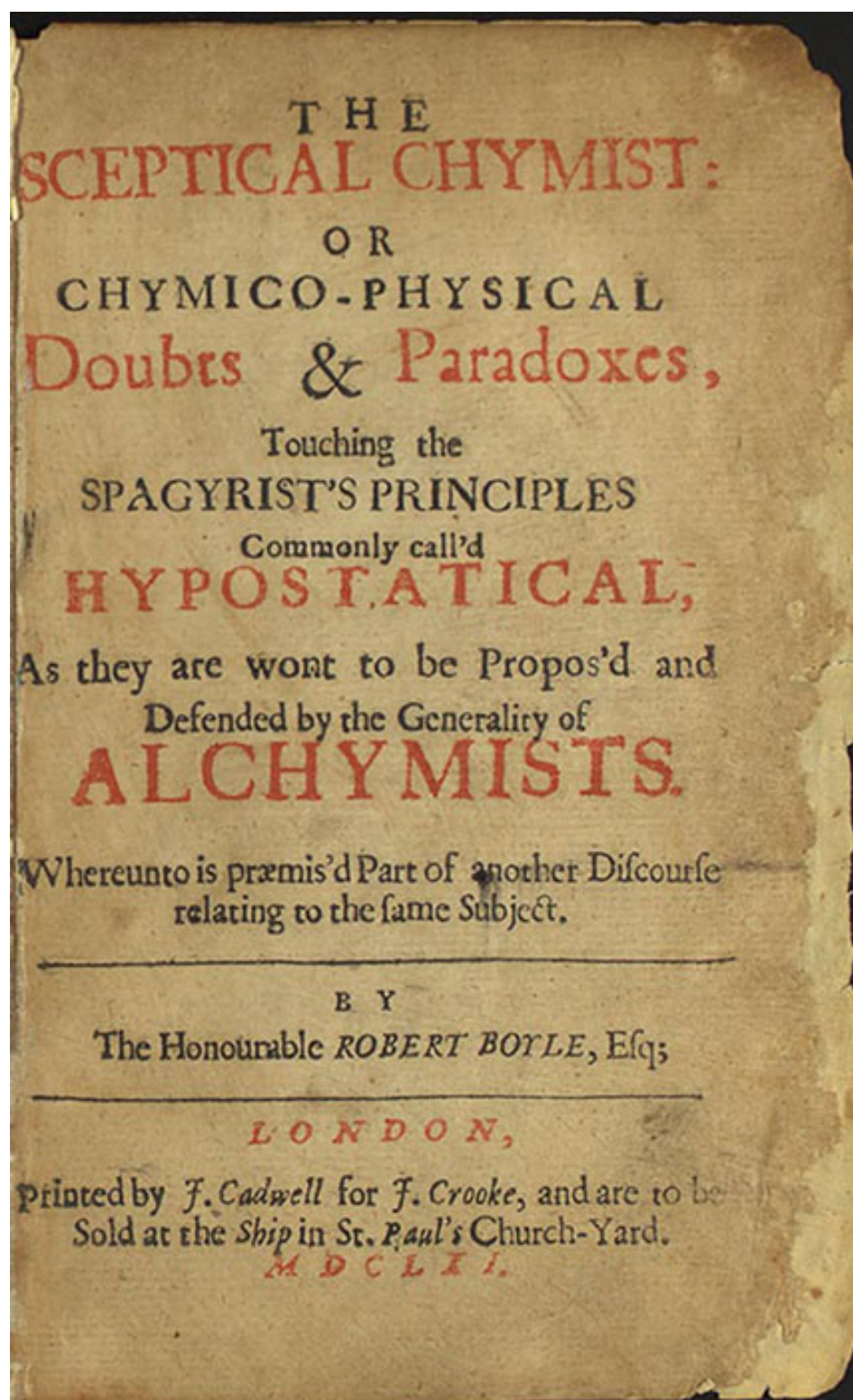


Figure 4.7: Frontpeice of Boyle's book *The Sceptical Chymist*. Like some of Galileo's books, it is written in the form of a dialogue.

#### 4.2. ROBERT BOYLE: THE LAST ALCHEMIST OR THE FIRST MODERN CHEMIST?61

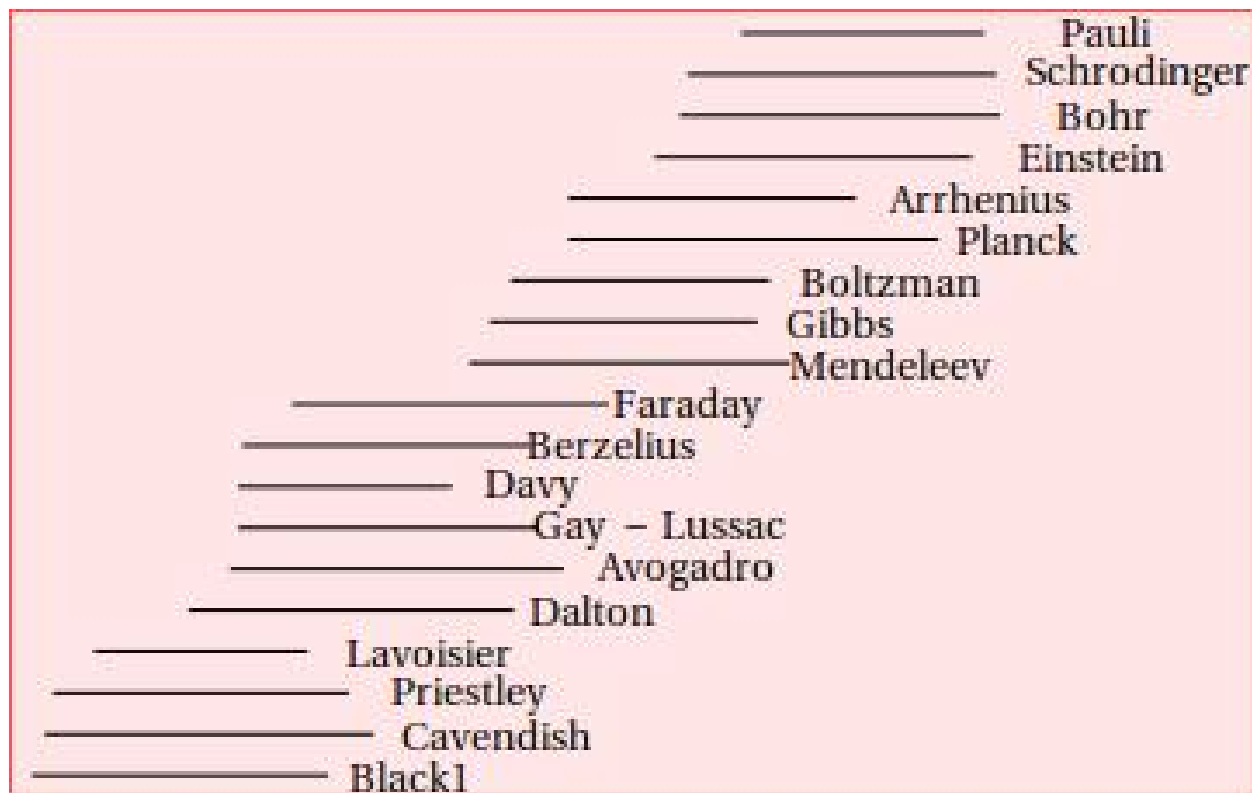


Figure 4.8: This figure shows the life spans of some of the pioneers of the Chemical Revolution. Many of these researchers were contemporaries. For example, Black and Cavendish were still alive when Faraday was a young man. The periodic table and its quantum mechanical interpretation, as well as the application of thermodynamics and statistical mechanics to chemistry, can be seen to be later developments.

### 4.3 The Chemical Revolution

Robert Boyle was the first important figure in what has been called the Chemical Revolution. This revolution is described in Chapters 5-11 of the present book, while later developments are discussed in Chapters 12-16. The time spans of lives of some of the pioneers of the Chemical Revolution are shown in Figure 4.8.

- Robert Boyle (1627-1691)
- Joseph Black (1728-1799)
- Henry Cavendish (1731-1810)
- Joseph Priestley (1733-1804)
- Antoine Lavoisier (1743-1794)
- John Dalton (1766-1844)
- Amedeo Avogadro (1776-1856)
- Joseph Gay-Lussac (1778-1850)
- Humphry Davy (1778-1829)
- Jöns Jacob Berzelius (1779-1848)
- Michael Faraday (1791-1867)
- Dmitri Mendeleev (1834-1907)
- Josiah Willard Gibbs (1839-1903)
- Ludwig Boltzmann (1844-1906)
- Max Planck (1858-1947)
- Svante Arrhenius (1859-1927)
- Albert Einstein (1879-1955)
- Niels Bohr (1885-1962)
- Erwin Schrödinger (1887-1961)
- Wolfgang Pauli (1900-1958)

#### More recent developments

- Wilhelm Conrad Röntgen (1845-1923)
- Sir William Henry Bragg (1862-1942)
- Gilbert N. Lewis (1875-1946)
- Sir William Lawrence Bragg (1880-1971)
- Erich Hückel (1896-1980)
- Robert S. Mulliken (1896-1986)
- Douglas Hartree (1897-1958)
- Vladimir A. Fock (1898-1974)
- Linus Pauling (1901-1994)
- John Desmond Bernal (1901-1971)
- Dorothy Crowfoot Hodgkin (1910-1994)
- Charles Coulson (1910-1974)
- Francis Crick (1916-2004)

- Maurice Wilkins (1916-2004)
- Per-Olov Löwdin (1916-2000)
- Sir John Kendrew (1917-1997)
- Clemens C.J. Roothaan (1918-2019)
- Alberte Pullman (1920-2011)
- Sir Geoffrey Wilkinson (1921-1996)
- James Dewey Watson (born in 1928)
- Rosalind Franklin (1929-1958)
- Dudley Robert. Herschbach (born in 1932)
- Jean-Marie Lehn (born in 1939)

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## Chapter 5

# BLACK, PRIESTLEY AND CAVENDISH

### 5.1 William Cullen

The two driving forces behind the Industrial Revolution were world trade and scientific discovery. During the 18th century, both these forces were especially strongly felt in Scotland and in the north-western part of England. The distilling industry in Scotland grew enormously because of world trade; and the resulting interest in what happens when liquids are vaporized and condensed produced one of the major scientific and technical developments of the Industrial Revolution.

The first step in this development was taken by William Cullen, a professor of medicine at the universities of Glasgow and Edinburgh. In a paper entitled *Of the Cold Produced by Evaporation* (1749), Cullen wrote that he had noticed that “...water and some other liquids, in evaporating, produce some degree of cold”.

Cullen therefore began to make experiments in which he dipped a thermometer in and out of a liquid and observed the drop in temperature. He noticed that the effect was increased by “...moving the thermometer very nimbly to and fro in the air; or if, while the ball was wet with spirit of wine, it was blown upon with a pair of bellows”. In this way, Cullen achieved a temperature 44 degrees below the freezing point of water. He next tried producing vacuums above various liquids with the help of an air pump:

“We set the vessel containing the ether”, Cullen wrote, “In another a little larger, containing water. Upon exhausting the receiver and the vessel’s remaining a few minutes *in vacuo*, we found the most part of the water frozen, and the vessel containing the ether surrounded with a thick crust of ice.”

Cullen had, in fact invented the refrigerator, and he gave the first known public demonstration of the device. However, it found no commercial application at the time.

## 5.2 Joseph Black

One of Cullen's favorite students at Edinburgh was Joseph Black (1728-1799). He became Cullen's scientific assistant, and later, in 1756, he was elected to the Chair of Medicine at Glasgow University. Continuing Cullen's work on the cold produced by evaporating liquids, Black discovered and studied quantitatively the phenomenon of latent heats, e.g., the very large quantities of heat which are necessary to convert ice into water, or to convert water into steam.

Black was led to his discovery of latent heats not only by Cullen's work, but also by his own observations on Scottish weather. Writing of the discovery, one of Black's friends at Glasgow recorded that "...since a fine winter day of sunshine did not at once clear the hills of snow, nor a frosty night suddenly cover the ponds with ice, Dr. Black was already convinced that much heat was absorbed and fixed in the water which slowly trickled from the wreaths of snow; and on the other hand, that much heat emerged from it while it was slowly changing into ice. For, during a thaw, a thermometer will always sink when removed from the air into melting snow; and during a severe frost it will rise when plunged into freezing water. Therefore in the first case, the snow is receiving heat, and in the last, the water is allowing it to emerge again."

Besides studying latent heats, Black also measured the specific heats of various substances, i.e. the amount of heat needed to raise their temperature by a given amount. These studies were important not only to the foundation of the science of thermodynamics, but also to James Watt's development of an improved steam engine, and hence to the Industrial revolution. Black was a close friend of James Watt, and supported his work, both with advice and financially.

Joseph Black also discovered and studied carbon dioxide,  $\text{CO}_2$ , which he called "fixed air". He found that this gas could be produced by treating limestone,  $\text{CaCO}_3$ , with acids, or by heating limestone. Black observed that this gas was heavier than air, and that it could not support animal life or combustion.

In 1766, Joseph Black succeeded his mentor, William Cullen, and became Professor of Medicine and Chemistry at the University of Edinburgh. His teaching duties then became so heavy that they put an end to his scientific research. However, he was a gifted teacher, and his lectures helped to spread the concept of accurate measurement in chemistry to a wide audience.

According to a contemporary observer, "He became one of the principal ornaments of the University; and his lectures were attended by an audience which continued increasing from year to year, for more than thirty years. It could not be otherwise. His personal appearance and manners were those of a gentleman, and peculiarly pleasing. His voice in lecturing was low, but fine; and his articulation so distinct, that he was perfectly well heard by an audience consisting of several hundreds. His discourse was so plain and perspicuous, his illustration by experiment so apposite, that his sentiments on any subject never could be mistaken even by the most illiterate; and his instructions were so clear of all hypothesis or conjecture, that the hearer rested on his conclusions with a confidence scarcely exceeded in matters of his own experience."

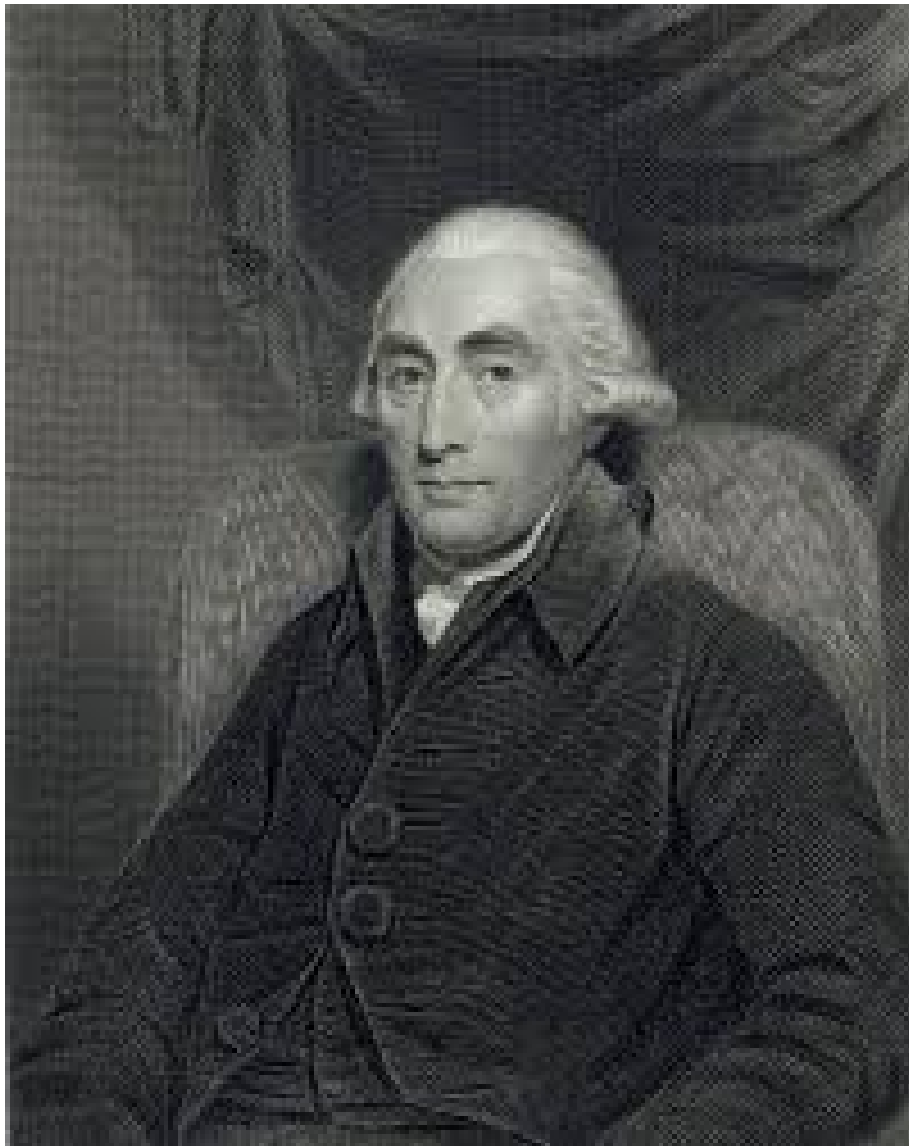


Figure 5.1: **Joseph Black (1728-1799).**

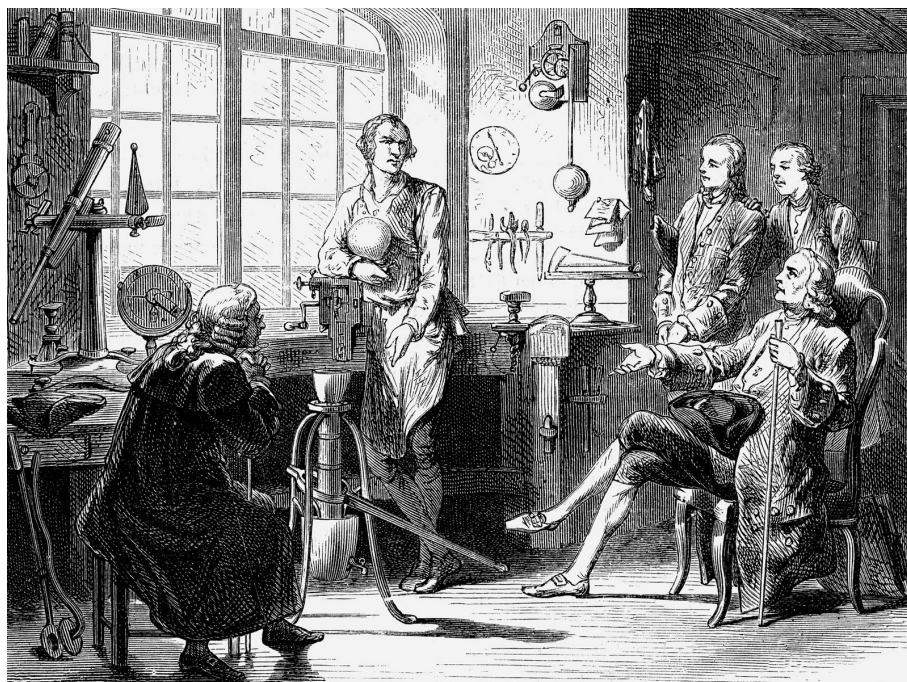


Figure 5.2: Black with friends in his laboratory.



Figure 5.3: One of Joseph Black's important contributions to chemistry was his invention of a highly accurate analytical balance.

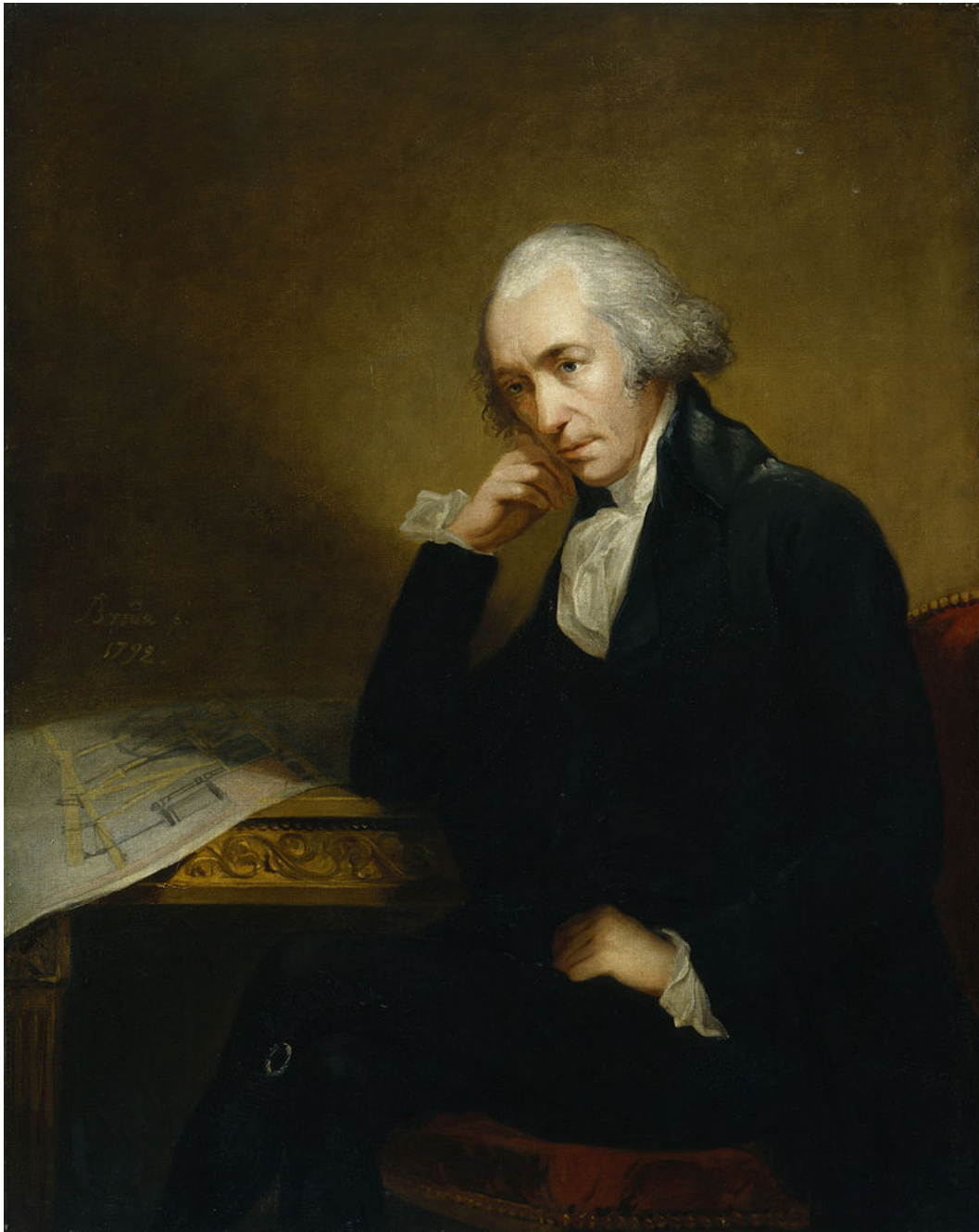


Figure 5.4: James Watt (1736-1819). Joseph Black's work on latent heats and specific heats contributed greatly to Watt's invention of an efficient steam engine, and hence the Industrial Revolution. Black was a close friend of Watt, and helped him both with advice and financial support.

### 5.3 Joseph Priestley

Joseph Priestley (1713-1804) was born in Yorkshire into a family of Dissenters. In those days, the Dissenters, who were Protestants outside the established Church of England, were discriminated against, and not allowed to hold public office or to vote.

After the early death of his mother, and his father's remarriage, Joseph Priestley went to live with a wealthy aunt and uncle. Recognizing the boy's highly precocious abilities his aunt and uncle gave him the best available education. He learned Greek, Latin, Hebrew, French, Italian, German, Aramaic and Arabic. His private tutor also introduced him to higher mathematics, natural philosophy, logic, and metaphysics.

In 1761, Joseph Priestley was given the post of tutor of modern languages and rhetoric at the Dissenting college, Warrington Academy. He soon made many friends there, including the famous potter, Josiah Wedgwood, with whom he corresponded for the remainder of his life.

A year later, Priestley married Mary Wilkinson, the sister of the industrialist John Wilkinson. Priestley wrote of her: "This proved a very suitable and happy connexion, my wife being a woman of an excellent understanding, much improved by reading, of great fortitude and strength of mind, and of a temper in the highest degree affectionate and generous; feeling strongly for others, and little for herself. Also, greatly excelling in every thing relating to household affairs, she entirely relieved me of all concern of that kind, which allowed me to give all my time to the prosecution of my studies, and the other duties of my station."

While at Warrington Academy, Priestley wrote many books. His *History of Electricity* became an influential standard text and it established his scientific reputation. On the basis of this book, he became a Fellow of the Royal Society.

### The chemistry of gases

Priestley's studies of the chemistry of gases were described as follows in an article by David A. Bassett<sup>1</sup>: "As Priestley expanded his studies in chemistry he became active in the field of pneumatic chemistry, the study of air and gases. Priestley was the first to isolate and characterize a number of gases, including oxygen, nitrogen, hydrogen chloride, ammonia, sulfur dioxide, carbon monoxide, nitric oxide, and nitrous oxide. Priestley's names for these compounds were different from the modern names, in part because he never adopted the oxygen theory of chemistry. The names he used were in terms of the older 'phlogiston theory.' Priestley did this work using very simple apparatuses, such as saucers, glasses, tubes, cylinders, and tubs of water or mercury."

Priestley noticed that the gas which we now call oxygen could support the breathing of a mouse for a very long time, and that it was unusually effective in supporting combustion. On a visit to Paris, he communicated these results to Antoine Lavoisier, who repeated and extended Priestley's experiments.

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<sup>1</sup><http://www.chemistryexplained.com/Pl-Pr/Priestley-Joseph.html>



Figure 5.5: Joseph Priestley (1733-1804) published 150 works on many subjects. As a theologian and philosopher, he contributed importantly to the founding of both the Unitarian and the Utilitarian movements. As a scientist, he wrote an influential *History of Electricity*, which described many of his own original experiments and an anticipation of Coulomb's Law. As a chemist, he isolated several gases, including oxygen. He also invented soda water and thus is the "father of the soft drinks industry".



Figure 5.6: Mary Priestley, in a portrait by Carl F. von Breda (1793). She was the daughter of ironmaster Isaac Wilkinson, and sister of industrialist John Wilkinson



Figure 5.7: The Birmingham mob burning Joseph Priestley's home.

### The Priestley Riots of 1791

On the 14th of July, 1791, Joseph Priestley's home in Birmingham was burned by a mob, which targeted Dissenters and those who supported the results of the French Revolution. The mob, which was tacitly condoned by Pitt's government, destroyed four Dissenting chapels, twenty-seven homes, and a number of businesses. Joseph Priestley fled with his family, first to London, and afterwards to the United States. He spent the last ten years of his life in Pennsylvania.

## 5.4 Henry Cavendish

Henry Cavendish (1731-1810) was born into the English nobility. His father, Lord John Cavendish, was the second son of the Duke of Devonshire, while his mother, Lady Anne de Grey, was the daughter of the Duke of Kent. Lady Anne died in 1733, and Henry Cavendish was brought up by his father, Lord John, whose interests were divided between politics and science. Henry Cavendish followed his father into scientific research, but, being shy to the point of eccentricity, not into politics. He attended Cambridge University for three years, but left without obtaining a degree, which was a common practice at the time.

### Father and son at the Royal Society

Starting in 1758, Lord John Cavendish began taking his son Henry to meetings of the Royal Society, of which he was a Fellow, and in 1760 Henry Cavendish also was elected to

be a Fellow of the Royal Society. Throughout his life, the younger Cavendish attended as many meetings as possible, and this was almost his only social activity.

## Contributions to chemistry

Like Black and Priestley, Henry Cavendish contributed importantly to the study of gas chemistry. Cavendish showed that the air exhaled by mammals when breathing is “fixed air”, i.e. carbon dioxide. He also isolated and studied hydrogen, which he called “inflammable air”. He produced hydrogen by reacting acids with metals, and correctly identified it as an element. He also correctly believed that when hydrogen is burned, two atoms of the element enter each molecule of water. He also measured the specific gravity and solubility in water of these gases. His results, reported in his 1778 paper *General Considerations on Acids*, won him the Copley Medal of the Royal Society.

In 1785, Cavendish made a series of very accurate studies of the composition of ordinary air. He concluded that ordinary air is a mixture of four parts of the gas that we now call nitrogen with one part of oxygen (again in modern terms). He also found a residue occupying 1/120-th the volume of the other two gases. About 100 years later, this small quantity of inert gas was identified as the element argon.

Cavendish also anticipated Dalton’s law of partial pressures, which states that the total pressure exerted by a mixture of gases is the sum of the pressures that each individual gas would exert if it occupied the total volume by itself. However, this was among his many unpublished results.

Henry Cavendish was among the first outside France to embrace Lavoisier anti-phlogiston theories. However, Cavendish disagreed with Lavoisier about the nature of heat. Following Newtonian mechanics, Cavendish developed a mathematical theory of heat as due to the motion of particles. His theory included the conservation of energy and the mechanical equivalent of heat.

## Weighing the earth

Cavendish made many important contributions to physics. Among them was his famous experiment to determine the density and total weight of the earth. To make this measurement, he used a sensitive torsion balance to measure the gravitational attraction between two spheres of lead. Cavendish was able to determine the gravitational attraction between these two spheres from the period of oscillation of the torsion balance. He found the average density of the earth to be 5.48 times greater than the density of water. His result was within one percent of the currently accepted figure.

Although he contributed importantly to many branches of physics, most of his results were unpublished, and credit for his discoveries went to others. After his death, his papers were carefully edited and published by the great physicist James Clerk Maxwell. At Maxwell’s insistence, the famous Cavendish Laboratory, built at Cambridge University with money donated by a relative of Henry Cavendish, was named after him.



Figure 5.8: The Hon. Henry Cavendish (1731-1810).



Figure 5.9: A drawing of Henry Cavendish.

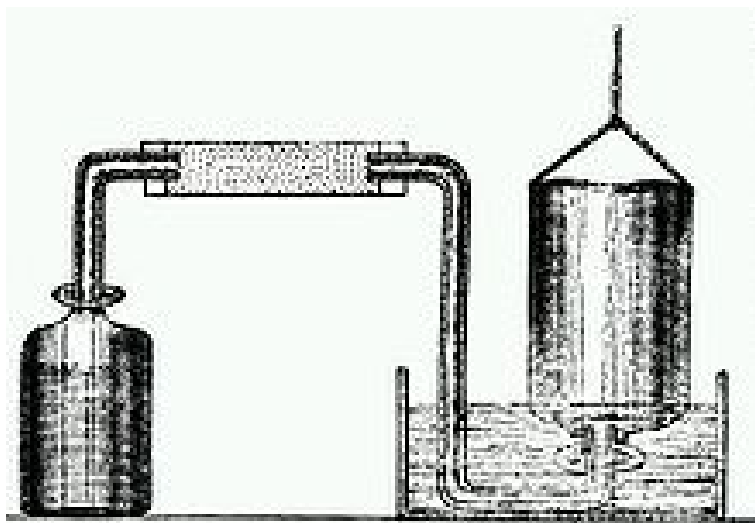


Figure 5.10: The apparatus used by Henry Cavendish to produce and collect hydrogen.

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# Chapter 6

## LAVOISIER

### 6.1 Lavoisier: “the father of modern chemistry”

Antoine-Laurent de Lavoisier (1743-1794) was born into a French noble family. At the age of five, after the death of his mother, he inherited a large fortune. When he was eleven years old, Lavoisier became a student at the Collège des Quatre-Nations, University of Paris, where he studied chemistry, botany, astronomy, and mathematics. He later obtained a degree in law, and was admitted to the bar, but he never practiced as a lawyer. Instead he returned to his earlier scientific interests, studying geology and participating in a geological survey of Alsace-Lorraine. In 1764, at the age of 21, he read his first paper to the French Academy of Sciences. It was on the chemical and physical properties of gypsum.

Lavoisier greatly admired the ideals of the Enlightenment, and he believed that scientific progress should be used for the betterment of the whole population, including all classes. His concern for the general welfare can be seen in his essay on the problem of urban street lighting, for which he received a gold medal from the king in 1766. He later designed an aqueduct to bring clean water to Paris from the river Yvette. When his plans were not carried out, he turned his attention to methods for purifying water from the Seine. and other problems of public hygiene and sanitation. Lavoisier also worked to improve the ventilation of hospitals and the living conditions of prisons. His other projects for public welfare included agricultural improvements. He founded the educational organizations Lycée Muse des Arts et Métiers, and he opened an expensive and sophisticated laboratory where young scientists were free to work.

Lavoisier spent large amounts of his own money on these projects, and the fortune that he had inherited from his mother would not have been sufficient. He had another source of income, however: He had invested massively in the Ferme générale, a tax-gathering company. This investment would later lead to his death under Robespierre’s Reign of Terror.

It should be mentioned that Lavoisier was a gifted administrator, and he was much in demand for the leadership of various governmental commissions. Perhaps his contributions to chemistry would have been still greater than they were, had it not been for these

administrative duties.

## Lavoisier's contributions to chemistry

Lavoisier's work was a turning point in the history of chemistry. He made the subject quantitative through his insistence on precise weighing of reactants and products and his methods for carrying out reactions within sealed flasks to prevent contamination from external sources. He also carefully measured the heat produced by chemical reactions.

Lavoisier's careful experiments with combustion put an end to the outdated and counter-intuitive "plogiston" theory - counter-intuitive because to explain experimental observations, the substance "plogiston" would need to have a negative mass. Lavoisier's studies of the role of oxygen in combustion put an end to this nonsense. His experiments also demonstrated that the respiration of an animal can be thought of as a slow form of combustion. Lavoisier also made very important contributions to chemistry by defining an element as a substance which cannot be further decomposed, and by introducing convenient conventions for chemical notation.

According to the New World Encyclopedia's article on Lavoisier, "Some of Lavoisier's most important experiments examined the nature of combustion, or burning. Through these experiments, he demonstrated that burning is a process that involves the combination of a substance with oxygen. He also demonstrated the role of oxygen in metal rusting, as well as its role in animal and plant respiration: working with Pierre-Simon Laplace, Lavoisier conducted experiments that showed that respiration was essentially a slow combustion of organic material using inhaled oxygen. Lavoisier's explanation of combustion replaced the phlogiston theory, which presumed that materials release a substance called phlogiston when they burn, a theory that was prominently held by Joseph Priestley during the latter part of the eighteenth century. Lavoisier studied Priestley's works and discussed the phenomenon of combustion with the English clergyman scientist who visited him in France. Due to Lavoisier's exacting measurements of the products of combustion, he was led to the conclusion that there was an element in the air which must combine with the materials being burned. He was able to determine the exact proportions of the element oxygen in the air by weighing and measuring the solids and gasses involved both before and after the experiments.

"Lavoisier's experiments were among the first truly quantitative chemical experiments ever performed; that is, he carefully weighed the reactants and products involved, a crucial step in the advancement of chemistry. He showed that, although matter can change its state in a chemical reaction, the quantity of matter is the same at the end as at the beginning of every chemical reaction. He burned phosphorus and sulfur in air, and proved that the products weighed more than the original. Nevertheless, the weight gained was lost from the air.

"These experiments provided evidence for the law of the conservation of matter, which was later formulated as the law of conservation of mass. It was only after the realization that matter can be neither created nor destroyed within a physical system that chemistry became an exact science."



Figure 6.1: Antoine Lavoisier and his wife, Marie-Anne Pierrette Paulze, by Jacques-Louis David, 1788.



Figure 6.2: Lavoisier explaining to his wife the results of an experiment on air, by Ernest Board.



Figure 6.3: A statue of Lavoisier in the Louvre.

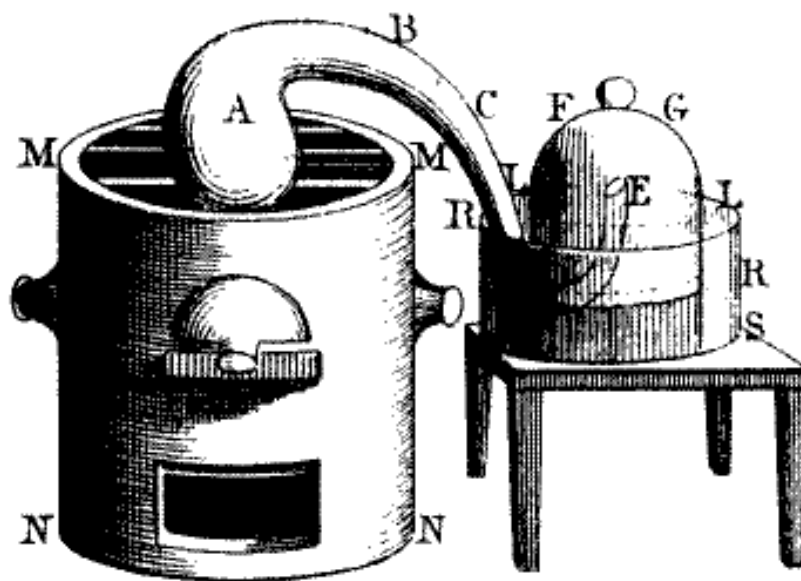


Figure 6.4: Lavoisier's experiment on the decomposition of air, engraved by his wife.

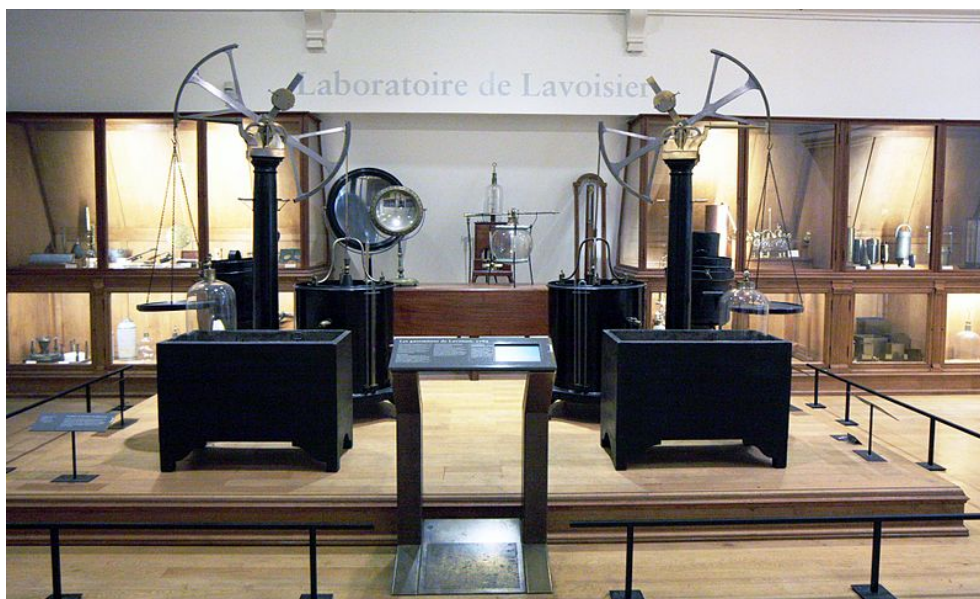


Figure 6.5: Lavoisier's laboratory, exhibited at the Musée des Arts et Métiers, Paris.

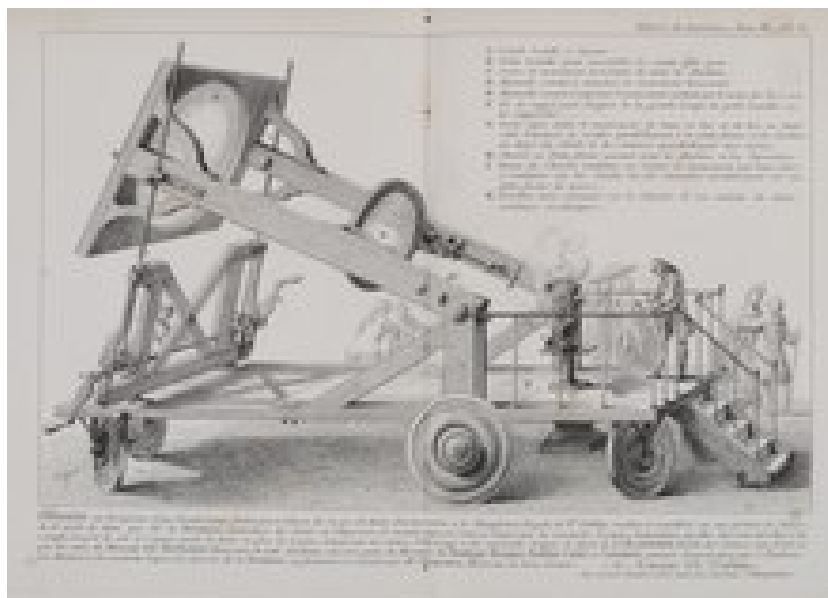


Figure 6.6: Lavoisier's solar furnace.



Figure 6.7: A statue of Lavoisier by Jules Dalou, 1866.

## Some quotations from the English translation of Lavoisier's book on chemistry

Lavoisier's book, *Elements of Chemistry* is available from Project Gutenberg. Here are a few quotations which illustrate how advanced his thinking was, compared with previous authors. He rejected both the idea that earth, air, fire and water were elements and also phlogiston theory, and made chemistry a quantitative science.

The metals, except gold, and sometimes silver, are rarely found in the mineral kingdom in their metallic state, being usually less or more saturated with oxygen, or combined with sulphur, arsenic, sulphuric acid, muriatic acid, carbonic acid, or phosphoric acid. Metallurgy, or the docimastic art, teaches the means of separating them from these foreign matters; and for this purpose we refer to such chemical books as treat upon these operations.

We are probably only acquainted as yet with a part of the metallic substances existing in nature, as all those which have a stronger affinity to oxygen, than charcoal possesses, are incapable of being reduced to the metallic state, and, consequently, being only presented to our observation under the form of oxyds, are confounded with earths. It is extremely probable that barytes, which we have just now arranged with earths, is in this situation; for in many experiments it exhibits properties nearly approaching to those of metallic bodies. It is even possible that all the substances we call earths may be only metallic oxyds, irreducible by any hitherto known process.

Those metallic bodies we are at present acquainted with, and which we can reduce to the metallic or reguline state, are the following seventeen:

1. Arsenic.
2. Molybdena.
3. Tungstein.
4. Manganese.
5. Nickel.
6. Cobalt.
7. Bismuth.
8. Antimony.
9. Zinc.
10. Iron.
11. Tin.
12. Lead.
13. Copper.
14. Mercury.
15. Silver.
16. Platina.
17. Gold.

It is necessary to remark, that earths and alkalies unite with acids to form neutral salts without the intervention of any medium, whereas metallic substances are incapable of forming this combination without being previously less or more oxygenated; strictly speaking, therefore, metals are not soluble in acids, but only metallic oxyds. Hence, when we put a metal into an acid for solution, it is necessary, in the first place, that it become oxygenated, either by attracting oxygen from the acid or from the water; or, in other words, that a metal cannot be dissolved in an acid unless the oxygen, either of the acid, or of the water mixed with it, has a stronger affinity to the metal than to the hydrogen or the acidifiable base; or, what amounts to the same thing, that no metallic solution can take place without a previous decomposition of the water, or the acid in which it is made. The explanation of the principal phenomena of metallic solution depends entirely upon this simple observation, which was overlooked even by the illustrious Bergman.

The first and most striking of these is the effervescence, or, to speak less equivocally, the disengagement of gas which takes place during the solution; in the solutions made in nitric acid this effervescence is produced by the disengagement of nitrous gas; in solutions with sulphuric acid it is either sulphurous acid gas or hydrogen gas, according as the oxydation of the metal happens to be made at the expence of the sulphuric acid or of the water. As both nitric acid and water are composed of elements which, when separate, can only exist in the gaseous form, at least in the common temperature of the atmosphere, it is evident that, whenever either of these is deprived of its oxygen, the remaining element must instantly expand and assume the state of gas; the effervescence is occasioned by this sudden conversion from the liquid to the gaseous state. The same decomposition, and consequent formation of gas, takes place when solutions of metals are made in sulphuric acid: In general, especially by the humid way, metals do not attract all the oxygen it contains; they therefore reduce it, not into sulphur, but into sulphurous acid, and as this acid can only exist as gas in the usual temperature, it is disengaged, and occasions effervescence.

The second phenomenon is, that, when the metals have been previously oxydated, they all dissolve in acids without effervescence: This is easily explained; because, not having now any occasion for combining with oxygen, they neither decompose the acid nor the water by which, in the former case, the effervescence is occasioned.



Plate IV (continued)

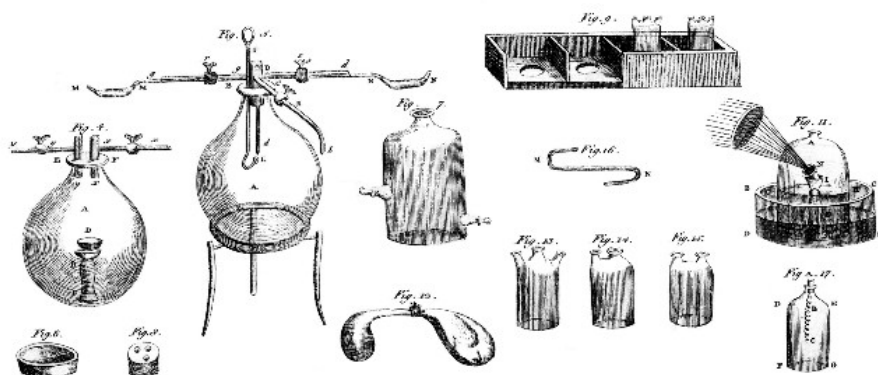


Plate V (continued)

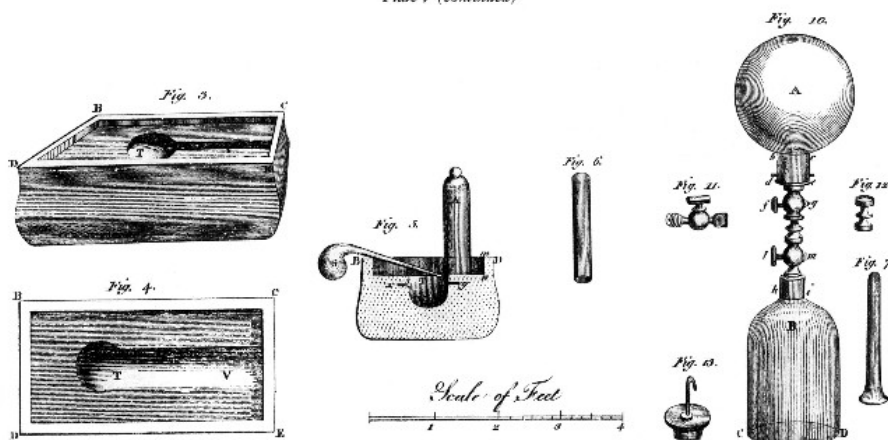


Plate VI

*Fig. 3.*

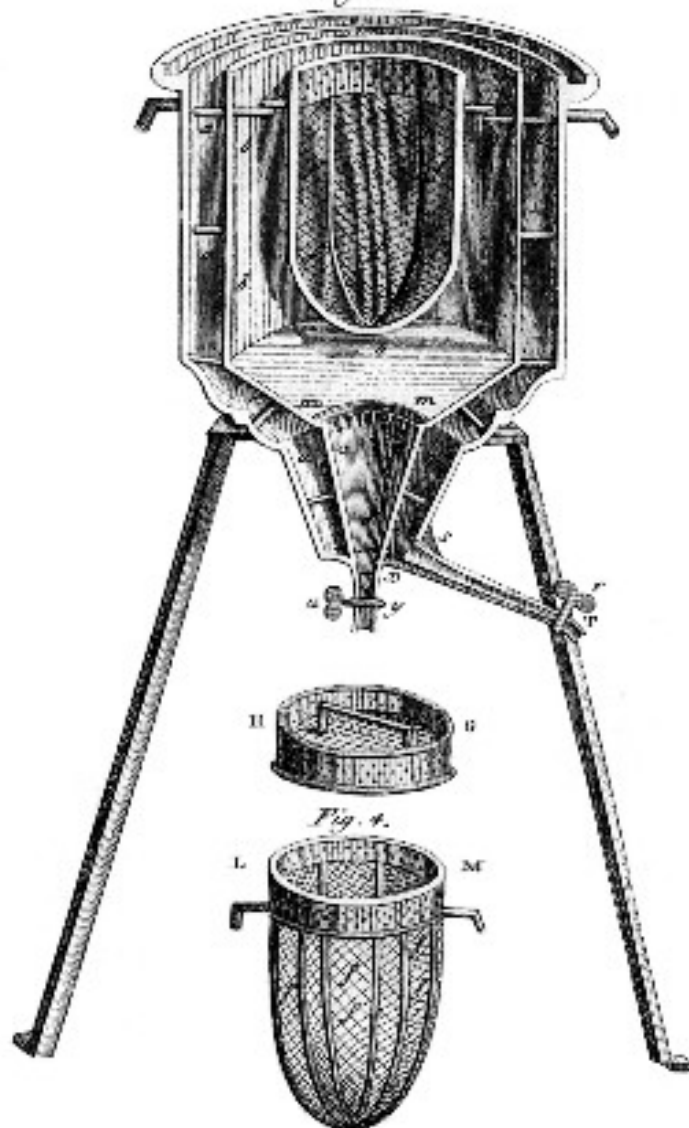
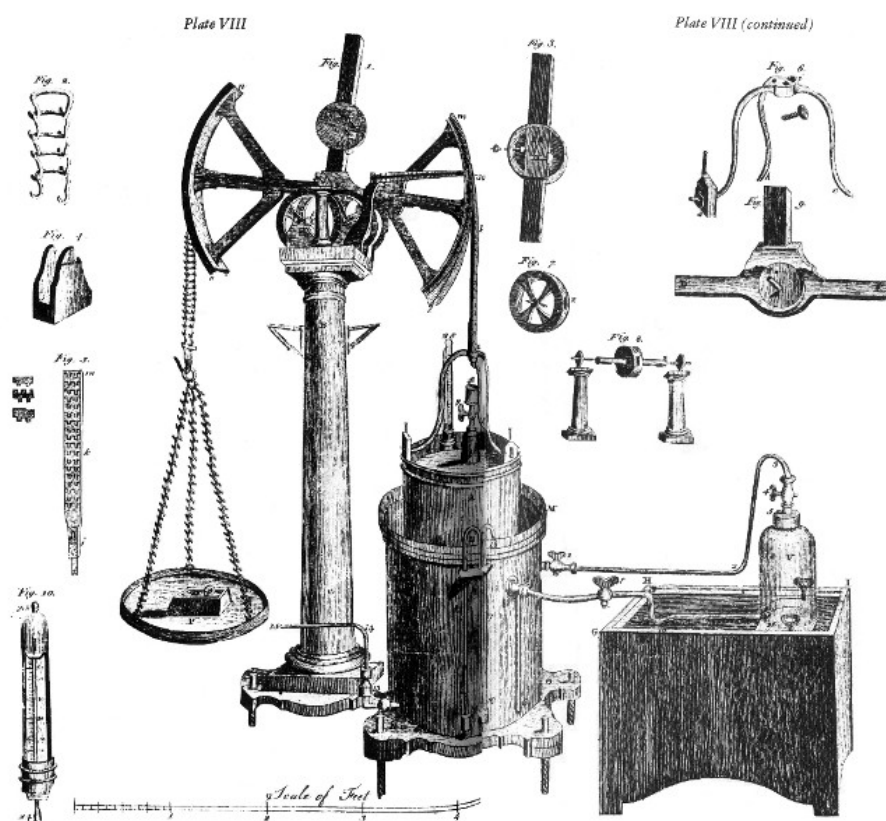
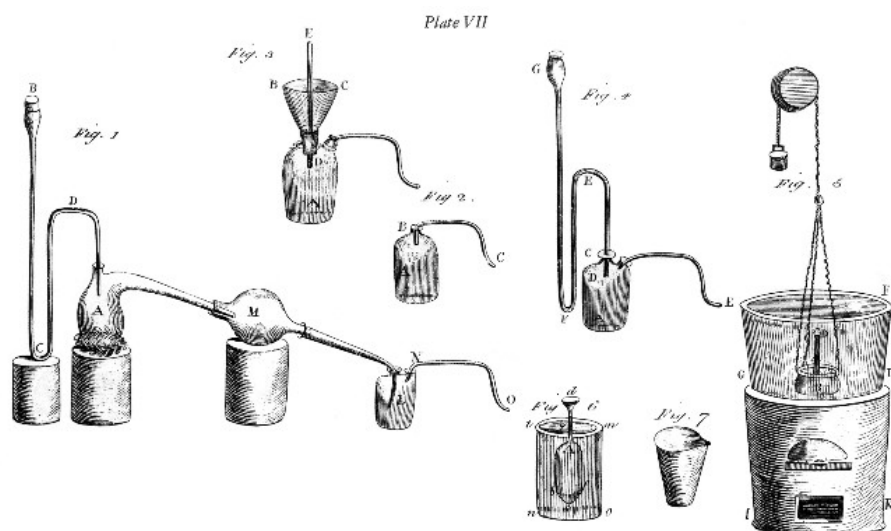


Fig. 9.



### Suggestions for further reading

1. Aykroyd, W. R. [1935] 1970. Three Philosophers (Lavoisier, Priestley and Cavendish). Westport, CT: Greenwood Press.
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4. Lavoisier, Antoine. 1965. *Elements of Chemistry*. New York: Dover Publications.
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# Chapter 7

## DALTON AND BERZELIUS

### 7.1 Atoms in chemistry

As we saw in an earlier chapter, atomism was originated by the Greek philosopher, Leucippus, in the 5th century B.C., and it was developed by his student Democritus. The atomists believed that all matter is composed of extremely small, indivisible particles (atoms). They believed that all the changes which we observe in matter are changes in the groupings of atoms, the atoms themselves being eternal.

The rational philosophy of Democritus was not very popular in his own time, but it was saved from being lost entirely by the Athenian philosopher Epicurus. Later, the Roman poet, Lucretius, published a long, philosophical poem, *De Natura Rerum*, in which he maintained that all things (even the gods!) are composed of atoms. In 1417, a single surviving manuscript copy of *De Natura Rerum* was discovered and printed.

The poem became very popular, and in this way, the ideas of Democritus were transmitted to the experimental scientists of the 17th century, almost all of whom were believers in the atomic theory of matter. Christian Huygens, for example, believed that light radiating from a flame is a wavelike disturbance produced by the violent motion of atoms in the flame. Sir Isaac Newton was also a believer in the atomic theory of matter. He believed (correctly) that chemical compounds are composed of atoms bonded together by forces which are fundamentally electrical in nature. The universally talented Robert Hooke came near to developing a kinetic theory of gases based on atomic ideas; but he lacked the mathematical power needed for such a theory.

At the beginning of the 19th century, an honest, ingenious, color-blind, devout, unmarried English provincial schoolteacher named John Dalton (1766-1814) gave the atomic theory of matter new force by relating it to the observed facts of chemistry. Dalton was born in Cumberland, the son of a Quaker weaver, and he remained in the North of England all his life. At the early age of 12, he became a teacher; and he remained a teacher in various Quaker schools until 1800, when he became the Secretary of the Manchester Literary and Philosophical Society.

One of Dalton's early scientific interests was in meteorology, and he recorded the capri-



Figure 7.1: Engraving of a painting of John Dalton.

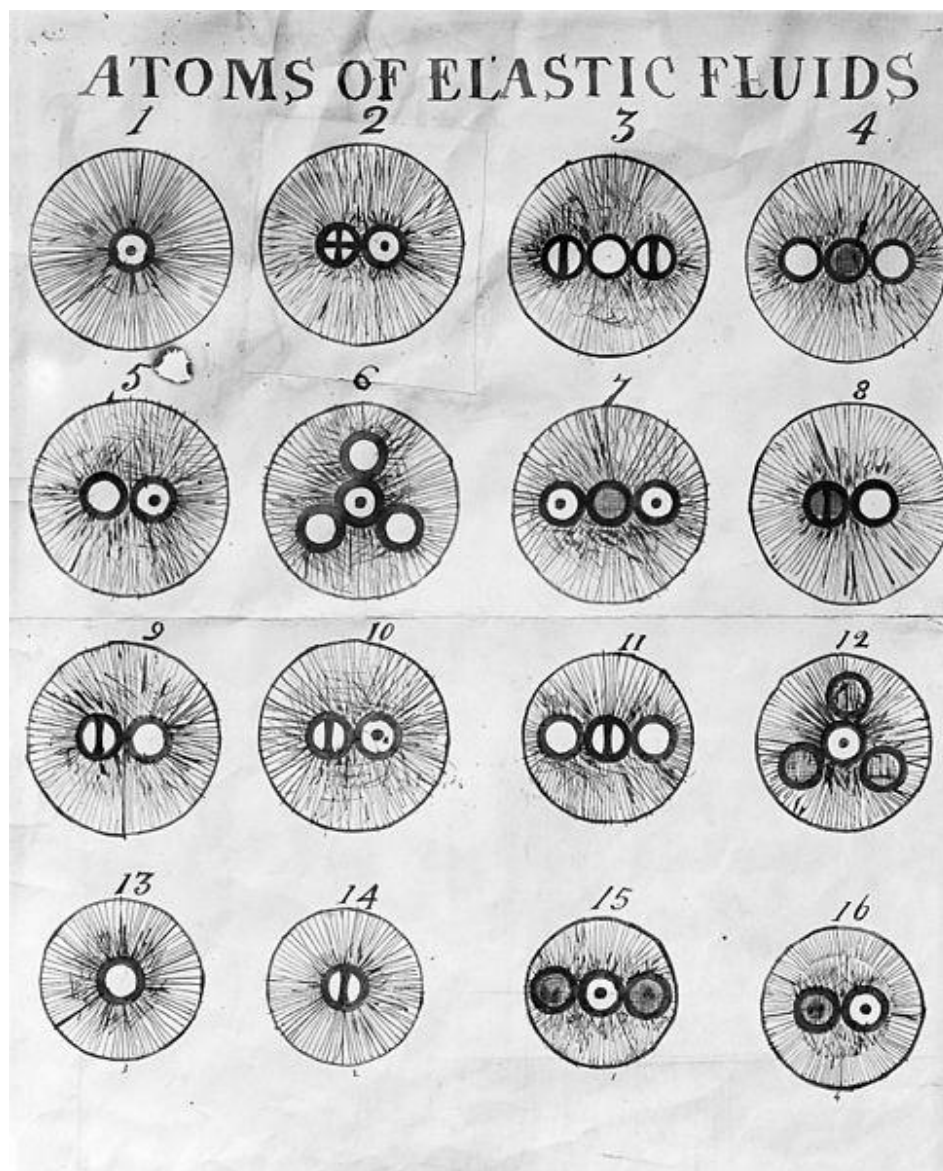


Figure 7.2: John Dalton: Composition and size of atoms, 1806.

cious weather of the Lake District in a diary which ultimately contained more than 200,000 entries. In speculating about water vapor in the atmosphere, John Dalton began to wonder why the various gases in the atmosphere did not separate into layers, since some of the gases in the mixture were less dense than others.

The only way that Dalton could explain the failure of the atmosphere to stratify was to imagine it as composed mainly of empty space through which atoms of the various gases moved almost independently, seldom striking one another. In this picture, he imagined each of the gases in the atmosphere as filling the whole available volume, almost as though the other gases in the mixture were not there.

Dalton believed the pressure on the walls of a vessel containing a mixture of gases to be due to the force of the atoms striking the walls; and he believed that each of the gases behaved as though the other gases were not there. Therefore he concluded that the total pressure must be the sum of the partial pressures, i.e. the sum of the pressures which would be exerted by each of the gases in the mixture if it occupied the whole volume by itself. This law, which he confirmed by experiment, is known as "Dalton's Law of Partial Pressures".

Convinced of the atomic picture by his studies of gases, John Dalton began to think about chemical reactions in terms of atoms. Here he made a bold guess - that all the atoms of a given element are of the same weight. He soon found that this hypothesis would explain one of the most important fact in chemistry, the fixed ratio of weights in which chemical elements combine to form compounds. (The law of definite proportions by weight in chemical reactions is known as "Proust's Law", after the French chemist, Joseph Louis Proust (1754-1826), who first proposed and defended it.)

In Dalton's view, molecules of the simplest compound formed from two elements ought to consist of one atom of the first element, united with one atom of the second element. For example, the simplest compound of carbon and oxygen should consist of one atom of carbon, bonded to one atom of oxygen (carbon monoxide). Dalton believed that besides such simple compounds, others with more complicated structure could also exist, (e.g. carbon dioxide).

By studying the weights of the elements which combined to form what he believed to be the simplest chemical compounds, Dalton was able to construct a table of the relative atomic weights of the elements. For example, knowing that 12 ounces of carbon combine with 16 ounces of oxygen to form carbon monoxide, Dalton could deduce that the ratio of the weight of a carbon atom to the weight of an oxygen atom must be 12/16. His table of relative atomic weights contained some errors, but the principle which he used in constructing it was not only correct, but also very important.

## 7.2 Gay-Lussac and Avogadro

In 1808, John Dalton published his table of atomic weights in a book entitled *A New System of Chemical Philosophy*. A year later, in 1809, the celebrated French chemist and balloonist, Joseph Louis Gay-Lussac (1778-1850), made public an important law concerning

the chemical reactions of gases: Gay-Lussac's experiments showed that the volumes of the reactants and the volumes of the products were related to each other by the ratios of simple whole numbers.

This law was strikingly similar to Proust's law of definite proportions by weight, on which Dalton had based his table of relative atomic weights. Gay-Lussac stated that his results were "very favorable to Dalton's ingenious ideas"; but there were problems in linking Dalton's ideas with Gay-Lussac's experiments.

Observation showed, for example, that one volume of hydrogen gas would unite with exactly the same volume of chlorine gas to form the gas of hydrochloric acid. The problem was that, if the temperature and pressure were kept constant, the resulting total volume of gas was the same after the reaction as before, although according to Dalton's ideas the number of particles should be cut in half!

This was a mystery which Dalton and Gay-Lussac failed to solve; but it was completely cleared up a year later, in 1810, by Amadeo Avogadro (1776-1856), Count of Quaregna and Professor of Philosophy at the University of Vercelli in Italy. Avogadro introduced a bold hypothesis - that a standard volume of any gas whatever, at room temperature and atmospheric pressure, contains a number of particles which is the same for every gas.

(Avogadro himself did not have any idea how many gas particles there are in a liter of gas; but we now know that at room temperature and atmospheric pressure, 22.4 liters contain 602,600,000,000,000,000,000 particles. This is the same as the number of atoms in a gram of hydrogen. To get some imaginative idea of the size of "Avogadro's number", we can think of the fact that the number of atoms in a drop of water is roughly the same as the number of drops of water in all the oceans in the world!)

Avogadro believed that the particles of a gas need not be single atoms, even if the gas contains only a single element. In this way, he could explain the mysterious proportions of volume observed by Gay-Lussac. for example, in the reaction where hydrogen and chlorine combine to form hydrochloric acid, Avogadro assumed that every molecule of hydrogen gas consist of two atoms joined together, and similarly, every molecule of chlorine gas consist of two atoms. Then, in the reaction in which hydrochloric acid is formed, the total number of molecules is not changed by the reaction, which fits with Gay-Lussac's observation that the volume occupied by the gasses is unchanged.

Although Avogadro completely solved the problem of reconciling Dalton's atomic ideas with Gay-Lussac's volume ratios, there was a period of 50 years during which most chemists ignored the atomic theories of Dalton and Avogadro. However, it hardly mattered that the majority of chemists where unconvinced, since the greatest chemist of the period, Jöns Jacob Berzelius (1779-1849), was an ardent disciple of Dalton's atomism. His belief more that made up for the other chemists' disbelief!



Figure 7.3: Count Amedeo Avogadro (1776-1856). Avogadro's law states that equal volumes of gases under the same conditions of temperature and pressure will contain the same number of gas molecules. Avogadro's number,  $6.02214076 \times 10^{23}$ , the number of particles in a *mole* of any substance, is named after him.

## 7.3 Berzelius: atomic weights; electronegativity

After studying medicine at the University of Uppsala in Sweden, Berzelius became a chemist; and over a period of ten years, between 1807 and 1817, he analyzed more than two thousand different chemical reactions. He showed that all these reactions follow Proust's law of definite proportions by weight. He also continued Dalton's work on relative atomic weights; and in 1828 he published the first reasonably accurate table of these weights.

Berzelius discovered and isolated several new elements, including cerium and thorium. He showed that by means of an electrochemical cell, elements could be divided into two types, according to the pole of the cell towards which they were attracted. He deduced from this that the forces holding atoms together in a molecule must be electrical in nature. Berzelius also invented modern chemical notation for molecules, in which the number of each species of atom is denoted by a subscript.



Figure 7.4: Jöns Jacob Berzelius (1779-1848).



Figure 7.5: **A monument to Berzelius in the center of Berzelii Park, Stockholm.**



Figure 7.6: A stamp from Grenada.



Figure 7.7: A Swedish stamp.



Figure 7.8: Some of the achievements of Berzelius.



Figure 7.9: Elements discovered by Berzelius.

## 7.4 The Karlsruhe Congress

Unfortunately, although Berzelius was a follower of Dalton, he did not appreciate the value of Avogadro's ideas; and therefore confusion about the distinction between atoms and molecules remained to plague chemistry until 1860. In that year, the first international scientific congress in history was held at Karlsruhe, Baden, to try to clear up the confusion about atomic weights. By that time, Dalton's atomic theory was widely accepted, but without Avogadro's clarifying ideas, it led to much confusion. In fact, the chemists of the period were almost at one another's throats, arguing about the correct chemical formulas for various compounds.

Among the delegates at the Karlsruhe Congress was the fiery Italian chemist, Stanislao Cannizzaro (1826-1910). He had been a revolutionist in 1848, and he was later to fight in the army of Garibaldi for the unification of Italy. Cannizzaro had read Avogadro's almost-forgotten papers; and he realized that Avogadro's hypothesis, together with Gay-Lussac's volume ratios, could be used to determine atomic weights unambiguously. He went to the congress filled with missionary zeal; and as a result of his efforts, most of the other delegates saw the light. One of the delegates, Lothar Meyer, said later: "The scales suddenly fell from my eyes, and they were replaced by a feeling of peaceful certainty."

Neither John Dalton nor Amadeo Avogadro lived to see the triumph of their theories at Karlsruhe, but towards the end of his life, John Dalton was much honored. He was given an honorary degree by Oxford University, invited to soirées by the Duke of Sussex, and presented to King William IV of England.

The presentation to the king involved some difficulty, since Dalton was forbidden by his Quaker religion to wear the sword required for court dress. Therefore it was arranged that he should be presented to the king wearing crimson academic robes from Oxford; but here again there was a difficulty: Bright colors were inconsistent with the simple clothes required by the Quakers. Dalton solved this problem by wearing the crimson robes anyway, and saying that he was colorblind, which was perfectly true!

## Suggestions for further reading

1. Frank Greenaway, *John Dalton and the Atom*, Heinemann, London (1966).
2. Sir Basil Schonland, *The Atomists, 1805-1933*, Clarendon Press, Oxford (1968).
3. F.J. Moore, *A History of Chemistry*, McGraw-Hill (1939).
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# Chapter 8

## DAVY AND FARADAY

### 8.1 Galvani and Volta

While Dalton's atomic theory was slowly gaining ground in chemistry, the world of science was electrified (in more ways than one) by the discoveries of Franklin, Galvani, Volta, Ørsted, Ampère, Coulomb and Faraday.

A vogue for electrical experiments had been created by the dramatic experiments of Benjamin Franklin (1706-1790), who drew electricity from a thundercloud, and thus showed that lightning is electrical in nature. Towards the end of the 18th century, almost every scientific laboratory in Europe contained some sort of machine for generating static electricity. Usually these static electricity generators consisted of a sphere of insulating material which could be turned with a crank and rubbed, and a device for drawing off the accumulated static charge. Even the laboratory of the Italian anatomist, Luigi Galvani (1737-1798), contained such a machine; and this was lucky, since it led indirectly to the invention of the electric battery.

In 1771, Galvani noticed that some dissected frog's legs on his work table twitched violently whenever they were touched with a metal scalpel while his electrostatic machine was running. Since Franklin had shown lightning to be electrical, it occurred to Galvani to hang the frog's legs outside his window during a thunderstorm. As he expected, the frog's legs twitched violently during the thunderstorm, but to Galvani's surprise, they continued to move even after the storm was over. By further experimentation, he found that what made the frog's legs twitch was a closed electrical circuit, involving the brass hook from which they were hanging, and the iron lattice of the window.

Galvani mentioned these experiments to his friend, the physicist Alessandro Volta (1745-1827). Volta was very much interested, but he could not agree with Galvani about the source of the electrical current which was making the frog's legs move. Galvani thought that the current was "animal electricity", coming from the frog's legs themselves, while Volta thought that it was the two different metals in the circuit which produced the current.

The argument over this question became bitter, and finally destroyed the friendship between the two men. Meanwhile, to prove his point, Volta constructed the first electrical

battery. This consisted of a series of dishes containing salt solution, connected with each other by bridges of metal. One end of each bridge was made of copper, while the other end was made of zinc. Thus, as one followed the circuit, the sequence was: copper, zinc, salt solution, copper, zinc, salt solution, and so on.

Volta found that when a closed circuit was formed by such an arrangement, a steady electrical current flowed through it. The more units connected in series in the battery, the stronger was the current. He next constructed a more compact arrangement, which came to be known as the “Voltaic pile”. Volta’s pile consisted of a disc of copper, a disc of zinc, a disc of cardboard soaked in salt solution, another disc of copper, another disc of zinc, another disc of cardboard soaked in salt solution, and so on. The more elements there were in the pile, the greater was the electrical potential and current which it produced.

The invention of the electric battery lifted Volta to a peak of fame where he remained for the rest of his life. He was showered with honors and decorations, and invited to demonstrate his experiments to Napoleon, who made him a count and a senator of the Kingdom of Lombardy. When Napoleon fell from power, Volta adroitly shifted sides, and he continued to receive honors as long as he lived.

In 1819, the Danish physicist, Hans Christian Ørsted (1777-1851), was demonstrating to his students the electrical current produced by a Voltaic pile. Suspecting some connection between electricity and magnetism, he brought a compass needle near to the wire carrying the current. To his astonishment, the needle turned from north, and pointed in a direction perpendicular to the wire. When he reversed the direction of the current, the needle pointed in the opposite direction.

Ørsted’s revolutionary discovery of a connection between electricity and magnetism was extended in France by André Marie Ampère (1775-1836). Ampère showed that two parallel wires, both carrying current, repel each other if the currents are in the same direction, but they attract each other if the currents are opposite. He also showed that a helical coil of wire carrying a current produces a large magnetic field inside the coil; and the more turns in the coil, the larger the field.

## 8.2 Sir Humphry Davy

News of the Voltaic pile spread like wildfire throughout Europe and started a series of revolutionary experiments both in physics and in chemistry. On March 20, 1800, Sir Joseph Banks, the President of the Royal Society, received a letter from Volta explaining the method of constructing batteries. On May 2 of the same year, the English chemist, William Nicholson (1755-1815), (to whom Banks had shown the letter), used a Voltaic pile to separate water into hydrogen and oxygen.

Shortly afterwards, the brilliant young English chemist, Sir Humphrey Davy (1778-1829), constructed a Voltaic pile with more than two hundred and fifty metal plates. On October 6, 1807, he used this pile to pass a current through molten potash, liberating a previously unknown metal, which he called potassium. During the year 1808, he isolated barium, strontium, calcium, magnesium and boron, all by means of Voltaic currents.



Figure 8.1: Sir Humphry Davy (1778-1829).

### 8.3 Michael Faraday

The electrochemical experiments of Davy, and the electromagnetic discoveries of Ørsted and Ampère, were further developed by the great experimental physicist and chemist, Michael Faraday (1791-1867). He was one of ten children of a blacksmith, and as a boy, he had little education. At the age of 14, he was sent out to work, apprenticed to a London bookbinder. Luckily, the bookbinder sympathized with his apprentice's desire for an education, and encouraged him to read the books in the shop (outside of working hours). Faraday's favorites were Lavoisier's textbook on chemistry, and the electrical articles in the *Encyclopedia Britannica*.

In 1812, when Michael Faraday was 21 years old, a customer in the bookshop gave him tickets to attend a series of lectures at the Royal Institution, which were to be given by the famous chemist Humphry Davy. At that time, fashionable London socialites (particularly ladies) were flocking to the Royal Institution to hear Davy. Besides being brilliant, he was also extremely handsome, and his lectures, with their dramatic chemical demonstrations, were polished to the last syllable.

Michael Faraday was, of course, thrilled to be present in the glittering audience, and he took careful notes during the series of lectures. These notes, to which he added beautiful colored diagrams, came to 386 pages. He bound the notes in leather and sent them to Sir Joseph Banks, the President of the Royal Society, hoping to get a job related to science. He received no reply from Banks, but, not discouraged, he produced another version of his notes, which he sent to Humphry Davy.

Faraday accompanied his notes with a letter saying that he wished to work in science because of "the detachment from petty motives and the unselfishness of natural philosophers". Davy told him to reserve judgement on that point until he had met a few natural philosophers, but he gave Faraday a job as an assistant at the Royal Institution.

In 1818, Humphry Davy was knighted because of his invention of the miner's safety lamp. He married a wealthy and fashionable young widow, resigned from his post as Director of the Royal Institution, and set off on a two-year excursion of Europe, taking Michael Faraday with him. Lady Davy regarded Faraday as a servant; but in spite of the humiliations which she heaped on him, he enjoyed the tour of Europe and learned much from it. He met, and talked with, Europe's most famous scientists; and in a sense, Europe was his university.

Returning to England, the modest and devoted Faraday finally rose to outshine Sir Humphry Davy, and he became Davy's successor as Director of the Royal Institution. Faraday showed enormous skill, intuition and persistence in continuing the electrical and chemical experiments begun by Davy.

In 1821, a year after H.C. Ørsted's discovery of the magnetic field surrounding a current-carrying wire, Michael Faraday made the first electric motor. His motor was simply a current-carrying wire, arranged so that it could rotate around the pole of a magnet; but out of this simple device, all modern electrical motors have developed. When asked what use his motor was, Faraday replied: "What use is a baby?"

Ørsted had shown that electricity could produce magnetism; and Faraday, with his



Figure 8.2: Michael Faraday in a portrait by Thomas Phillips.

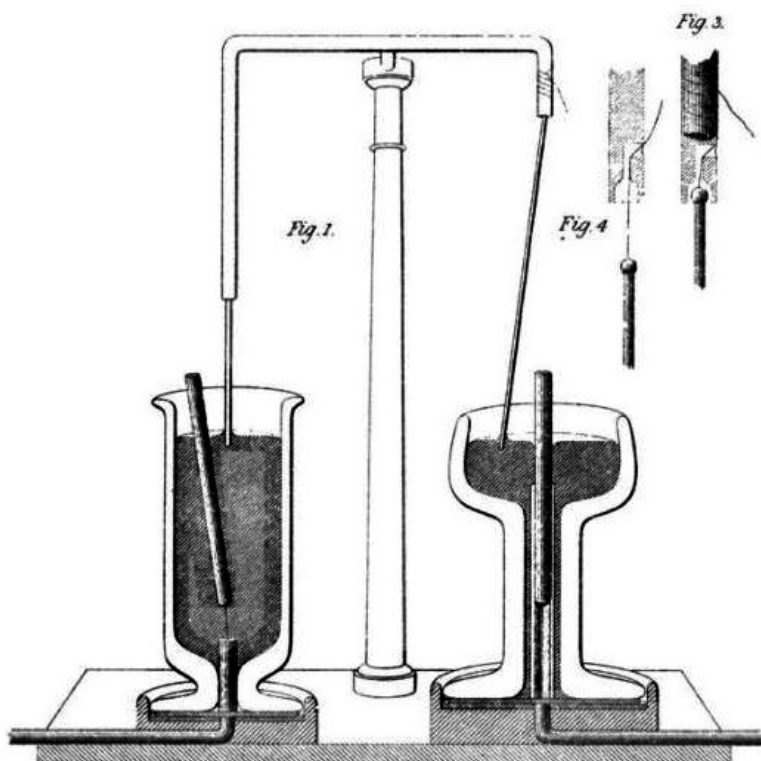


Figure 8.3: Faraday's experiment showing that an electric current could produce mechanical rotation in a magnetic field. This was the first electric motor! On the right side of the figure, a current-carrying rod rotates about a fixed magnet in a pool of mercury. On the left, the rod is fixed and the magnet rotates.

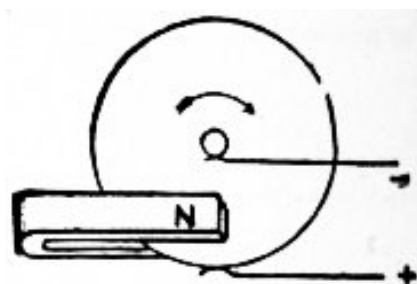


Figure 8.4: Faraday also showed that a copper disc, rotating between the poles of a magnet could produce an electric current.

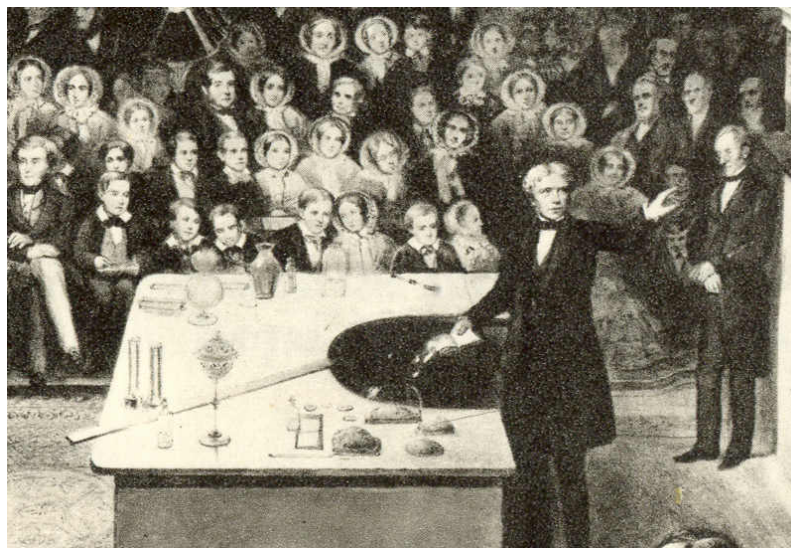


Figure 8.5: A Christmas lecture at the Royal Institution by Michael Faraday.

strong intuitive grasp of the symmetry of natural laws, believed that the relationship could be reversed. He believed that magnetism could be made to produce electricity. In 1822, he wrote in his notebook: “Convert magnetism to electricity”. For almost ten years, he tried intermittently to produce electrical currents with strong magnetic fields, but without success. Finally, in 1831, he discovered that a *changing* magnetic field would produce a current.

Faraday had wrapped two coils of wire around a soft iron ring; and he discovered that at precisely the instant when he started a current flowing in one of the coils, a momentary current was induced in the other coil. When he stopped the current in the first coil, so that the magnetic field collapsed, a momentary current in the opposite direction was induced in the second coil.

Next, Faraday tried pushing a permanent magnet in and out of a coil of wire; and he found that during the time when the magnet was in motion, so that the magnetic field in the coil was changing, a current was induced in the coil. Finally, Faraday made the first dynamo in history by placing a rotating copper disc between the poles of a magnet. He demonstrated that when the disc rotated, an electrical current flowed through a circuit connecting the center with the edge. He also experimented with static electricity, and showed that insulating materials become polarized when they are placed in an electric field.

Faraday continued the experiments on electrolysis begun by Sir Humphry Davy. He showed that when an electrical current is passed through a solution, the quantities of the chemical elements liberated at the anode and cathode are directly proportional to the total electrical charge passed through the cell, and inversely proportional to the valence of the elements. He realized that these laws of electrolysis supported Dalton’s atomic hypothesis, and that they also pointed to the existence of an indivisible unit of electrical charge.

Faraday believed (correctly) that light is an electromagnetic wave; and to prove the connection of light with the phenomena of electricity and magnetism, he tried for many years to change light by means of electric and magnetic fields. Finally, towards the end of his career, he succeeded in rotating the plane of polarization of a beam of light passing through a piece of heavy glass by placing the glass in a strong magnetic field. This phenomenon is now known as the "Faraday effect".

Because of his many contributions both to physics and to chemistry (including the discovery of benzene and the first liquefaction of gases), and especially because of his contributions to electromagnetism and electrochemistry, Faraday is considered to be one of the greatest masters of the experimental method in the history of science. He was also a splendid lecturer. Fashionable Londoners flocked to hear his discourses at the Royal Institution, just as they had flocked to hear Sir Humphry Davy. Prince Albert, Queen Victoria's husband, was in the habit of attending Faraday's lectures, bringing with him Crown Prince Edward (later Edward VII).

As Faraday grew older, his memory began to fail, probably because of mercury poisoning. Finally, his unreliable memory forced him to retire from scientific work. He refused both an offer of knighthood and the Presidency of the Royal Society, remaining to the last the simple, modest and devoted worker who had first gone to assist Davy at the Royal Institution.

## Suggestions for further reading

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3. E.T. Whittaker, *A History of the Aether and Electricity*, Cambridge University Press (1953).
4. D.K.C. Macdonald, *Faraday, Maxwell and Kelvin*, Heinemann, London (1964).
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# Chapter 9

## BOLTZMANN, GIBBS AND ARRHENIUS

### 9.1 The second law of thermodynamics

The second law of thermodynamics was discovered by Nicolas Leonard Sadi Carnot (1796-1832) and elaborated by Rudolf Clausius (1822-1888) and William Thomson (later Lord Kelvin, 1824-1907). Carnot came from a family of distinguished French politicians and military men, but instead of following a political career, he studied engineering. In 1824, his only scientific publication appeared - a book with the title *Reflections on the Motive Power of Fire*. Although it was ignored for the first few years after its publication, this single book was enough to secure Carnot a place in history as the founder of the science of thermodynamics. In his book, Carnot introduced a scientific definition of work which we still use today - “weight lifted through a height”; in other words, force times distance.

At the time when Carnot was writing, much attention was being given to improving the efficiency of steam engines. Although James Watt’s steam engines were far more efficient than previous models, they still could only convert between 5 % and 7 % of the heat energy of their fuels into useful work. Carnot tried to calculate the theoretical maximum of the efficiency of steam engines, and he was able to show that an engine operating between the temperatures  $T_1$  and  $T_2$  could at most attain

$$\text{maximum efficiency} = \frac{T_1 - T_2}{T_1} \quad (9.1)$$

Here  $T_1$  is the temperature of the input steam, and  $T_2$  is the temperature of the cooling water. Both these temperatures are absolute temperatures, i.e., temperatures proportional to the volume of a given quantity of gas at constant pressure.

Carnot died of cholera at the age of 36. Fifteen years after his death, the concept of absolute temperature was further clarified by Lord Kelvin (1824-1907), who also helped to bring Carnot’s work to the attention of the scientific community.

Building on the work of Carnot, the German theoretical physicist Rudolph Clausius was able to deduce an extremely general law. He discovered that the ratio of the heat

content of a closed system to its absolute temperature always increases in any process. He called this ratio the entropy of the system. In the notation of modern thermodynamics, the change in entropy  $dS$  when a small amount of heat  $dq$  is transferred to a system is given by

$$dS = \frac{dq}{dT} \quad (9.2)$$

Let us imagine a closed system consisting of two parts, one at temperature  $T_1$ , and the other part at a lower temperature  $T_2$ . If a small amount of heat  $dq$  flows from the warmer part to the cooler one, the small resulting change in entropy of the total system will be

$$dS = \frac{dq}{T_1} - \frac{dq}{T_2} > 0 \quad (9.3)$$

According to Clausius, since heat never flows spontaneously from a colder object to a warmer one, the entropy of a closed system always increases; that is to say,  $dS$  is always positive. As heat continues to flow from the warmer part of the system to the cooler part, the system's energy becomes less and less available for doing work. Finally, when the two parts have reached the same temperature, no work can be obtained. When the parts differed in temperature, a heat engine could in principle be run between them, making use of the temperature difference; but when the two parts have reached the same temperature, this possibility no longer exists. The law stating that the entropy of a closed system always increases is called the second law of thermodynamics.

## 9.2 Statistical mechanics

Besides his monumental contributions to electromagnetic theory, the English physicist James Clerk Maxwell (1831-1879) also helped to lay the foundations of statistical mechanics. In this enterprise, he was joined by the Austrian physicist Ludwig Boltzmann (1844-1906) and by an American, Josiah Willard Gibbs, whom we will discuss later.

As a young student, Boltzmann read Maxwell's paper on the velocity distributions of molecules in a gas, and he spent the remainder of his life developing these Maxwell's initiative into the science of statistical mechanics. Boltzmann was able to derive the following equation hold for the particles in a perfect (non-interacting) gas:

$$\frac{n_i}{N} = \frac{e^{-\epsilon_i/kT}}{\sum_i e^{-\epsilon_i/kT}} \quad (9.4)$$

Here  $n_i$  represents the number of particles in a state with energy  $\epsilon_i$ , while  $N$  is the total number of particles.  $T$  is the absolute temperature, and  $k$ , which is called *Boltzmann's constant*, has a dimension such that the dimension of  $kT$  is energy.

Like Maxwell, Boltzmann also interpreted an increase in entropy as an increase in disorder; and like Maxwell he was a firm believer in atomism at a time when this belief was by no means universal. For example, Ostwald and Mach, both important figure in

German science at that time, refused to believe in the existence of atoms, in spite of the fact that Dalton's atomic ideas had proved to be so useful in chemistry. Towards the end of his life, Boltzmann suffered from periods of severe depression, perhaps because of attacks on his scientific work by Ostwald and others. In 1906, while on vacation near Trieste, he committed suicide - ironically, just a year before the French physicist J.B. Perrin produced irrefutable evidence of the existence of atoms.

When a system is in thermodynamic equilibrium, its entropy has reached a maximum; but if it is not in equilibrium, its entropy has a lower value. For example, let us think of the case which was studied by Clausius when he introduced the concept of entropy: Clausius imagined an isolated system, divided into two parts, one of which has a temperature  $T_1$ , and the other a lower temperature,  $T_2$ . When heat is transferred from the hot part to the cold part, the entropy of the system increases; and when equilibrium is finally established at some uniform intermediate temperature, the entropy has reached a maximum. The difference in entropy between the initial state of Clausius' system and its final state is a measure of how far away from thermodynamic equilibrium it was initially. From the discussion given above, we can see that it is also possible to interpret this entropy difference as the system's initial content of thermodynamic information.

Similarly, when a photon from the sun reaches (for example) a drop of water on the earth, the initial entropy of the system consisting of the photon plus the drop of water is smaller than at a later stage, when the photon's energy has been absorbed and shared among the water molecules, with a resulting very slight increase in the temperature of the water. This entropy difference can be interpreted as the quantity of thermodynamic information which was initially contained in the photon-drop system, but which was lost when the photon's free energy was degraded into heat. Equation (4.32) allows us to express this entropy difference in terms of bits. For example, if the photon energy is 2 electronvolts, and if the water drop is at a temperature of 298.15 degrees Kelvin, then  $\Delta S = 112.31$  bits; and this amount of thermodynamic information is available in the initial state of the system. In our example, the information is lost; but if the photon had instead reached the leaf of a plant, part of its energy, instead of being immediately degraded, might have been stabilized in the form of high-energy chemical bonds. When a part of the photon energy is thus stabilized, not all of the thermodynamic information which it contains is lost; a part is conserved and can be converted into other forms of information.



Figure 9.1: The English physicist James Clerk Maxwell (1831-1879). Together with Ludwig Boltzmann, he was one of the founders of statistical mechanics. Maxwell took the first step in a paper on the velocity distributions of molecules in a gas.



Figure 9.2: The Austrian physicist Ludwig Boltzmann (1844-1906), the co-founder of statistical mechanics. As a young student, Boltzmann read Maxwell's paper on velocity distributions, and he spent the remainder of his life developing these ideas into the science of statistical mechanics.

### 9.3 Gibbs free energy

At the beginning of this chapter, we mentioned that the American physicist Josiah Willard Gibbs (1839-1903) made many contributions to thermodynamics and statistical mechanics. In 1863, Gibbs received from Yale the first Ph.D. in engineering granted in America, and after a period of further study in France and Germany, he became a professor of mathematical physics at Yale in 1871, a position which he held as long as he lived. During the period between 1876 and 1878, he published a series of papers in the *Transactions of the Connecticut Academy of Sciences*. In these papers, about 400 pages in all, Gibbs applied thermodynamics to chemical reactions. (The editors of the *Transactions of the Connecticut Academy of Sciences* did not really understand Gibbs' work, but, as they said later, "We knew Gibbs, and we took his papers on faith".)

Because the journal was an obscure one, and because Gibbs' work was so highly mathematical, it remained almost unknown to European scientists for a long period. However, in 1892 Gibbs' papers were translated into German by Ostwald, and in 1899 they were translated into French by Le Chatelier; and then the magnitude of Gibbs' contribution was finally recognized. One of his most important innovations was the definition of a quantity which we now call "Gibbs free energy". This quantity allows one to determine whether or not a chemical reaction will take place spontaneously.

Chemical reactions usually take place at constant pressure and constant temperature. If a reaction produces a gas as one of its products, the gas must push against the pressure of the earth's atmosphere to make a place for itself. In order to take into account the work done against external pressure in energy relationships, the German physiologist and physicist Hermann von Helmholtz introduced a quantity (which we now call heat content or enthalpy) defined by

$$H = U + PV \quad (9.5)$$

where  $U$  is the internal energy of a system,  $P$  is the pressure, and  $V$  is the system's volume.

Gibbs went one step further than Helmholtz, and defined a quantity which would also take into account the fact that when a chemical reaction takes place, heat is exchanged with the surroundings. Gibbs defined his free energy by the relation

$$G = U + PV - TS \quad (9.6)$$

or

$$G = H - TS \quad (9.7)$$

where  $S$  is the entropy of a system,  $H$  is its enthalpy, and  $T$  is its temperature.

Gibbs' reason for introducing the quantity  $G$  is as follows: The second law of thermodynamics states that in any spontaneous process, the entropy of the universe increases. Gibbs invented a simple model of the universe, consisting of the system (which might, for example, be a beaker within which a chemical reaction takes place) in contact with a large thermal reservoir at constant temperature. The thermal reservoir could, for example, be a water bath so large that whatever happens in the chemical reaction, the temperature of

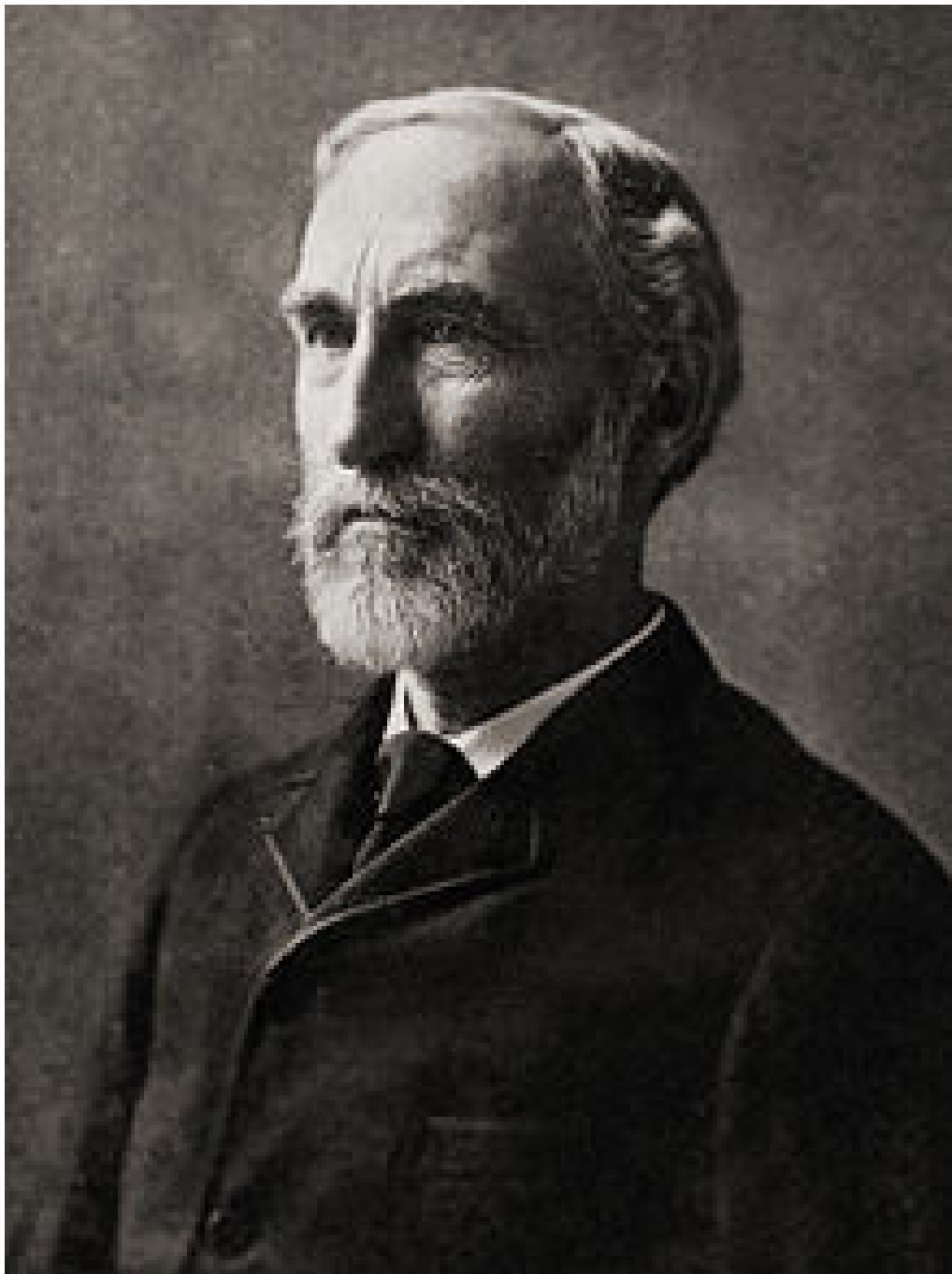


Figure 9.3: Josiah Willard Gibbs (1839-1903). He found a way to apply thermodynamics to chemistry.

the bath will remain essentially unaltered. In Gibbs' simplified model, the entropy change of the universe produced by the chemical reaction can be split into two components:

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{bath} \quad (9.8)$$

Now suppose that the reaction is endothermic (i.e. it absorbs heat). Then the reaction beaker will absorb an amount of heat  $\Delta H_{system}$  from the bath, and the entropy change of the bath will be

$$\Delta S_{bath} = -\frac{\Delta H_{system}}{T} \quad (9.9)$$

Combining (4.36) and (4.37) with the condition requiring the entropy of the universe to increase, Gibbs obtained the relationship

$$\Delta S_{universe} = \Delta S_{system} - \frac{\Delta H_{system}}{T} > 0 \quad (9.10)$$

The same relationship also holds for exothermic reactions, where heat is transferred in the opposite direction. Combining equations (4.38) and (4.35) yields

$$\Delta G_{system} = -T\Delta S_{universe} < 0 \quad (9.11)$$

Thus, the Gibbs free energy for a system must decrease in any spontaneous chemical reaction or process which takes place at constant temperature and pressure. We can also see from equation (4.39) that Gibbs free energy is a measure of a system's content of thermodynamic information. If the available free energy is converted into heat, the quantity of thermodynamic information  $\Delta S_{universe} = -\Delta G_{system}/T$  is lost, and we can deduce that in the initial state of the system, this quantity of information was available. Under some circumstances the available thermodynamic information can be partially conserved. In living organisms, chemical reactions are coupled together, and Gibbs free energy, with its content of thermodynamic information, can be transferred from one compound to another, and ultimately converted into other forms of information.

Measured values of the "Gibbs free energy of formation",  $\Delta G_f^\circ$ , are available for many molecules. To construct tables of these values, the change in Gibbs free energy is measured when the molecules are formed from their constituent elements. The most stable states of the elements at room temperature and atmospheric pressure are taken as zero points. For example, water in the gas phase has a Gibbs free energy of formation

$$\Delta G_f^\circ(H_2O) = -228.59 \frac{\text{kJ}}{\text{mol}} \quad (9.12)$$

This means that when the reaction



takes place under standard conditions, there is a change in Gibbs free energy of  $\Delta G^\circ = -228.59 \text{ kJ/mol}$ <sup>1</sup>. The elements hydrogen and oxygen in their most stable states at room

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<sup>1</sup> The superscript  $^\circ$  means "under standard conditions", while kJ is an abbreviation for joule $\times 10^3$ .

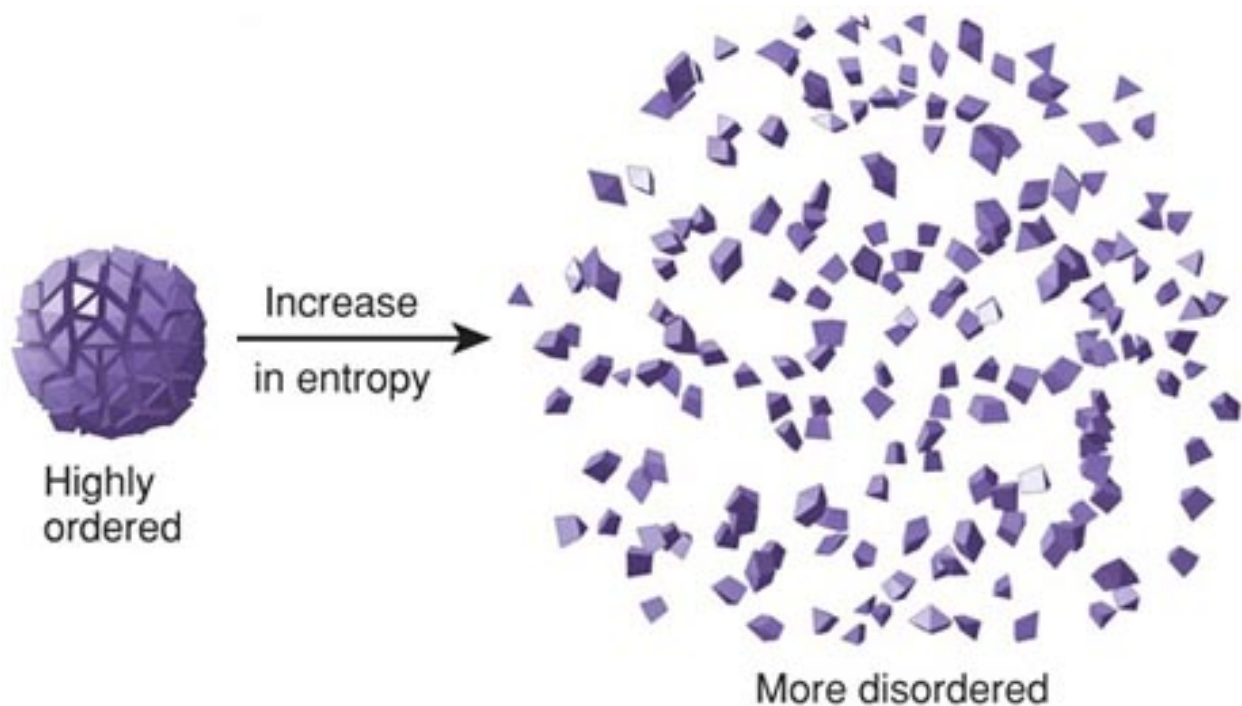


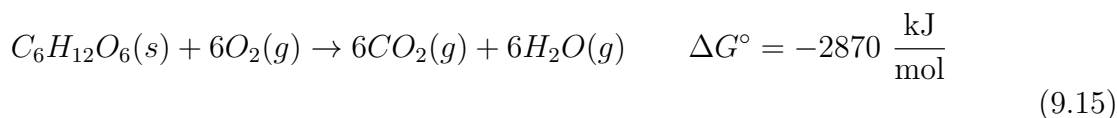
Figure 9.4: According to the second law of thermodynamics, the entropy of the universe constantly increases. Increase of entropy corresponds to increase of disorder, and also to increase of statistical probability. Living organisms on the earth are able to achieve a high degree of order and highly improbable structures because the earth is not a closed system. It constantly receives free energy (i.e. energy capable of doing work) from the sun, and this free energy can be thought of as carrying thermodynamic information, or “negative entropy”.

temperature and atmospheric pressure are taken as the zero points for Gibbs free energy of formation. Since  $\Delta G^\circ$  is negative for the reaction shown in equation (4.41), the reaction is spontaneous. In general, the change in Gibbs free energy in a chemical reaction is given by

$$\Delta G^\circ = \sum_{\text{products}} \Delta G_f^\circ - \sum_{\text{reactants}} \Delta G_f^\circ \quad (9.14)$$

where  $\Delta G_f^\circ$  denotes the Gibbs free energy of formation.

As a second example, we can consider the reaction in which glucose is burned:



From equation (4.29) it follows that in this reaction,

$$-\frac{\Delta G^\circ}{T} = 1670 \frac{\text{bits}}{\text{molecule}} \quad (9.16)$$

If the glucose is simply burned, this amount of information is lost; but in a living organism, the oxidation of glucose is usually coupled with other reactions in which a part of the available thermodynamic information is stored, or utilized to do work, or perhaps converted into other forms of information.

The oxidation of glucose illustrates the importance of enzymes and specific coupling mechanisms in biology. A lump of glucose can sit for years on a laboratory table, fully exposed to the air. Nothing will happen. Even though the oxidation of glucose is a spontaneous process - even though the change in Gibbs free energy produced by the reaction would be negative - even though the state of the universe after the reaction would be much more probable than the initial state, the reaction does not take place, or at least we would have to wait an enormously long time to see the glucose oxidized, because the reaction pathway is blocked by potential barriers.

Now suppose that the lump of glucose is instead eaten by a girl working in the laboratory. (She likes sweet things, and can't resist eating a lump of sugar when she sees one.) In her body, the glucose will be oxidized almost immediately, because enzymes will lower the potential barriers along the reaction path. However, only part of the available free energy, with its content of thermodynamic information, will be degraded into heat. A large part will be coupled to the synthesis of ATP in the girl's mitochondria. The high-energy phosphate bonds of the ATP molecules will carry the available thermodynamic information further. In the end, a large part of the free energy made available by the glucose oxidation will be used to drive molecular machinery and to build up the statistically unlikely (information-containing) structures of the girl's body.

## What is life?

*What is Life?* That was the title of a small book published by the physicist Erwin Schrödinger in 1944. Schrödinger (1887-1961) was born and educated in Austria. In

1926 he shared the Nobel Prize in Physics<sup>2</sup> for his contributions to quantum theory (wave mechanics). Schrödinger's famous wave equation is as fundamental to modern physics as Newton's equations of motion are to classical physics.

When the Nazis entered Austria in 1938, Schrödinger opposed them, at the risk of his life. To escape arrest, he crossed the Alps on foot, arriving in Italy with no possessions except his knapsack and the clothes which he was wearing. He traveled to England; and in 1940 he obtained a position in Ireland as Senior Professor at the Dublin Institute for Advanced Studies. There he gave a series of public lectures upon which his small book is based.

In his book, *What is Life?*, Schrödinger developed the idea that a gene is a very large information-containing molecule which might be compared to an aperiodic crystal. He also examined in detail the hypothesis (due to Max Delbrück) that X-ray induced mutations of the type studied by Hermann Muller can be thought of as photo-induced transitions from one isomeric conformation of the genetic molecule to another. Schrödinger's book has great historic importance, because Francis Crick (whose education was in physics) was one of the many people who became interested in biology as a result of reading it. Besides discussing what a gene might be in a way which excited the curiosity and enthusiasm of Crick, Schrödinger devoted a chapter to the relationship between entropy and life.

"What is that precious something contained in our food which keeps us from death? That is easily answered," Schrödinger wrote, "Every process, event, happening - call it what you will; in a word, everything that is going on in Nature means an increase of the entropy of the part of the world where it is going on. Thus a living organism continually increases its entropy - or, as you may say, produces positive entropy, which is death. It can only keep aloof from it, i.e. alive, by continually drawing from its environment negative entropy - which is something very positive as we shall immediately see. What an organism feeds upon is negative entropy. Or, to put it less paradoxically, the essential thing in metabolism is that the organism succeeds in freeing itself from all the entropy it cannot help producing while alive..."<sup>3</sup>

"Entropy, taken with a negative sign, is itself a measure of order. Thus the device by which an organism maintains itself stationary at a fairly high level of orderliness (= fairly low level of entropy) really consists in continually sucking orderliness from its environment. This conclusion is less paradoxical than it appears at first sight. Rather it could be blamed for triviality. Indeed, in the case of higher animals we know the kind of orderliness they feed upon well enough, viz. the extremely well-ordered state of matter state in more or less complicated organic compounds which serve them as foodstuffs. After utilizing it, they return it in a very much degraded form - not entirely degraded, however, for plants can still make use of it. (These, of course, have their most powerful source of 'negative entropy' in the sunlight.)" At the end of the chapter, Schrödinger added a note in which he said that if he had been writing for physicists, he would have made use of the concept of free energy;

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<sup>2</sup> with P.A.M. Dirac

<sup>3</sup> The Hungarian-American biochemist Albert Szent-Györgyi, who won a Nobel prize for isolating vitamin C, and who was a pioneer of Bioenergetics, expressed the same idea in the following words: "We need energy to fight against entropy".

but he judged that this concept might be difficult or confusing for a general audience.

In the paragraphs which we have quoted, Schrödinger focused on exactly the aspect of life which is the main theme of the present book: All living organisms draw a supply of thermodynamic information from their environment, and they use it to “keep aloof” from the disorder which constantly threatens them. In the case of animals, the information-containing free energy comes in the form of food. In the case of green plants, it comes primarily from sunlight. The thermodynamic information thus gained by living organisms is used by them to create configurations of matter which are so complex and orderly that the chance that they could have arisen in a random way is infinitesimally small.

John von Neumann invented a thought experiment which illustrates the role which free energy plays in creating statistically unlikely configurations of matter. Von Neumann imagined a robot or automaton, made of wires, electrical motors, batteries, etc., constructed in such a way that when floating on a lake stocked with its component parts, it will reproduce itself.<sup>4</sup> The important point about von Neumann’s automaton is that it requires a source of free energy (i.e., a source of energy from which work can be obtained) in order to function. We can imagine that the free energy comes from electric batteries which the automaton finds in its environment. (These are analogous to the food eaten by animals.) Alternatively we can imagine that the automaton is equipped with photocells, so that it can use sunlight as a source of free energy, but it is impossible to imagine the automaton reproducing itself without some energy source from which work can be obtained to drive its reproductive machinery. If it could be constructed, would von Neumann’s automaton be alive? Few people would say yes. But if such a self-reproducing automaton could be constructed, it would have some of the properties which we associate with living organisms.

The autocatalysts which are believed to have participated in molecular evolution had some of the properties of life. They used “food” (i.e., energy-rich molecules in their environments) to reproduce themselves, and they evolved, following the principle of natural selection. The autocatalysts were certainly precursors of life, approaching the borderline between non-life and life.

Is a virus alive? We know, for example, that the tobacco mosaic virus can be taken to pieces. The proteins and RNA of which it is composed can be separated, purified, and stored in bottles on a laboratory shelf. At a much later date, the bottles containing the separate components of the virus can be taken down from the shelf and incubated together, with the result that the components assemble themselves in the correct way, guided by steric and electrostatic complementarity. New virus particles are formed by this process of autoassembly, and when placed on a tobacco leaf, the new particles are capable of reproducing themselves. In principle, the stage where the virus proteins and RNA are purified and placed in bottles could be taken one step further: The amino acid sequences of the proteins and the base sequence of the RNA could be determined and written down.

Later, using this information, the parts of the virus could be synthesized from amino acids and nucleotides. Would we then be creating life? Another question also presents

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<sup>4</sup> In Chapter 8 we will return to von Neumann’s self-replicating automaton and describe it in more detail.

itself: At a certain stage in the process just described, the virus seems to exist only in the form of information - the base sequence of the RNA and the amino acid sequence of the proteins. Can this information be thought of as the idea of the virus in the Platonic sense? (Pythagoras would have called it the “soul” of the virus.) Is a computer virus alive? Certainly it is not so much alive as a tobacco mosaic virus. But a computer virus can use thermodynamic information (supplied by an electric current) to reproduce itself, and it has a complicated structure, containing much cybernetic information.

Under certain circumstances, many bacteria form spores, which do not metabolize, and which are able to exist without nourishment for very long periods - in fact for millions of years. When placed in a medium containing nutrients, the spores can grow into actively reproducing bacteria. There are examples of bacterial spores existing in a dormant state for many millions of years, after which they have been revived into living bacteria. Is a dormant bacterial spore alive?

Clearly there are many borderline cases between non-life and life; and Aristotle seems to have been right when he said, “Nature proceeds little by little from lifeless things to animal life, so that it is impossible to determine either the exact line of demarcation, or on which side of the line an intermediate form should lie.” However, one theme seems to characterize life: It is able to convert the thermodynamic information contained in food or in sunlight into complex and statistically unlikely configurations of matter. A flood of information-containing free energy reaches the earth’s biosphere in the form of sunlight. Passing through the metabolic pathways of living organisms, this information keeps the organisms far away from thermodynamic equilibrium (“which is death”). As the thermodynamic information flows through the biosphere, much of it is degraded into heat, but part is converted into cybernetic information and preserved in the intricate structures which are characteristic of life. The principle of natural selection ensures that as this happens, the configurations of matter in living organisms constantly increase in complexity, refinement and statistical improbability. This is the process which we call evolution, or in the case of human society, progress.

## 9.4 Svante Arrhenius

Svante Augustus Arrhenius was born in Wik Castle, Sweden in 1859, the son of Svante Gustav and Carolina Thunberg Arrhenius. He was a child prodigy, who without encouragement from his parents, taught himself to read at the age of 3. As a very young child, he also became an arithmetical prodigy by watching his father add numbers in his account books.

Arrhenius started research at the University of Uppsala, but he was dissatisfied with the instruction in physics and chemistry. In 1881 he moved to the Swedish Academy of Sciences in Stockholm. There he produced a Ph.D. dissertation which focused on conductivity of electrolytes. The dissertation was so contrary to the chemical ideas of the time that it was accepted only grudgingly by the committee judging it, and Arrhenius was only granted a 4th class degree. Nevertheless, the 56 propositions put forward in the dissertation are



Figure 9.5: **Svante Arrhenius (1859-1927) was one of the main founders of physical chemistry and a pioneer of climate science. He was related to climate activist Greta Thunberg, and Greta's father is named after him.**

universally accepted today, almost entirely without modification, and they won Arrhenius the 1903 Nobel Prize in Chemistry.

Michael Faraday (1791-1867) had previously shown that charged particles, which he named “ions”, could carry an electrical current through a solution. Arrhenius developed Faraday's concept of ions by demonstrating that when salts are dissolved in water, ions are present even without an electrical current. He also defined acids to be substances which produce solutions in which  $\text{H}^+$  ions predominate, while in bases, when dissolved, produce solutions in which  $\text{OH}^-$  ions predominate.

In chemical reaction theory, Arrhenius introduced the idea of an activation energy,  $E_a$ , which can be thought of as the height of an energy barrier which must be surmounted in order for the reaction to take place. Thus most chemical reactions become more probable when the temperature  $T$  is raised, since the rapid motion of the reactants at higher temperatures can supply the energy needed to overcome the reaction barrier  $E_a$ . Arrhenius connected the concept of activation energy with the statistical mechanics of Ludwig Boltzmann (1844-1906) by means of his famous equation:

$$K = A e^{-E_a/RT}$$

In the Arrhenius equation,  $K$  is the reaction rate,  $A$  is a constant proportional to the frequency of reactant collisions with the proper orientation,  $T$  is the absolute temperature, and  $R$  is the constant that appears in the equation of state of a perfect gas,  $PV = nRT$ .

## Climate science

Wikipedia states that “In developing a theory to explain the ice ages, Arrhenius, in 1896, was the first to use basic principles of physical chemistry to calculate estimates of the extent to which increases in atmospheric carbon dioxide (CO<sub>2</sub>) will increase Earth’s surface temperature through the greenhouse effect.

“These calculations led him to conclude that human-caused CO<sub>2</sub> emissions, from fossil-fuel burning and other combustion processes, are large enough to cause global warming. This conclusion has been extensively tested, winning a place at the core of modern climate science.

“Arrhenius, in this work, built upon the prior work of other famous scientists, including Joseph Fourier, John Tyndall and Claude Pouillet. Arrhenius wanted to determine whether greenhouse gases could contribute to the explanation of the temperature variation between glacial and inter-glacial periods. Arrhenius used infrared observations of the moon - by Frank Washington Very and Samuel Pierpont Langley at the Allegheny Observatory in Pittsburgh - to calculate how much of infrared (heat) radiation is captured by CO<sub>2</sub> and water (H<sub>2</sub>O) vapour in Earth’s atmosphere...

“Based on information from his colleague Arvid Högbom, Arrhenius was the first person to predict that emissions of carbon dioxide from the burning of fossil fuels and other combustion processes were large enough to cause global warming. In his calculation Arrhenius included the feedback from changes in water vapor as well as latitudinal effects, but he omitted clouds, convection of heat upward in the atmosphere, and other essential factors. His work is currently seen less as an accurate quantification of global warming than as the first demonstration that increases in atmospheric CO<sub>2</sub> will cause global warming, everything else being equal.”

## Suggestions for further reading

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# Chapter 10

## MENDELEEV

### 10.1 Mendeléev and the periodic table

Among the distinguished delegates listening to Cannizzaro at the Karlsruhe Congress in 1860, was the brilliant young Russian chemist, Dmitri Ivanovich Mendeléev (1834-1907). He had been born in Tobolsk, Siberia, the youngest child in a family of 14 (some accounts even say 17!). His grandfather had brought the first printing press to Siberia, and had published Siberia's first newspaper. His father had been the principal of the high-school in Tobolsk, before blindness forced his retirement. Mendeléev's mother, a part-Mongol woman of incredible energy, then set up a glass factory to support her large family.

When Mendeléev was in his teens, two disasters struck the family: His father died and the glass factory burned down. His mother then gathered her last remaining strength, and traveled to St. Petersburg, where a friend of her dead husband obtained a university place for her favorite son, Dmitri. Soon afterward, she died.

After graduating from the university at the top of his class, Dmitri Mendeléev went to Germany to do postgraduate work under Bunsen, (the inventor of the spectroscope and the "Bunsen burner"). In 1860, he attended the First International Congress of Chemistry at Karlsruhe; and like Lothar Meyer, he was profoundly impressed by Cannizzaro's views on atomic weights. In 1861, Mendeléev published a textbook entitled *Organic Chemistry*, which won him the Demidov Prize of the Petersburg Academy of Sciences.

Returning to St. Petersburg, (where he became a professor of chemistry in 1866), Mendeléev began to arrange the elements in order of their atomic weights. He soon noticed that when the elements were arranged in this way, their chemical properties showed a periodic variation. Arranged in order of their atomic weights, the first few elements were hydrogen, (helium was then unknown), lithium, beryllium, boron, carbon, nitrogen, oxygen and fluorine. Mendeléev noticed that lithium was a very active metal, with a valence (combining power) of 1; beryllium was a metal, with valence 2; boron had valence 3; and carbon had valence 4. Next came the non-metals: nitrogen with valence 3; oxygen with valence 2; and finally came fluorine, a very active non-metal with valence 1.

Continuing along the list of elements, arranged in order of their atomic weights, Mendeléev

came next to sodium, a very active metal with valence 1; magnesium, a metal with valence 2; aluminum, with valence 3; silicon, with valence 4; phosphorus, a non-metal, with valence 3; sulphur, a non-metal with valence 2; and finally chlorine, a very active non-metal with valence 1. Mendeléev realized that there is a periodicity in the chemical properties of the elements: The elements of the first period, arranged in order of increasing atomic weight, had the valences 1,2,3,4,3,2,1. The second period exhibited the same pattern: 1,2,3,4,3,2,1.

When he arranged all of the known elements in a table which exhibited the periodicity of their chemical properties, Mendeléev could see that there were some gaps. These gaps, he reasoned, must correspond to undiscovered elements! By studying the rows and columns of his periodic table, he calculated the chemical properties and the approximate atomic weights which these yet-unknown elements ought to have.

Mendeléev's predictions, made in 1869, were dramatically confirmed a decade later, when three of the elements whose discovery he had prophesied were actually found, and when their atomic weights and chemical properties turned out to be exactly as he had predicted! The discovery of these elements made Mendeléev world-famous, and it was clear that his periodic table contained some deep truth. However, the underlying meaning of the periodic table was not really understood; and it remained a mystery until it was explained by quantum theory in 1926.

Remembering his work on the periodic table, Mendeleev wrote: "I saw in a dream a table where all elements fell into place as required. Awakening, I immediately wrote it down on a piece of paper, only in one place did a correction later seem necessary."

For the eight elements whose properties he predicted, Mendeleev used Sanskrit prefaces to relate them to known elements. For example, he called germanium (then undiscovered) *ekasilicon*, while gallium became *ekaaluminium* and scandium *ekaboron*.

Dmitri Mendeleev made many other contributions to science besides the periodic table. For example, he investigated the composition and properties of petroleum and founded Russia's petroleum industry. He recognized the importance of petroleum as a starting point for the synthesis of organic compounds, and remarked that burning petroleum as a fuel "would be akin to firing up a kitchen stove with bank notes".

The Russian historian of science Lev Chugaev has characterized Mendeleev as "a chemist of genius, first-class physicist, a fruitful researcher in the fields of hydrodynamics, meteorology, geology, certain branches of chemical technology (explosives, petroleum, and fuels, for example) and other disciplines adjacent to chemistry and physics, a thorough expert of chemical industry and industry in general, and an original thinker in the field of economy." Mendeleev was one of the founders, in 1869, of the Russian Chemical Society. He worked on the theory and practice of protectionist trade and on agriculture."

Shortly after Mendeleev's publication of his periodic table of the known elements and his prediction of the properties of several as yet undiscovered ones, Lothar Meyer, in Germany, published a very similar, independently-derived table, but without Mendeleev's predictions.



Figure 10.1: Dmitri Mendeleev, (1834-1907) in an early portrait.

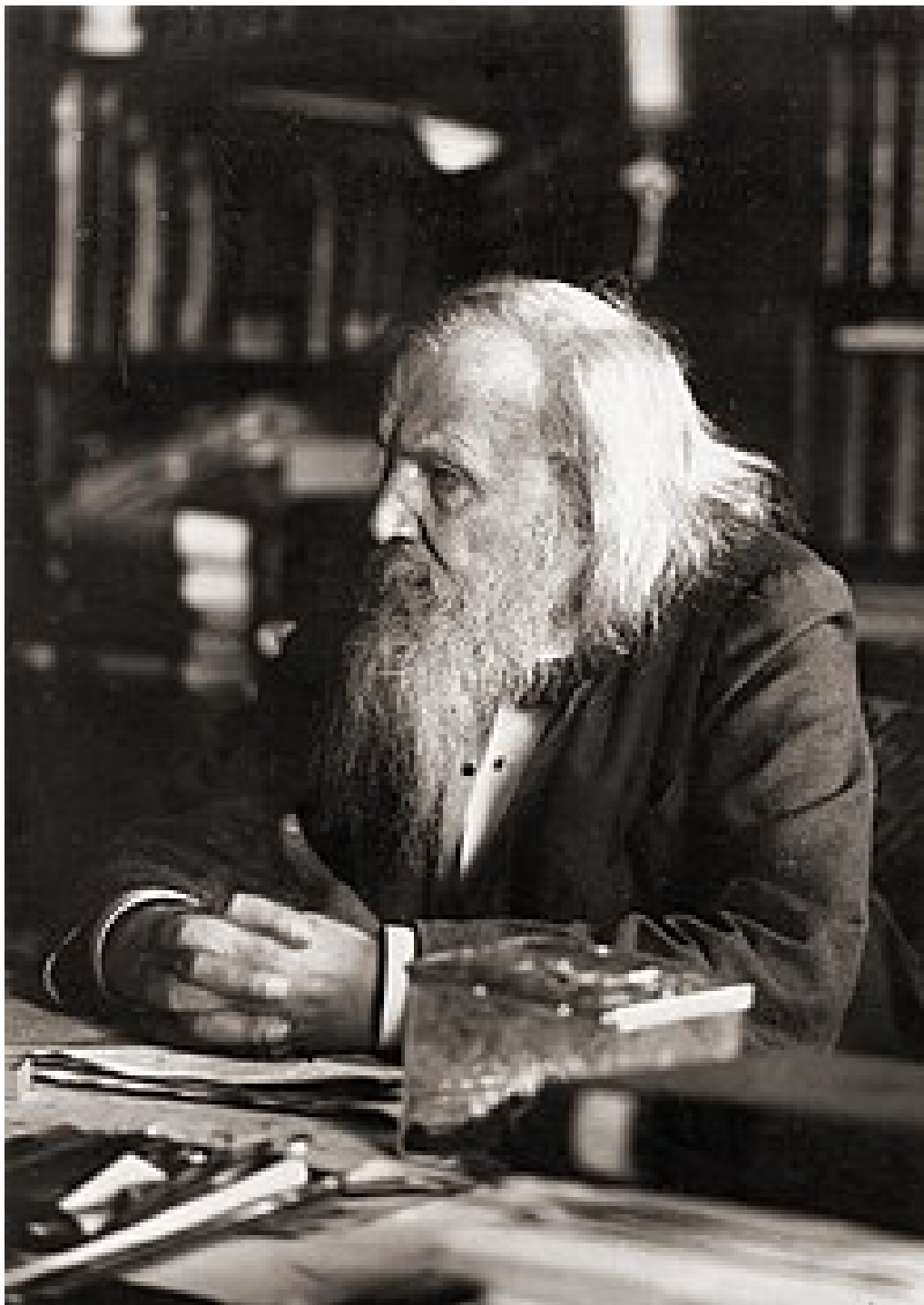


Figure 10.2: Dmitri Mendeleev in 1897.



Figure 10.3: Julius Lothar Meyer (1830-1895). He independently proposed a periodic table almost identical to that of Mendeleév, but published slightly later. Both men had worked with Robert Bunsen.

|          |          |          |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |
|----------|----------|----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| 1<br>H   |          |          |           |           |           |           |           |           |           |           |           |           |           |           |           |           | 2<br>He   |
| 3<br>Li  | 4<br>Be  |          |           |           |           |           |           |           |           |           |           | 5<br>B    | 6<br>C    | 7<br>N    | 8<br>O    | 9<br>F    | 10<br>Ne  |
| 11<br>Na | 12<br>Mg |          |           |           |           |           |           |           |           |           |           | 13<br>Al  | 14<br>Si  | 15<br>P   | 16<br>S   | 17<br>Cl  | 18<br>Ar  |
| 19<br>K  | 20<br>Ca | 21<br>Sc | 22<br>Ti  | 23<br>V   | 24<br>Cr  | 25<br>Mn  | 26<br>Fe  | 27<br>Co  | 28<br>Ni  | 29<br>Cu  | 30<br>Zn  | 31<br>Ga  | 32<br>Ge  | 33<br>As  | 34<br>Se  | 35<br>Br  | 36<br>Kr  |
| 37<br>Rb | 38<br>Sr | 39<br>Y  | 40<br>Zr  | 41<br>Nb  | 42<br>Mo  | 43<br>Tc  | 44<br>Ru  | 45<br>Rh  | 46<br>Pd  | 47<br>Ag  | 48<br>Cd  | 49<br>In  | 50<br>Sn  | 51<br>Sb  | 52<br>Te  | 53<br>I   | 54<br>Xe  |
| 55<br>Cs | 56<br>Ba | -71      | 72<br>Hf  | 73<br>Ta  | 74<br>W   | 75<br>Re  | 76<br>Os  | 77<br>Ir  | 78<br>Pt  | 79<br>Au  | 80<br>Hg  | 81<br>Tl  | 82<br>Pb  | 83<br>Bi  | 84<br>Po  | 85<br>At  | 86<br>Rn  |
| 87<br>Fr | 88<br>Ra | -103     | 104<br>Rf | 105<br>Db | 106<br>Sg | 107<br>Bh | 108<br>Hs | 109<br>Mt | 110<br>Ds | 111<br>Rg | 112<br>Cn | 113<br>Nh | 114<br>Fl | 115<br>Mc | 116<br>Lv | 117<br>Ts | 118<br>Og |

|          |          |          |          |          |          |          |          |          |          |          |           |           |           |           |
|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|-----------|-----------|-----------|-----------|
| 57<br>La | 58<br>Ce | 59<br>Pr | 60<br>Nd | 61<br>Pm | 62<br>Sm | 63<br>Eu | 64<br>Gd | 65<br>Tb | 66<br>Dy | 67<br>Ho | 68<br>Er  | 69<br>Tm  | 70<br>Yb  | 71<br>Lu  |
| 89<br>Ac | 90<br>Th | 91<br>Pa | 92<br>U  | 93<br>Np | 94<br>Pu | 95<br>Am | 96<br>Cm | 97<br>Bk | 98<br>Cf | 99<br>Es | 100<br>Fm | 101<br>Md | 102<br>No | 103<br>Lr |

|                                                                       |                                                 |
|-----------------------------------------------------------------------|-------------------------------------------------|
| Known in antiquity                                                    | akw Seaborg published his periodic table (1945) |
| also known when (akw) Lavoisier published his list of elements (1789) | also known (ak) up to 2000                      |
| akw Mendeleev published his periodic table (1869)                     | ak to 2012                                      |
| akw Deming published his periodic table (1923)                        |                                                 |

Figure 10.4: The periodic table of the elements.

**Suggestions for further reading**

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# Chapter 11

## QUANTUM THEORY AND THE PERIODIC TABLE

### 11.1 The Geiger-Marsden scattering experiment

In 1911, a young research student named Ernest Marsden joined Ernest Rutherford's research group at Manchester University, and Rutherford had to find a project for him. What happened next, in Rutherford's own words, was as follows:

"One day, Geiger came to me and said, 'Don't you think that young Marsden, whom I'm training in radioactive methods, ought to begin a small research?' Now I had thought that too, so I said, 'Why not let him see if any alpha-particles can be scattered through a large angle?' I may tell you in confidence that I did not believe that they would be, since we knew that the alpha-particle was a very fast, massive particle, with a great deal of energy; and you could show that if the scattering was due to the accumulated effect of a number of small scattering, the chance of an alpha-particle's being scattered backward was very small."

"Then I remember two or three days later, Geiger coming to me in great excitement and saying, 'We have been able to get some of the alpha-particles coming backwards'. It was quite the most incredible event that has ever happened to me in my life. It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you."

"On consideration, I realized that this scattering backwards must be the result of a single collision, and when I made calculations, I found that it was impossible to get anything of that order of magnitude unless you took a system in which the greater part of the mass of the atom was concentrated in a minute nucleus."

"It was then that I had the idea of an atom with a minute massive center carrying a charge. I worked out mathematically what laws the scattering should obey, and found that the number of particles scattered through a given angle should be proportional to the thickness of the scattering foil, the square of the nuclear charge, and inversely proportional to the fourth power of the velocity. These deductions were later verified by Geiger and

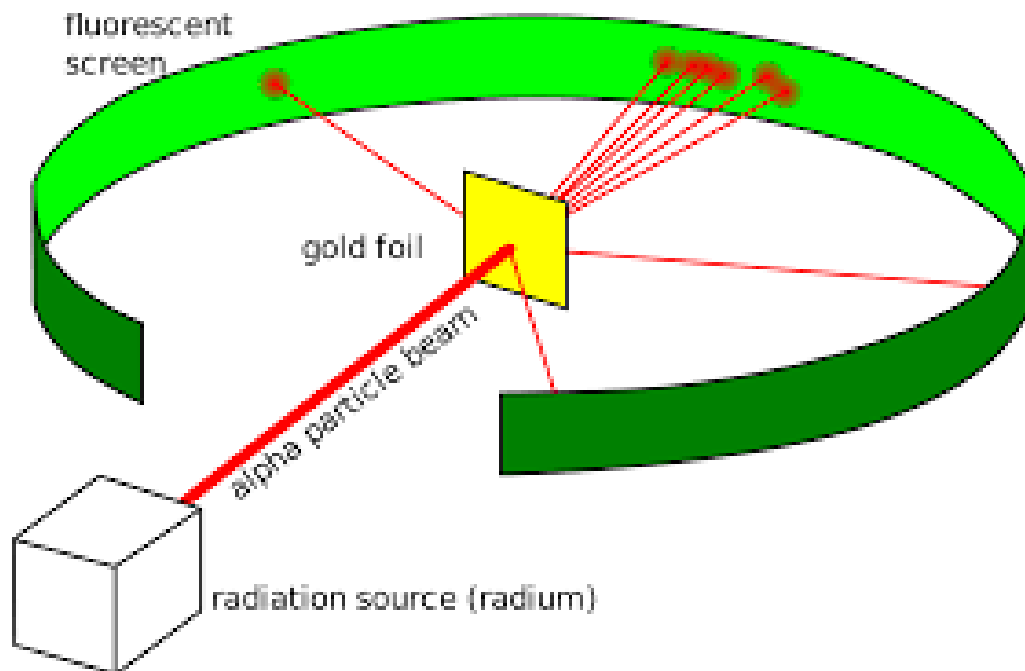


Figure 11.1: The Geiger-Marsden scattering experiment. To Rutherford's great surprise, the experiment showed that some of the alpha particles were scattered backwards. After treating the problem mathematically, Rutherford concluded that most of the mass of an atom must be concentrated in a very small, positively-charged nucleus, around which the much lighter electrons circulate in orbits.

Marsden in a series of beautiful experiments.”

## 11.2 Planck, Einstein and Bohr

According to the model proposed by Rutherford in 1911, every atom has an extremely tiny nucleus, which contains almost all of the mass of the atom. Around this tiny but massive nucleus, Rutherford visualized light, negatively-charged electrons circulating in orbits, like planets moving around the sun. Rutherford calculated that the diameter of the whole atom had to be several thousand times as large as the diameter of the nucleus.

Rutherford's model of the atom explained beautifully the scattering experiments of Geiger and Marsden, but at the same time it presented a serious difficulty: According to Maxwell's equations, the electrons circulating in their orbits around the nucleus ought to produce electromagnetic waves. It could easily be calculated that the electrons in Rutherford's atom ought to lose all their energy of motion to this radiation, and spiral in towards the nucleus. Thus, according to classical physics, Rutherford's atom could not be stable. It had to collapse.

Niels Bohr became aware of this paradox when he worked at Rutherford's Manchester

laboratory during the years 1911-1913. Bohr was not at all surprised by the failure of classical concepts when applied to Rutherford's nuclear atom. Since he had been educated in Denmark, he was more familiar with the work of German physicists than were his English colleagues at Manchester. In particular, Bohr had studied the work of Max Planck (1858-1947) and Albert Einstein (1879-1955).

Just before the turn of the century, the German physicist, Max Planck, had been studying theoretically the electromagnetic radiation coming from a small hole in an oven. The hole radiated as though it were an ideally black body. This "black body radiation" was very puzzling to the physicists of the time, since classical physics failed to explain the frequency distribution of the radiation and its dependence on the temperature of the oven.

In 1901, Max Planck had discovered a formula which fitted beautifully with the experimental measurements of the frequency distribution of black body radiation; but in order to derive his formula, he had been forced to make a radical assumption which broke away completely from the concepts of classical physics.

Planck had been forced to assume that light (or, more generally, electromagnetic radiation of any kind) can only be emitted or absorbed in amounts of energy which Planck called "quanta". The amount of energy in each of these "quanta" was equal to the frequency of the light multiplied by a constant,  $h$ , which came to be known as "Planck's constant".

This was indeed a strange assumption! It seemed to have been pulled out of thin air; and it had no relation whatever to anything that had been discovered previously in physics. The only possible justification for Planck's quantum hypothesis was the brilliant success of his formula in explaining the puzzling frequency distribution of the black body radiation. Planck himself was greatly worried by his own radical break with classical concepts, and he spent many years trying unsuccessfully to relate his quantum hypothesis to classical physics.

In 1905, Albert Einstein published a paper in the *Annalen der Physik* in which he applied Planck's quantum hypothesis to the photoelectric effect. (At that time, Einstein was 25 years old, completely unknown, and working as a clerk at the Swiss Patent Office.) The photoelectric effect was another puzzling phenomenon which could not in any way be explained by classical physics. The German physicist Lenard had discovered in 1903 that light with a frequency above a certain threshold could knock electrons out of the surface of a metal; but below the threshold frequency, nothing at all happened, no matter how long the light was allowed to shine.

Using Planck's quantum hypothesis, Einstein offered the following explanation for the photoelectric effect: A certain minimum energy was needed to overcome the attractive forces which bound the electron to the metal surface. This energy was equal to the threshold frequency multiplied by Planck's constant. Light with a frequency equal to or higher than the threshold frequency could tear an electron out of the metal; but the quantum of energy supplied by light of a lower frequency was insufficient to overcome the attractive forces.

Einstein later used Planck's quantum formula to explain the low-temperature behavior of the specific heats of crystals, another puzzling phenomenon which defied explanation by classical physics. These contributions by Einstein were important, since without this supporting evidence it could be maintained that Planck's quantum hypothesis was an *ad*



Figure 11.2: Niels Bohr and Albert Einstein in a photo by Paul Ehrenfest.

*hoc* assumption, introduced for the sole purpose of explaining black body radiation.

As a student, Niels Bohr had been profoundly impressed by the radical ideas of Planck and Einstein. In 1912, as he worked with Rutherford at Manchester, Bohr became convinced that the problem of saving Rutherford's atom from collapse could only be solved by means of Planck's quantum hypothesis.

Returning to Copenhagen, Bohr continued to struggle with the problem. In 1913, he found the solution: The electrons orbiting around the nucleus of an atom had "angular momentum". Assuming circular orbits, the angular momentum was given by the product of the mass and velocity of the electron, multiplied by the radius of the orbit. Bohr introduced a quantum hypothesis similar to that of Planck: He assumed that the angular momentum of an electron in an allowed orbit, (multiplied by  $2\pi$ ), had to be equal to an integral multiple of Planck's constant. The lowest value of the integer,  $n=1$ , corresponded to the lowest allowed orbit. Thus, in Bohr's model, the collapse of Rutherford's atom was avoided.

Bohr calculated that the binding energies of the various allowed electron orbits in a hydrogen atom should be a constant divided by the square of the integer  $n$ ; and he calculated the value of the constant to be 13.5 electron-Volts. This value fit exactly the observed ionization energy of hydrogen. After talking with the Danish spectroscopist, H.M. Hansen, Bohr realized with joy that by combining his formula for the allowed orbital energies with the Planck-Einstein formula relating energy to frequency, he could explain the mysterious line spectrum of hydrogen.

When Niels Bohr published all this in 1913, his paper produced agonized cries of "foul!" from the older generation of physicists. When Lord Rayleigh's son asked him if he had seen Bohr's paper, Rayleigh replied: "Yes, I have looked at it; but I saw that it was of no



Figure 11.3: Another photo of Bohr and Einstein by Ehrenfest.

use to me. I do not say that discoveries may not be made in that sort of way. I think very likely they may be. But it does not suit me.” However, as more and more atomic spectra and properties were explained by extensions of Niels Bohr’s theories, it became clear that Planck, Einstein and Bohr had uncovered a whole new stratum of phenomena, previously unsuspected, but of deep and fundamental importance.

### 11.3 Atomic numbers

Bohr’s atomic theory soon received strong support from the experiments of one of the brightest of Rutherford’s bright young men - Henry Moseley (1887-1915). Moseley came from a distinguished scientific family. Not only his father, but also both his grandfathers, had been elected to the Royal Society. After studying at Oxford, where his father had once been a professor, Moseley found it difficult to decide where to do his postgraduate work. Two laboratories attracted him: the great J.J. Thomson’s Cavendish Laboratory at Cambridge, and Rutherford’s laboratory at Manchester. Finally, he decided on Manchester, because of the revolutionary discoveries of Rutherford, who two years earlier had won the 1908 Nobel Prize for Chemistry.

Rutherford’s laboratory was like no other in the world, except J.J. Thomson’s. In fact, Rutherford had learned much about how to run a laboratory from his old teacher, Thomson. Rutherford continued Thomson’s tradition of democratic informality and cheerfulness. Like Thomson, he had a gift for infecting his students with his own powerful scientific curiosity, and his enthusiastic enjoyment of research.

Thomson had also initiated a tradition for speed and ingenuity in the improvisation of experimental apparatus - the so-called “sealing-wax and string” tradition - and Rutherford continued it. Niels Bohr, after working with Rutherford, was later to continue the tradition of informality and enthusiasm at the Institute for Theoretical Physics which Bohr founded in Copenhagen in 1920.

Niels Bohr had shown that the binding energies of the allowed orbits in a hydrogen atom are equal to Rydberg’s constant,  $R$  (named after the distinguished Swedish spectroscopist, Johannes Robert Rydberg), divided by the square of an integral “quantum number”,  $n$ . He had also shown that for heavier elements, the constant,  $R$ , is equal to the square of the nuclear charge,  $Z$ , multiplied by a factor which is the same for all elements. The constant,  $R$ , could be observed in Moseley’s studies of X-ray spectra: Since X-rays are produced when electrons are knocked out of inner orbits and outer electrons fall in to replace them, Moseley could use the Planck-Einstein relationship between frequency and energy to find the energy difference between the orbits, and Bohr’s theory to relate this to  $R$ .

Moseley found complete agreement with Bohr’s theory. He also found that the nuclear charge,  $Z$ , increased regularly in integral steps as he went along the rows of the periodic table: Hydrogen had  $Z=1$ , helium  $Z=2$ , lithium  $Z=3$ , and so on up to uranium with  $Z=92$ . The 92 electrons of a uranium atom made it electrically neutral, exactly balancing the charge of the nucleus. The number of electrons of an element, and hence its chemical properties, Moseley found, were determined uniquely by its nuclear charge, which Moseley

called the “atomic number”.

Moseley’s studies of the nuclear charges of the elements revealed that a few elements were missing. In 1922, Niels Bohr received the Nobel Prize for his quantum theory of the atom; and he was able to announce at the presentation ceremony that one of Moseley’s missing elements had been found at his institute. Moseley, however, was dead. He was one of the ten million young men whose lives were needlessly thrown away in Europe’s most tragic blunder - the First World War.

## 11.4 A wave equation for matter

In 1926, the difficulties surrounding the “old quantum theory” of Max Planck, Albert Einstein and Niels Bohr were suddenly solved, and its true meaning was understood. Two years earlier, a French aristocrat, Louis de Broglie, writing his doctoral dissertation at the Sorbonne in Paris, had proposed that very small particles, such as electrons, might exhibit wavelike properties. The ground state and higher excited states of the electron in Bohr’s model of the hydrogen atom would then be closely analogous to the fundamental tone and higher overtones of a violin string.

Almost the only person to take de Broglie’s proposal seriously was Albert Einstein, who mentioned it in one of his papers. Because of Einstein’s interest, de Broglie’s matter-waves came to the attention of other physicists. The Austrian theoretician, Erwin Schrödinger, working at Zürich, searched for the underlying wave equation which de Broglie’s matter-waves obeyed.

Schrödinger’s gifts as a mathematician were so great that it did not take him long to solve the problem. The Schrödinger wave equation for matter is now considered to be more basic than Newton’s equations of motion. The wavelike properties of matter are not apparent to us in our daily lives because the wave-lengths are extremely small in comparison with the sizes of objects which we can perceive. However, for very small and light particles, such as electrons moving in their orbits around the nucleus of an atom, the wavelike behavior becomes important.

Schrödinger was able to show that Niels Bohr’s atomic theory, including Bohr’s seemingly arbitrary quantization of angular momentum, can be derived by solving the wave equation for the electrons moving in the attractive field of the nucleus. The allowed orbits of Bohr’s theory correspond in Schrödinger’s theory to harmonics, similar to the fundamental harmonic and higher overtones of an organ pipe or a violin string. (If Pythagoras had been living in 1926, he would have rejoiced to see the deepest mysteries of matter explained in terms of harmonics!)

There is an interesting story about Erwin Schrödinger’s derivation of his famous wave equation. According to the solid state physicist Felix Bloch, Peter Debye was chairing a symposium in Zürich, Switzerland, at which de Broglie’s waves were being discussed. At one point during the symposium, Debye said: “Well, if there are waves associated with every particle, there must be a wave equation.” Then, turning to Schrödinger, he said: “You, Erwin. You’re not doing anything important at the moment. Why don’t you find



Figure 11.4: Louis Victor Pierre Raymond, duc de Broglie, (1892-1987).



Figure 11.5: **Erwin Schrödinger (1887-1961).**

the wave equation obeyed by de Broglie's waves?"

During the following weekend, the whole group started off for a skiing trip. "Come with us, Erwin!", they said, but Schrödinger replied: "No, forgive me, I think I will stay here and work." By the end of the weekend he had derived his famous non-relativistic wave equation. He had first tried a relativistic equation (now known as the Klein-Gordon equation), but had rejected it because he believed that the equation had to be first-order in time.

Later, Felix Bloch asked Peter Debye, "Aren't you sorry that you didn't derive the wave equation yourself, instead of giving the job to Schrödinger?" Debye replied wistfully, "At least I was right about the need for a wave equation, wasn't I?"

## 11.5 The Pauli exclusion principle and the periodic table

Bohr himself believed that a complete atomic theory ought to be able to explain the chemical properties of the elements in Mendeléev's periodic system. Bohr's 1913 theory failed to pass this test, but the new de Broglie-Schrödinger theory succeeded! Through the work of Pauli, Heitler, London, Slater, Pauling, Hund, Mulliken, Hückel and others, who applied Schrödinger's wave equation to the solution of chemical problems, it became apparent that the wave equation could indeed (in principle) explain all the chemical properties of matter.

The solutions to Schrödinger's wave equation for an electron moving in the field of a nucleus are called *atomic orbitals*, and the first few of them are shown in Figure 11.6. They are analogous to the harmonics of a violin string or an organ pipe, except the they are three-dimensional. The electron had been shown to have a magnetic moment, and in a magnetic field, it was found to orient itself either in the direction of an applied magnetic field, or in the opposite direction - either "spin-up" or "spin-down". This effect could be observed in the splitting of the lines in atomic spectra in the presence of an applied magnetic field. The "spin" and magnetic moment of electrons were completely explained in 1928 by P.A.M. Dirac's relativistic wave equation.

Meanwhile, the Austrian physicist Wolfgang Pauli proposed his famous *exclusion principle*, which explained the periodic table and the chemical properties of the elements. According to the Pauli exclusion principle, in the lowest energy state of an atom, the electrons fill the atomic orbitals in the order (1s), (2p), (3d), ... Two electrons are allowed in each linearly independent orbital, one with spin up and the other with spin down. This leads to the following electron configurations for the elements:

- Hydrogen; (1s); very active metal; valence=1
- Helium; (1s)<sup>2</sup>; noble (inert) gas; valence=0
- Lithium; (1s)<sup>2</sup>(2p)<sup>1</sup>; very active metal; valence=1
- Beryllium; (1s)<sup>2</sup>(2p)<sup>2</sup>; metal; valence=2
- Boron; (1s)<sup>2</sup>(2p)<sup>3</sup>; less active metal; valence=3

- Carbon;  $(1s)^2(2p)^4$ ; intermediate; valence=4
- Nitrogen;  $(1s)^2(2p)^5$ ; less active nonmetal; valence=5
- Oxygen;  $(1s)^2(2p)^6$ ; nonmetal; valence=6
- Fluorine;  $(1s)^2(2p)^7$ ; very active nonmetal; valence=7
- Neon;  $(1s)^2(2p)^8$ ; noble gas; valence=0
- Sodium;  $(1s)^2(2p)^8(2s)^1$ ; very active metal; valence=1

In chemical reactions, the metals tend to give away their outer-shell electrons, while the non-metals tend to accept electrons. The most active metals, hydrogen, lithium, sodium, potassium, rubidium and cesium, all have a single electron in their outer shell, and they tend to give this electron away. The most active nonmetals, fluorine, chlorine, bromine and iodine, all are missing a single electron to complete their outer shell. We can notice that common table salt, is a cubic crystal structure formed from  $\text{Na}^+$  ions and  $\text{Cl}^-$  ions. When it is dissolved in water, the sodium-chloride crystal dissociates into  $\text{Na}^+$  ions, complexed with water molecules and  $\text{Cl}^-$  ions, also forming complexes with water. We see here the strong tendency of very active metals to give up their outer shell electron and to form positive ions, while very active nonmetals have an equally strong tendency to form negative ions. Helium, neon, argon, krypton, and radon, all with completely filled outer shell, are unreactive noble gases, with no tendency at all to give away or accept electrons or to form ions.

## The Hartree-Fock equations

The application of the Schrödinger equation to our understanding of chemical reactivity and the periodic table was made quantitative through the work of Douglas Hartree (1897-1958) and Vladimir A. Fock (1898-1974).

Douglas Hartree was born in Cambridge, England, where his father was a professor of engineering at Cambridge University and his mother was the mayor of the city. In his work on the electronic structure of atoms, Hartree visualized the electrons moving in both the attractive field of the atomic nucleus and in a repulsive potential produced collectively by all the electrons. Hartree's method for treating this problem was to make an initial guess of the size of the atomic orbitals (Figure 11.6) occupied by the electrons. He then calculated the repulsive potential that would result, and combined it with the nuclear attraction potential. Solving the Schrödinger equation for the an electron moving in this new potential, he obtained a set of improved atomic orbitals, and from these he could calculate an improved total potential. He continued to iterate this process until the change resulting from successive iterations became very small, at which point he described the electrical field in which the electrons moved as being *self-consistent*. Hartree called his procedure the Self-Consistent-Field (or SCF) Method. He published his first results in 1927, only a year after Schrödinger's discovery of his wave equation.

The Russian physicist Vladimir A. Fock was able to refine Hartree's method by postulating that the total electronic wave function of an atom or molecule had to be antisymmetric with respect to the exchange of the coordinates of any two electrons in the system. When

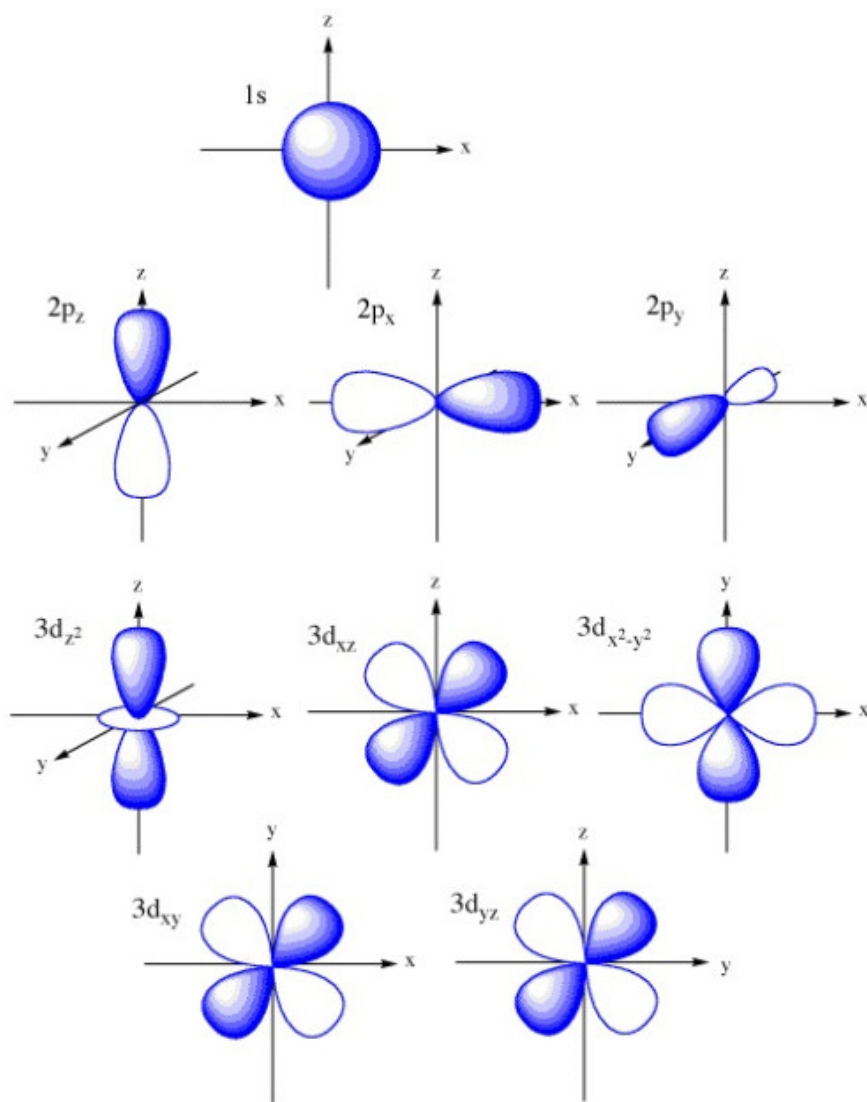


Figure 11.6: Atomic orbitals.

|               |          |          |                       |           |           |             |           |           |           |           |           |                   |           |            |           |            |            |
|---------------|----------|----------|-----------------------|-----------|-----------|-------------|-----------|-----------|-----------|-----------|-----------|-------------------|-----------|------------|-----------|------------|------------|
| 1<br>H        |          |          |                       |           |           |             |           |           |           |           |           |                   |           |            |           |            | 2<br>He    |
| 3<br>Li       | 4<br>Be  |          |                       |           |           |             |           |           |           |           |           | 5<br>B            | 6<br>C    | 7<br>N     | 8<br>O    | 9<br>F     | 10<br>Ne   |
| 11<br>Na      | 12<br>Mg |          |                       |           |           |             |           |           |           |           |           | 13<br>Al          | 14<br>Si  | 15<br>P    | 16<br>S   | 17<br>Cl   | 18<br>Ar   |
| 19<br>K       | 20<br>Ca | 21<br>Sc | 22<br>Ti              | 23<br>V   | 24<br>Cr  | 25<br>Mn    | 26<br>Fe  | 27<br>Co  | 28<br>Ni  | 29<br>Cu  | 30<br>Zn  | 31<br>Ga          | 32<br>Ge  | 33<br>As   | 34<br>Se  | 35<br>Br   | 36<br>Kr   |
| 37<br>Rb      | 38<br>Sr | 39<br>Y  | 40<br>Zr              | 41<br>Nb  | 42<br>Mo  | 43<br>Tc    | 44<br>Ru  | 45<br>Rh  | 46<br>Pd  | 47<br>Ag  | 48<br>Cd  | 49<br>In          | 50<br>Sn  | 51<br>Sb   | 52<br>Te  | 53<br>I    | 54<br>Xe   |
| 55<br>Cs      | 56<br>Ba | *        | 72<br>Hf              | 73<br>Ta  | 74<br>W   | 75<br>Re    | 76<br>Os  | 77<br>Ir  | 78<br>Pt  | 79<br>Au  | 80<br>Hg  | 81<br>Tl          | 82<br>Pb  | 83<br>Bi   | 84<br>Po  | 85<br>At   | 86<br>Rn   |
| 87<br>Fr      | 88<br>Ra | **       | 104<br>Rf             | 105<br>Db | 106<br>Sg | 107<br>Bh   | 108<br>Hs | 109<br>Mt | 110<br>Ds | 111<br>Rg | 112<br>Cn | 113<br>Uut        | 114<br>Fl | 115<br>Uup | 116<br>Lv | 117<br>Uus | 118<br>Uuo |
| 119<br>Uun    |          |          |                       |           |           |             |           |           |           |           |           |                   |           |            |           |            |            |
|               |          |          | 57<br>La              | 58<br>Ce  | 59<br>Pr  | 60<br>Nd    | 61<br>Pm  | 62<br>Sm  | 63<br>Eu  | 64<br>Gd  | 65<br>Tb  | 66<br>Dy          | 67<br>Ho  | 68<br>Er   | 69<br>Tm  | 70<br>Yb   | 71<br>Lu   |
|               |          |          | 89<br>Ac              | 90<br>Th  | 91<br>Pa  | 92<br>U     | 93<br>Np  | 94<br>Pu  | 95<br>Am  | 96<br>Cm  | 97<br>Bk  | 98<br>Cf          | 99<br>Es  | 100<br>Fm  | 101<br>Md | 102<br>No  | 103<br>Lr  |
| Alkali metals |          |          | Alkaline earth metals |           |           | Lanthanides |           |           | Actinides |           |           | Transition metals |           |            |           |            |            |
| Poor metals   |          |          | Metalloids            |           |           | Nonmetals   |           |           | Halogens  |           |           | Noble gases       |           |            |           |            |            |

red

blue

Figure 11.7: The periodic table of the elements.

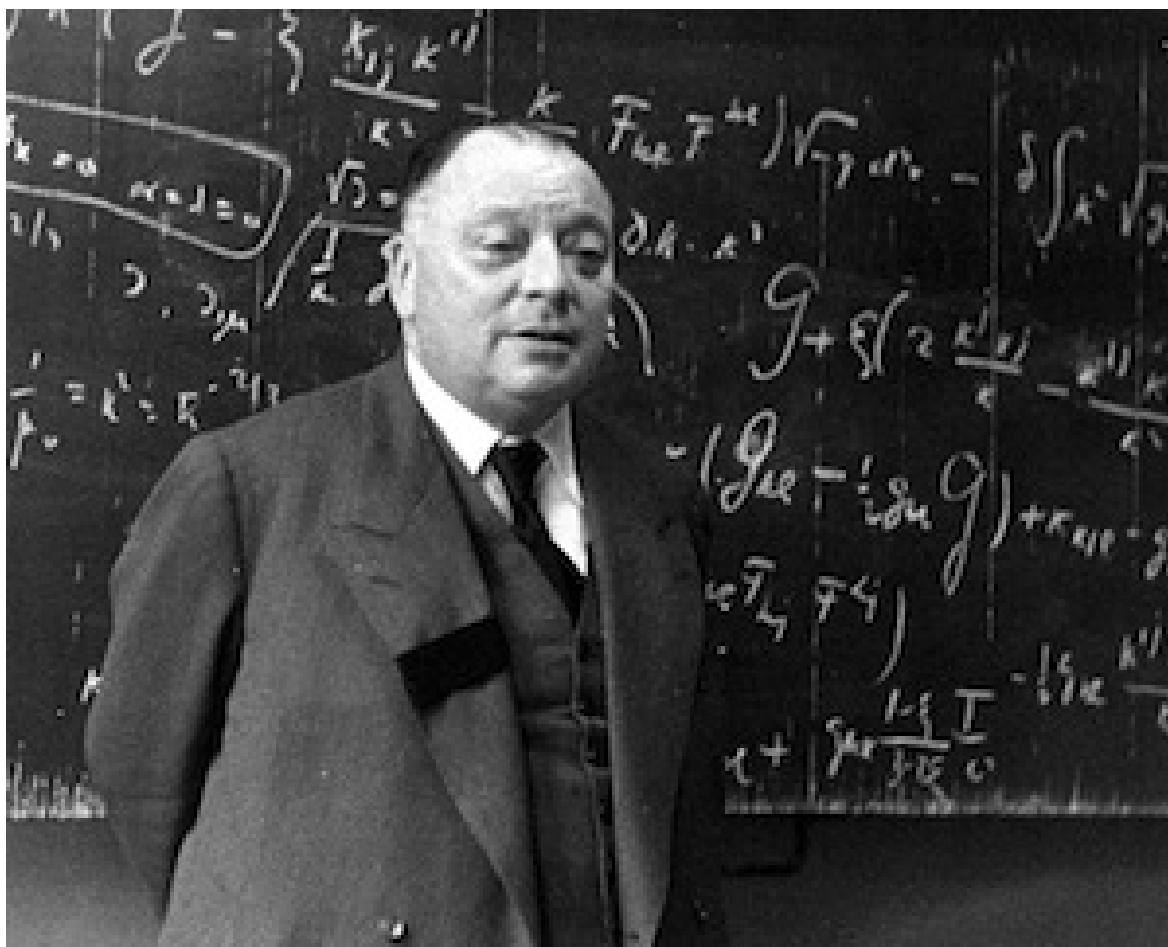


Figure 11.8: **Wolfgang Pauli (1900-1958).**

spin was included in the wave function, this requirement led in a natural way to the exclusion principle postulated by Wolfgang Pauli. When combined with Hartree's SCF method, Fock's antisymmetry requirement led to more accurate results and better agreement between theory and experiment. However, the Hartree-Fock SCF equations were much more difficult to solve. Later Clemens C.J. Roothaan (1918-2019) converted the Hartree-Fock equations into a matrix form suitable for solution by digital computers. The method in use today is thus known as the Hartree-Fock-Roothaan SCF Method. When applied to molecules, it is called the Hartree-Fock-Roothaan LCAO SCF Method. The LCAO in the name stands for the fact that molecular orbitals are represented as Linear Combinations of Atomic Orbitals.



Figure 11.9: **Douglas Hartree** (1897-1958).



Figure 11.10: Vladimir A. Fock (1898-1974).

### Suggestions for further reading

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# Chapter 12

## X-RAY CRYSTALLOGRAPHY

### 12.1 Roentgen's discovery of X-rays

In 1895, while the work leading to the discovery of the electron was still going on, a second revolutionary discovery was made. In the autumn of that year, Wilhelm Konrad Roentgen (1845-1923), the head of the department of physics at the University of Würzburg in Bavaria, was working with a discharge tube, repeating some of the experiments of Crookes.

Roentgen was especially interested in the luminescence of certain materials when they were struck by cathode rays. He darkened the room, and turned on the high voltage. As the current surged across the tube, a flash of light came from an entirely different part of the room! To Roentgen's astonishment, he found that a piece of paper which he had coated with barium platinocyanide was glowing brightly, even though it was so far away from the discharge tube that the cathode rays could not possibly reach it!

Roentgen turned off the tube, and the light from the coated paper disappeared. He turned on the tube again, and the bright glow on the screen reappeared. He carried the coated screen into the next room. Still it glowed! Again he turned off the tube, and again the screen stopped glowing. Roentgen realized that he had discovered something completely strange and new. Radiation of some kind was coming from his discharge tube, but the new kind of radiation could penetrate opaque matter!

Years later, when someone asked Roentgen what he thought when he discovered X-rays, he replied: "I didn't think. I experimented!" During the next seven weeks he experimented like a madman; and when he finally announced his discovery in December, 1895, he was able to report all of the most important properties of X-rays, including their ability to ionize gases and the fact that they cannot be deflected by electric or magnetic fields. Roentgen correctly believed X-rays to be electromagnetic waves, just like light waves, but with very much shorter wavelength.

It turned out that X-rays were produced by electrons from the cathode of the discharge tube. These electrons were accelerated by the strong electric field as they passed across the tube from the cathode (the negative terminal) to the anode (the positive terminal).



*Dr. W. C. Roentgen*

Figure 12.1: Wilhelm Konrad Roentgen (1845-1923). Wellcome Images.



Figure 12.2: X-ray photograph by W.K. Roentgen. Wellcome Images.

They struck the platinum anode with very high velocity, knocking electrons out of the inner parts of the platinum atoms. As the outer electrons fell inward to replace these lost inner electrons, electromagnetic waves of very high frequency were emitted.

On January 23, 1896, Roentgen gave the first public lecture on X-rays; and in this lecture he demonstrated to his audience that X-ray photographs could be used for medical diagnosis. When Roentgen called for a volunteer from the audience, the 79 year old physiologist, Rudolf von Kölliker stepped up to the platform, and an X-ray photograph was taken of the old man's hand. The photograph, still in existence, shows the bones beautifully.

Wild enthusiasm for Roentgen's discovery swept across Europe and America, and soon many laboratories were experimenting with X-rays. The excitement about X-rays led indirectly to a third revolutionary discovery - radioactivity.

## 12.2 Bragg father and son

Sir William Henry Bragg (1862-1942) graduated from Trinity College, Cambridge University. with first class honors in mathematics in 1885. In that year, at the age of 25, he was appointed Professor of Mathematics and Experimental Physics at the University of Adelaide in Australia. In 1908, Bragg returned to England after 23 years in Australia.



Figure 12.3: Max von Laue (1879-1960).

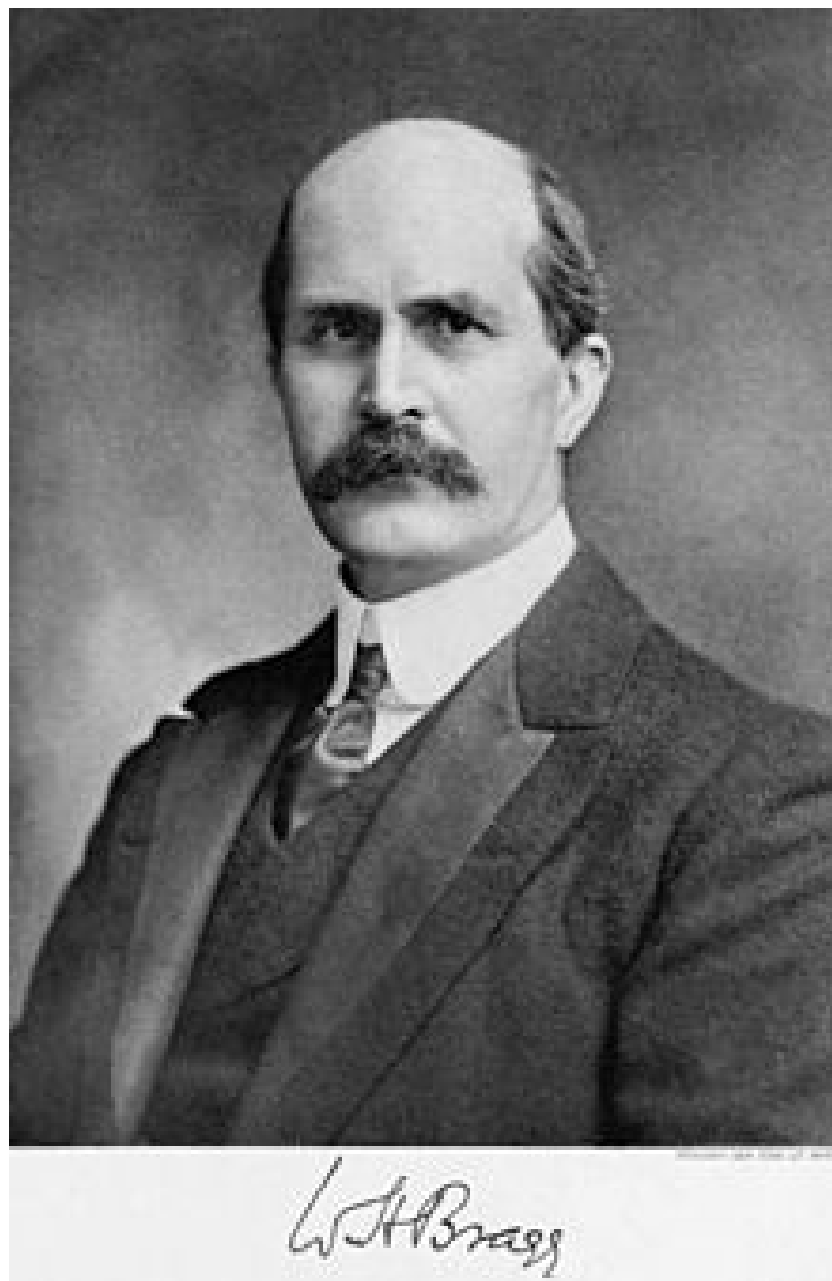


Figure 12.4: Sir William Henry Bragg (1862-1942). He and his son, Lawrence Bragg shared the 1915 Nobel Prize in Physics “for their services to the analysis of crystal structure by means of X-rays”. He studied with J.J. Thomson at Cambridge University after having won a scholarship to Trinity College in 1885. X-ray crystallography, pioneered by Bragg and his son, has proved to be enormously important both in chemistry and in biology. It has allowed us to understand the structure of both organic and inorganic molecules, and initiated the science of molecular biology.

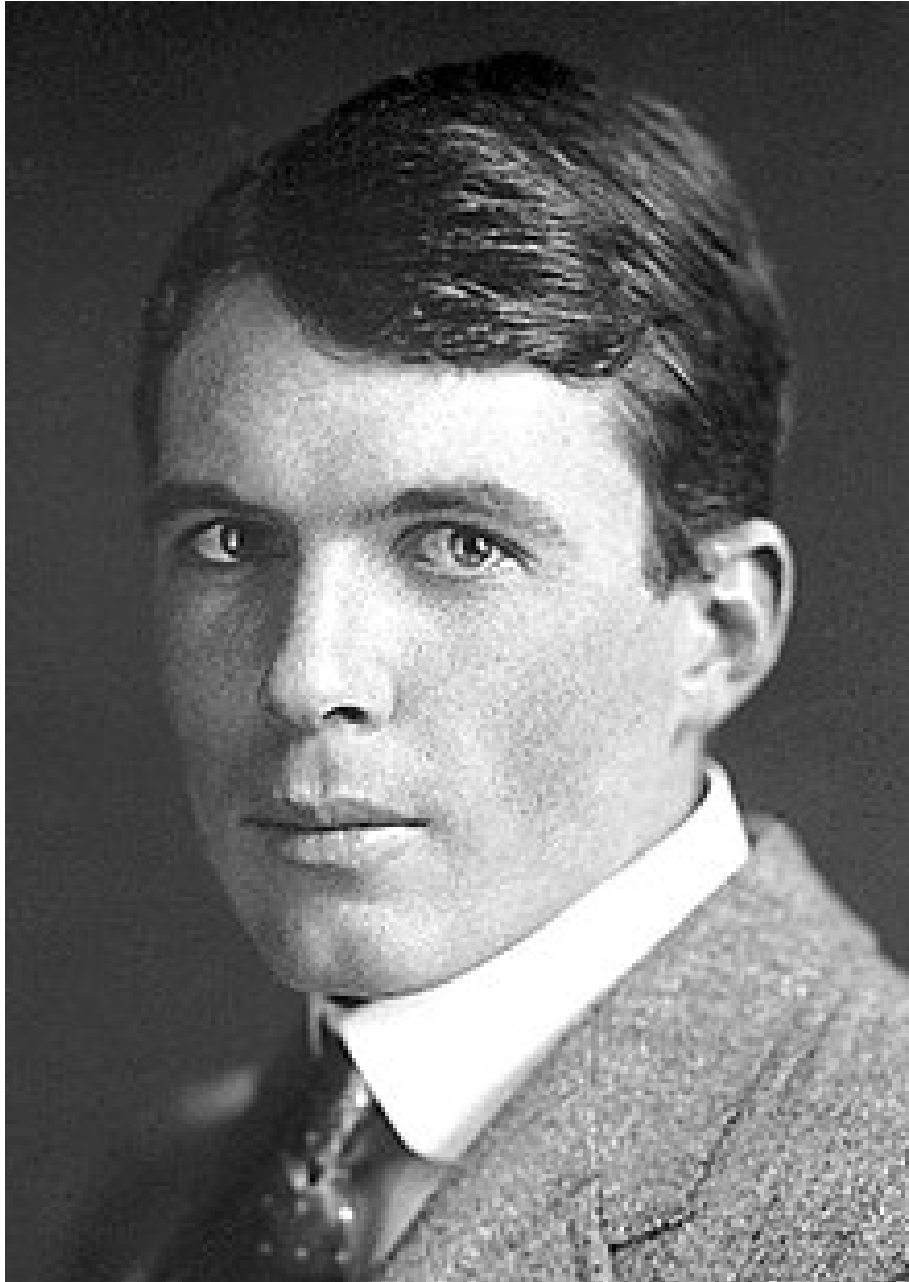


Figure 12.5: Sir William Lawrence Bragg (1890-1971).

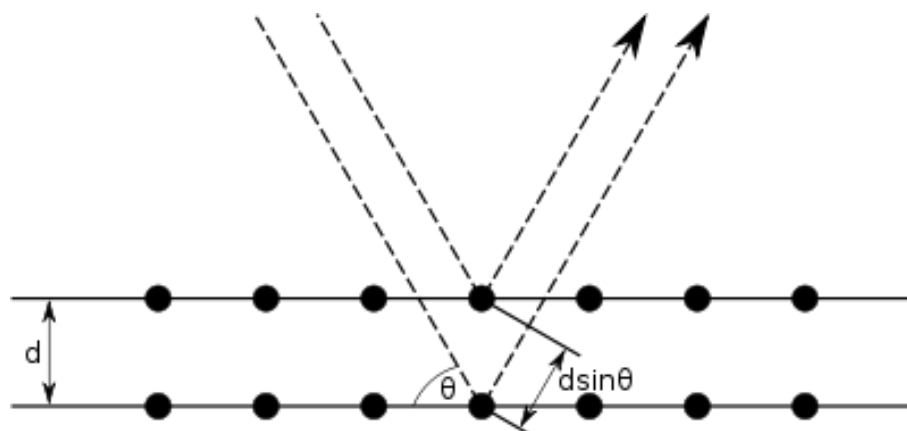


Figure 12.6: **Bragg's law of diffraction.** Two beams with identical wavelength and phase approach a crystalline solid and are scattered off two different atoms within it. The lower beam traverses an extra length of  $2d \sin \theta$ . Constructive interference occurs when this length is equal to an integer multiple of the wavelength of the radiation.

## 12.3 J.D. Bernal and Dorothy Crowfoot Hodgkin

In England, J.D. Bernal and Dorothy Crowfoot Hodgkin pioneered the application of X-ray diffraction methods to the study of complex biological molecules. In 1949, Hodgkin determined the structure of penicillin; and in 1955, she followed this with the structure of vitamin B12. In 1960, Max Perutz and John C. Kendrew obtained the structures of the blood proteins myoglobin and hemoglobin. This was an impressive achievement for the Cambridge crystallographers, since the hemoglobin molecule contains roughly 12,000 atoms.

The structure obtained by Perutz and Kendrew showed that hemoglobin is a long chain of amino acids, folded into a globular shape, like a small, crumpled ball of yarn. They found that the amino acids with an affinity for water were on the outside of the globular molecule; while the amino acids for which contact with water was energetically unfavorable were hidden on the inside. Perutz and Kendrew deduced that the conformation of the protein - the way in which the chain of amino acids folded into a 3-dimensional structure - was determined by the sequence of amino acids in the chain.

In 1966, D.C. Phillips and his co-workers at the Royal Institution in London found the crystallographic structure of the enzyme lysozyme (an egg-white protein which breaks down the cell walls of certain bacteria). Again, the structure showed a long chain of amino acids, folded into a roughly globular shape. The amino acids with hydrophilic groups were on the outside, in contact with water, while those with hydrophobic groups were on the inside. The structure of lysozyme exhibited clearly an active site, where sugar molecules of bacterial cell walls were drawn into a mouth-like opening and stressed by electrostatic forces, so that bonds between the sugars could easily be broken.

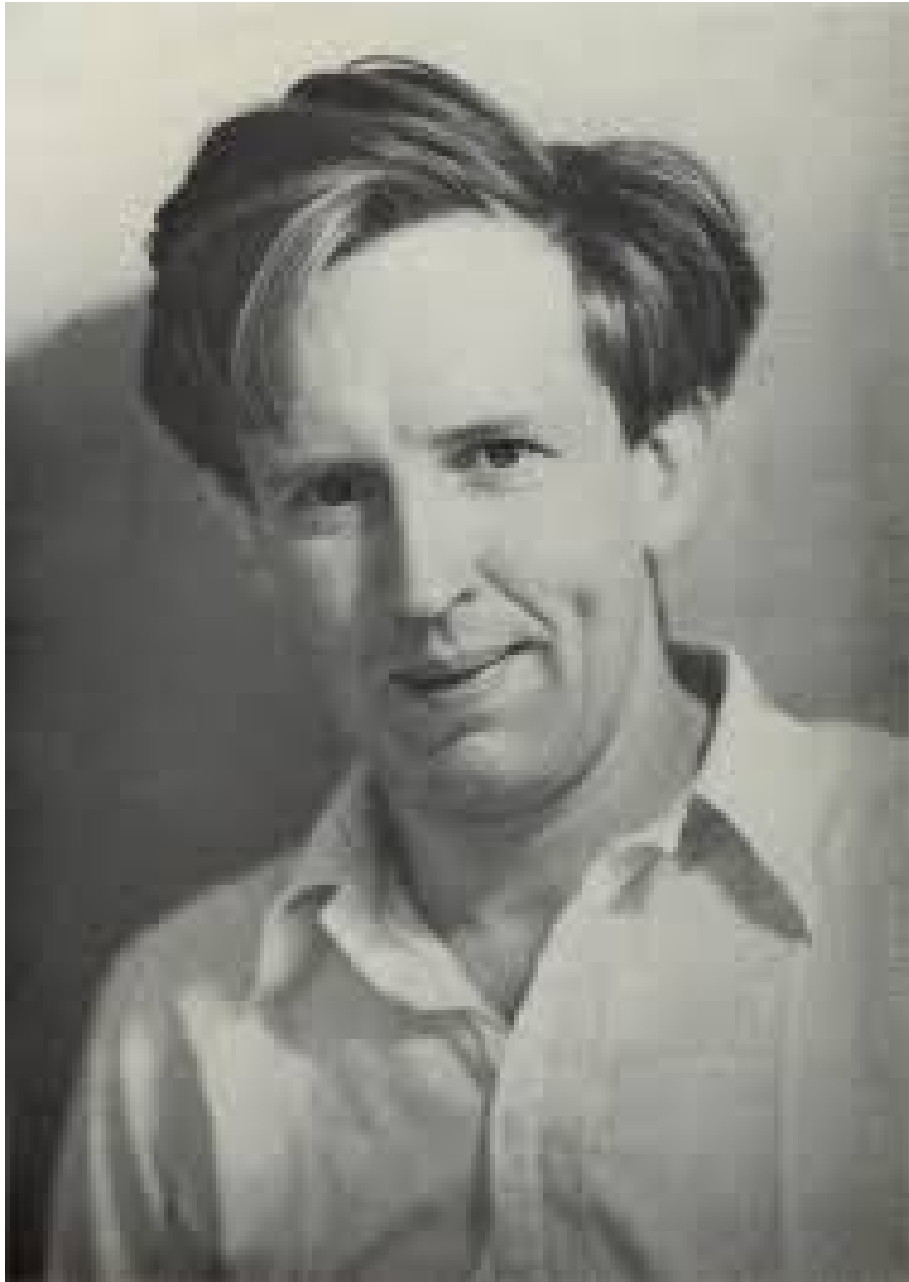


Figure 12.7: J.D. Bernal, (1901-1971).



Figure 12.8: Dorothy Crowfoot Hodgkin (1910-1994). She and her mentor J.D Bernal were a great pioneers in the application of X-ray crystallography to determination of the structure of biological molecules, such as proteins. She was awarded the Nobel Prize in Chemistry in 1964.



Figure 12.9: **Sir John C. Kendrew (1917-1997) with an unfinished model of myoglobin.** He shared the 1962 Nobel Prize in Chemistry with Perutz, Crick, Watson and Wilkins.

## 12.4 The structure of DNA: Molecular biology

The discovery of the molecular structure of DNA was an event of enormous importance for genetics, and for biology in general. The structure was a revelation! The giant, helical DNA molecule was like a twisted ladder: Two long, twisted sugar-phosphate backbones formed the outside of the ladder, while the rungs were formed by the base pairs, A, T, G and C. The base adenine (A) could only be paired with thymine (T), while guanine (G) fit only with cytosine (C). Each base pair was weakly joined in the center by hydrogen bonds - in other words, there was a weak point in the center of each rung of the ladder - but the bases were strongly attached to the sugar-phosphate backbone. In their 1953 paper, Crick and Watson wrote:

"It has not escaped our notice that the specific pairing we have postulated suggests a possible copying mechanism for genetic material". Indeed, a sudden blaze of understanding illuminated the inner workings of heredity, and of life itself.

If the weak hydrogen bonds in the center of each rung were broken, the ladderlike DNA macromolecule could split down the center and divide into two single strands. Each single strand would then become a template for the formation of a new double-stranded molecule.

Because of the specific pairing of the bases in the Watson-Crick model of DNA, the two strands had to be complementary. T had to be paired with A, and G with C. Therefore, if the sequence of bases on one strand was (for example) TTTGCTAAAGGTGAACCA... , then the other strand necessarily had to have the sequence AAACGATTTCCACTTGGT... The Watson-Crick model of DNA made it seem certain that all the genetic information

needed for producing a new individual is coded into the long, thin, double-stranded DNA molecule of the cell nucleus, written in a four-letter language whose letters are the bases, adenine, thymine, guanine and cytosine.

In 1956, George Emil Palade of the Rockefeller Institute used electron microscopy to study subcellular particles rich in RNA (ribosomes). Ribosomes were found to consist of two subunits - a smaller subunit, with a molecular weight one million times the weight of a hydrogen atom, and a larger subunit with twice this weight.

It was shown by means of radioactive tracers that a newly synthesized protein molecule is attached temporarily to a ribosome, but neither of the two subunits of the ribosome seemed to act as a template for protein synthesis. Instead, Palade and his coworkers found that genetic information is carried from DNA to the ribosome by a messenger RNA molecule (mRNA). Electron microscopy revealed that mRNA passes through the ribosome like a punched computer tape passing through a tape-reader. It was found that the adapter molecules, whose existence Crick had postulated, were smaller molecules of RNA; and these were given the name "transfer RNA" (tRNA). It was shown that, as an mRNA molecule passes through a ribosome, amino acids attached to complementary tRNA adaptor molecules are added to the growing protein chain.

The solution of the DNA structure in 1953 initiated a new kind of biology - molecular biology. This new discipline made use of recently-discovered physical techniques - X-ray diffraction, electron microscopy, electrophoresis, chromatography, ultracentrifugation, radioactive tracer techniques, autoradiography, electron spin resonance, nuclear magnetic resonance and ultraviolet spectroscopy. In the 1960's and 1970's, molecular biology became the most exciting and rapidly-growing branch of science.

Since DNA was known to carry the genetic message, coded into the sequence of the four nucleotide bases, A, T, G and C, and since proteins were known to be composed of specific sequences of the twenty amino acids, it was logical to suppose that the amino acid sequence in a protein was determined by the base sequence of DNA. The information somehow had to be read from the DNA and used in the biosynthesis of the protein.

It was known that, in addition to DNA, cells also contain a similar, but not quite identical, polynucleotide called ribonucleic acid (RNA). The sugar-phosphate backbone of RNA was known to differ slightly from that of DNA; and in RNA, the nucleotide thymine (T) was replaced by a chemically similar nucleotide, uracil (U). Furthermore, while DNA was found only in cell nuclei, RNA was found both in cell nuclei and in the cytoplasm of cells, where protein synthesis takes place. Evidence accumulated indicating that genetic information is first transcribed from DNA to RNA, and afterwards translated from RNA into the amino acid sequence of proteins.

The crystallographic determination of the structures of DNA and RNA and proteins opened the way for a new field of science, Molecular Biology, now one of the most rapidly developing of all research fields.

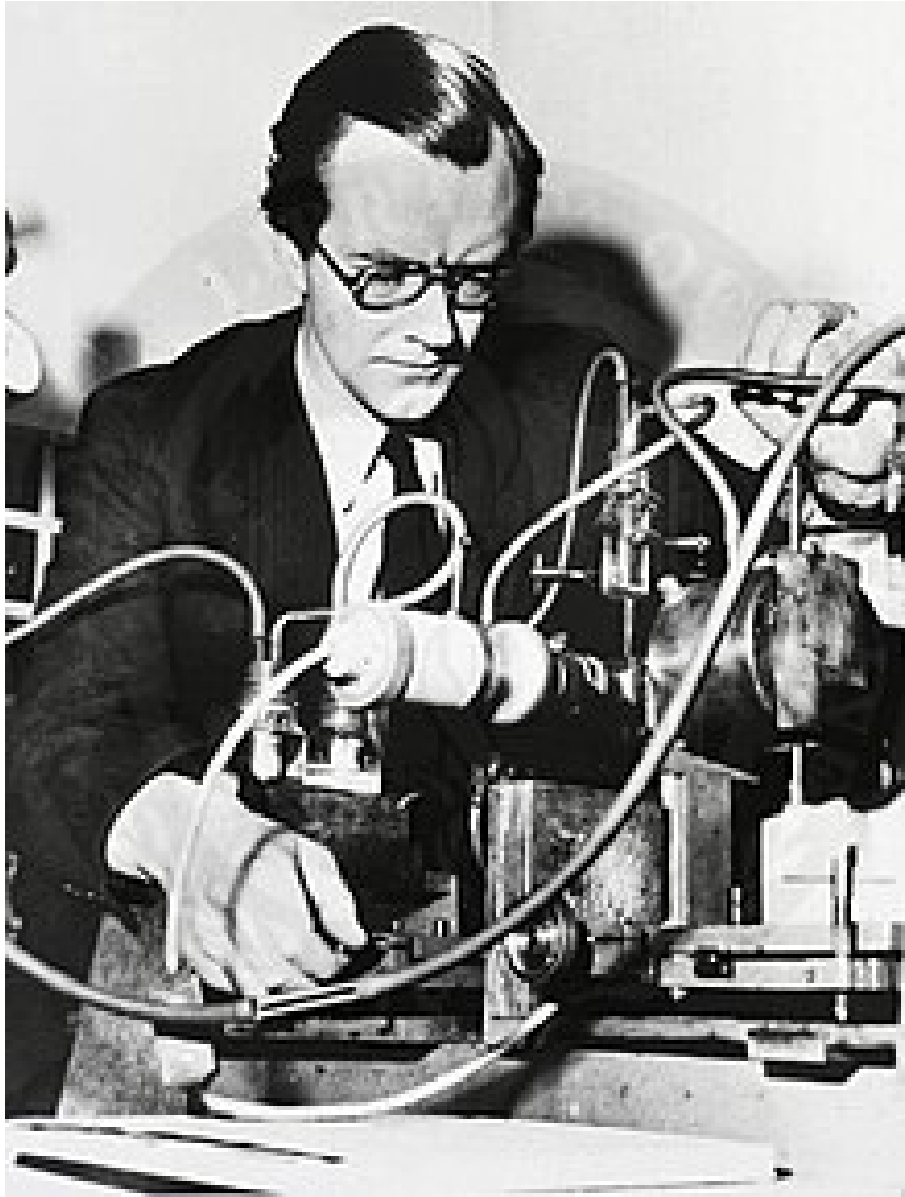


Figure 12.10: Maurice Wilkins (1916-2004). He applied to DNA the X-ray diffraction methods pioneered by Dorothy Hodgkin. It was his work, and that of Rosalind Franklin, together with Linus Pauling's model-building methods, that enabled Crick and Watson to correctly solve the structure of DNA. He shared the 1962 Nobel Prize in Physiology or Medicine with them.



Figure 12.11: Rosalind Franklin (1920-1958). It was one of her high-quality diffraction photographs, taken in Maurice Wilkins' laboratory, that proved to be critical for the DNA structure. She might have shared the Nobel Prize with Wilkins, Crick and Watson, but before this could be considered by the committee, she died of ovarian cancer.

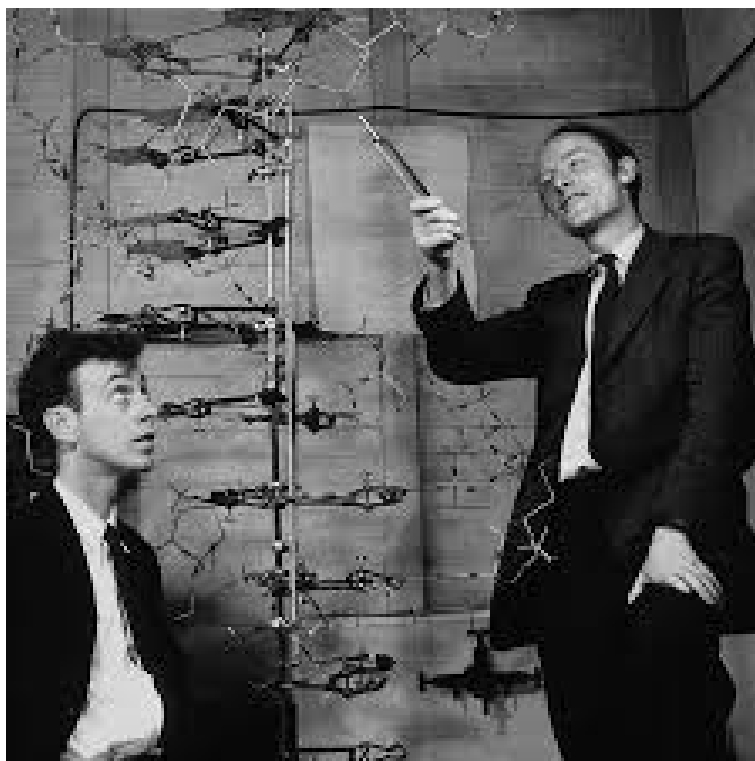


Figure 12.12: Francis Crick (1916-2004) and James Dewey Watson (born 1928) at the Cavendish Laboratory with their model of DNA. After their discovery of the structure of DNA, it became clear that it was this molecule that carried genetic information between generations.

### Suggestions for further reading

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12. James D. Watson, *The Double Helix*, Athenium, New York (1968).
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14. F. Crick, *Central dogma of molecular biology*, Nature, **227**, 561-563 (1970).
15. David Freifelder (editor), *Recombinant DNA, Readings from the Scientific American*, W.H. Freeman and Co. (1978).
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# Chapter 13

## WILKINSON

### 13.1 A revival of inorganic chemistry

#### Excerpts from Sir Geoffrey Wilkinson's Nobel autobiography

I was born in Springside, a village close to Todmorden in west Yorkshire on July 14th, 1921. The house where I was born and indeed most of the village has been demolished by the local council as being unfit for habitation. My father, and his father, also Geoffrey, were both master house painters and decorators, the latter, youngest of twelve children having migrated from Boroughbridge in Yorkshire about 1880. My mother's family were originally of hill farming stock but many of my relations were weavers in the local cotton mills and indeed my mother went into the mill at an early age. My first introduction to chemistry came at a quite early age through my mother's elder brother. A well known organist and choirmaster he had married into a family that owned a small chemical company making Epsom and Glauber's salt for the pharmaceutical industry. I used to play around in their small laboratory as well as go with my uncle on visits to various chemical companies.

The oldest of three children, I was educated in the local council primary school and after winning a County Scholarship in 1932, went to Todmorden Secondary School. This small school has had an unusual record of scholarly achievement, including two Nobel Laureates within 25 years. I actually had the same Physics teacher as Sir John Cockcroft, but physics was never my favourite subject.

In 1939 I obtained a Royal Scholarship for study at the Imperial College of Science and Technology where I graduated in 1941. As it was wartime, I was directed to stay on and did some research under the supervision of my predecessor, Professor H.V.A. Briscoe. In late 1942, Professor F.A. Paneth was recruiting young chemists for the nuclear energy project which I joined. I was sent out to Canada in January 1943 and remained in Montreal and later Chalk River until I could leave in 1946. Having been attracted by the prospect



Figure 13.1: Professor Sir Geoffrey Wilkinson (1921-1996).

of California, I wrote to, and was accepted by Professor Glenn T. Seaborg. For the next four years in Berkeley I was engaged mostly on nuclear taxonomy and made many new neutron deficient isotopes using the cyclotrons of the Radiation Laboratory.

On a visit in 1949 to England, Briscoe advised me that I was unlikely to get an academic position in England in nuclear chemistry so that when I went as Research Associate to the Massachusetts Institute of Technology in 1950, I began to return to my first interest as a student - transition metal complexes such as carbonyls and olefin complexes.

In 1951 I was offered an Assistant Professorship at Harvard University, largely because of my nuclear background. I was at Harvard from September 1951 until I returned to England in December, 1955, with a sabbatical break of nine months in Copenhagen in Professor Jannik Bjerrum's laboratory as a John Simon Guggenheim Fellow. At Harvard, I still did some nuclear work on excitation functions for protons on cobalt but I had already begun to work on olefin complexes so that I was primed for the appearance of the celebrated Kealy and Pauson note on dicyclopentadienyliron in *Nature* in early 1952.

In June 1955, I was appointed to the chair of Inorganic Chemistry at Imperial College in the University of London, which, at that time was the only established chair in the subject in the United Kingdom and took up the position in January 1956. I have been at the College ever since and have worked, with a relatively few students and postdoctoral fellows, almost entirely on the

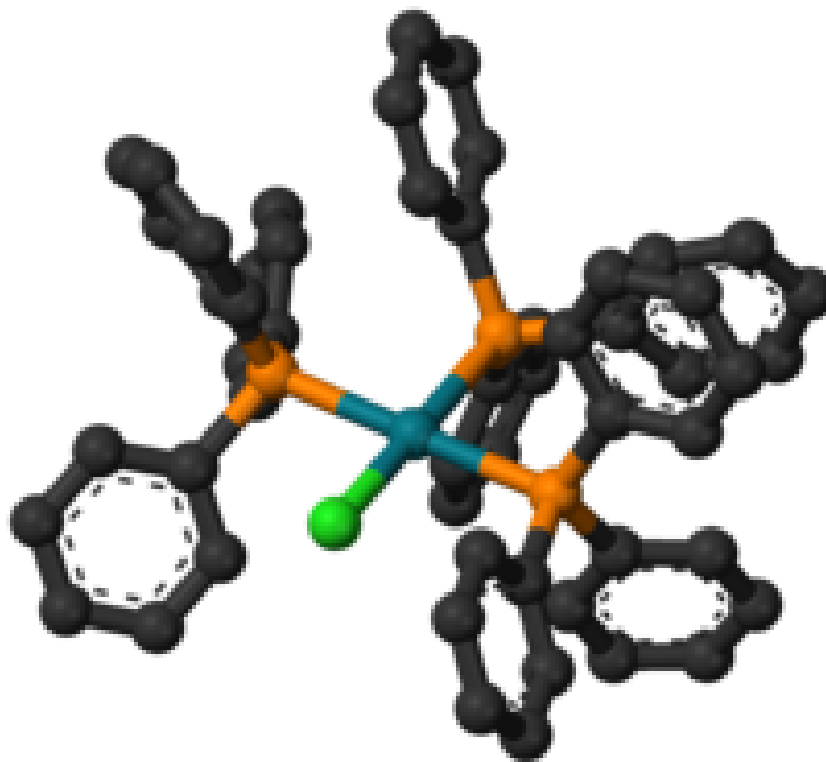


Figure 13.2: Wilkinson's catalyst,  $\text{RhCl}(\text{PPh}_3)_3$ .

complexes of transition metals. I have been much interested in the complex chemistry of ruthenium, rhodium and rhenium, in compounds of unsaturated hydrocarbons and with metal to hydrogen bonds. The latter led to work on homogeneous catalytic reactions such as hydrogenation and hydroformylation of olefins.

### Organometallic catalysts

The catalysts for which Sir Geoffrey Wilkinson was awarded the 1973 Nobel Prize in Chemistry (shared with Ernst Otto Fischer) are organometallic “sandwich compounds”. A typical catalyst of this type is the ferrocene molecule, shown in Figure 13.3. In this molecule, an iron atom is sandwiched between two  $\text{C}_5\text{H}_5$  rings. Other catalysts first synthesized by Prof. Wilkinson make use of various organic ring systems, and various transition metals. These catalysts have proved to me immensely valuable to chemical industries.

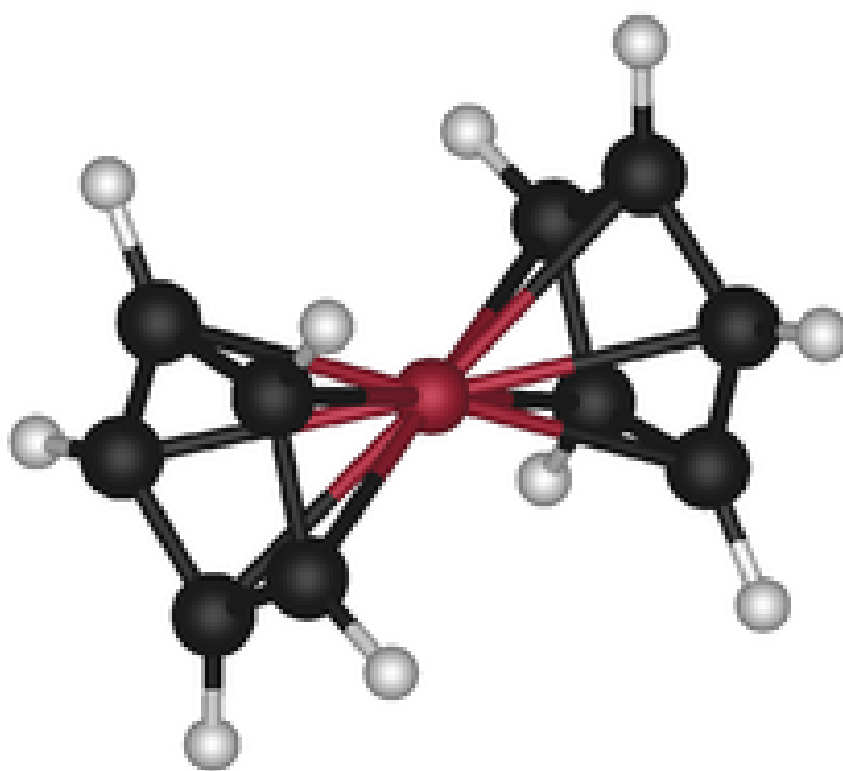


Figure 13.3: The structure of ferrocene  $\text{Fe}(\text{C}_5\text{H}_5)_2$ .



Figure 13.4: This beautiful old Victorian building was the Chemistry Department of Imperial College when I started to work there. Sadly it was later torn down and replaced by a modern building.

## Some personal memories of Prof. Wilkinson

I have many memories about Prof. Wilkinson and his family, because I continued to see them very regularly even after I moved to Denmark. Lady Wilkinson came from a much-respected Danish academic family. Her father was the Rector of the Pharmaceutical College of the University of Copenhagen, and her brother later held the same position. Lady Wilkinson first studied pharmacology. After she had finished that education, she took a degree in biochemistry at the University of California in Berkeley under the famous biochemist Melvin Calvin.

It was at Berkeley's International House that she met Prof. Wilkinson. At a celebration of Saint Lucia Day at International House she looked so beautiful in a white dress with a crown of burning candles that he immediately fell in love with her. They remained unusually devoted to each other as long as they both lived. When Prof. Wilkinson died in 1996, Lady Wilkinson was completely heartbroken, and she remained inconsolable for several years afterwards.

In London, Lady Wilkinson had a dream job, writing books on the history of medicine for the Wellcome Trust. She wrote a number of books while holding this position, for example histories of virology, and histories of the relationship between human diseases and animal diseases. Her daughter, Prof. Anne Wilkinson, later followed in her footsteps, doing research on the history of medicine and public health for the Wellcome Trust.

Because of Lady Wilkinson's Danish roots, the family always spent two months each year at their summer house in Tisvilde, about 50 kilometers north of Copenhagen. These were not exactly holidays for Prof. Wilkinson. He always took with him massive amounts of scientific reading, which he ploughed through and used both for his own research and to update Cotton and Wilkinson, *Basic Inorganic Chemistry*.

When I came to the University of Copenhagen in 1973, the Wilkinsons proposed an arrangement where I became a sort of caretaker for their summer house. My family and I could use it whenever they were not there. In return I should do the chores that had to be done each year, cutting the grass on the 3000 square meter grounds with a scythe, planting flowers in the garden and weeding it, eliminating grass and moss from the terrace, and putting varnish on the floors, and so on.

My wife and I had lunch with the Wilkinsons every year when they arrived in Denmark. Their summer house was very near to the one that belonged to the Bohr family. When Lady Wilkinson was a young girl, there were only a handful of summer houses in Tisvilde, and the few people who spent their summers there knew each other very well. Lady Wilkinson remembered how Niels Bohr's five sons sometimes teased her by throwing pine cones after her. Sometimes when I was at the summer house before the Wilkinsons arrived, one or another of Niels Bohr's sons would come to the door and ask if the Wilkinsons were there.

My family and I will always remember the great kindness which Prof. Sir Geoffrey Wilkinson and Lady Lise Wilkinson showed to us over very many years.

### Suggestions for further reading

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# Chapter 14

## HERSCHBACH

### 14.1 Molecular beam experiments

One of the early pioneers of molecular beam experiments was the German-American physicist Otto Stern (1888-1969). Because of his Jewish ancestry, Stern left Germany when Hitler came to power. and moved to the United states, first to the Carnegie Institute of Technology, and later to the University of California in Berkeley. His experiments on molecular beam methods, and his discovery of spin quantization earned him 82 nominations for the Nobel Prize in Physics, which he finally won in 1943 “for his contribution to the development of the molecular ray method, and his discovery of the magnetic moment of the proton”.

#### Production of molecular beams

Molecular beams are produced by allowing a gas at high pressure to expand quickly into a region of lower pressure. In this way, a beam of gas particles moving in approximately the same direction and with approximately the same velocity can be produced.

#### Chemical reaction mechanisms

Molecular beams have many applications. They have been used to fabricate thin films, quantum wells and quantum dots. Molecular beams were used by Isador Rabi to measure the magnetic moments of isotopes, and by Charles H. Townes to produce a maser. In 1986, Dudley R. Herschbach, Yuan T. Lee and John C. Polanyi were jointly awarded the Nobel Prize in Chemistry for their use of crossed molecular beams to determine the mechanisms of chemical reactions.



Figure 14.1: Otto Stern (1888-1969).



Figure 14.2: Dudley R. Herschbach (born in 1932).

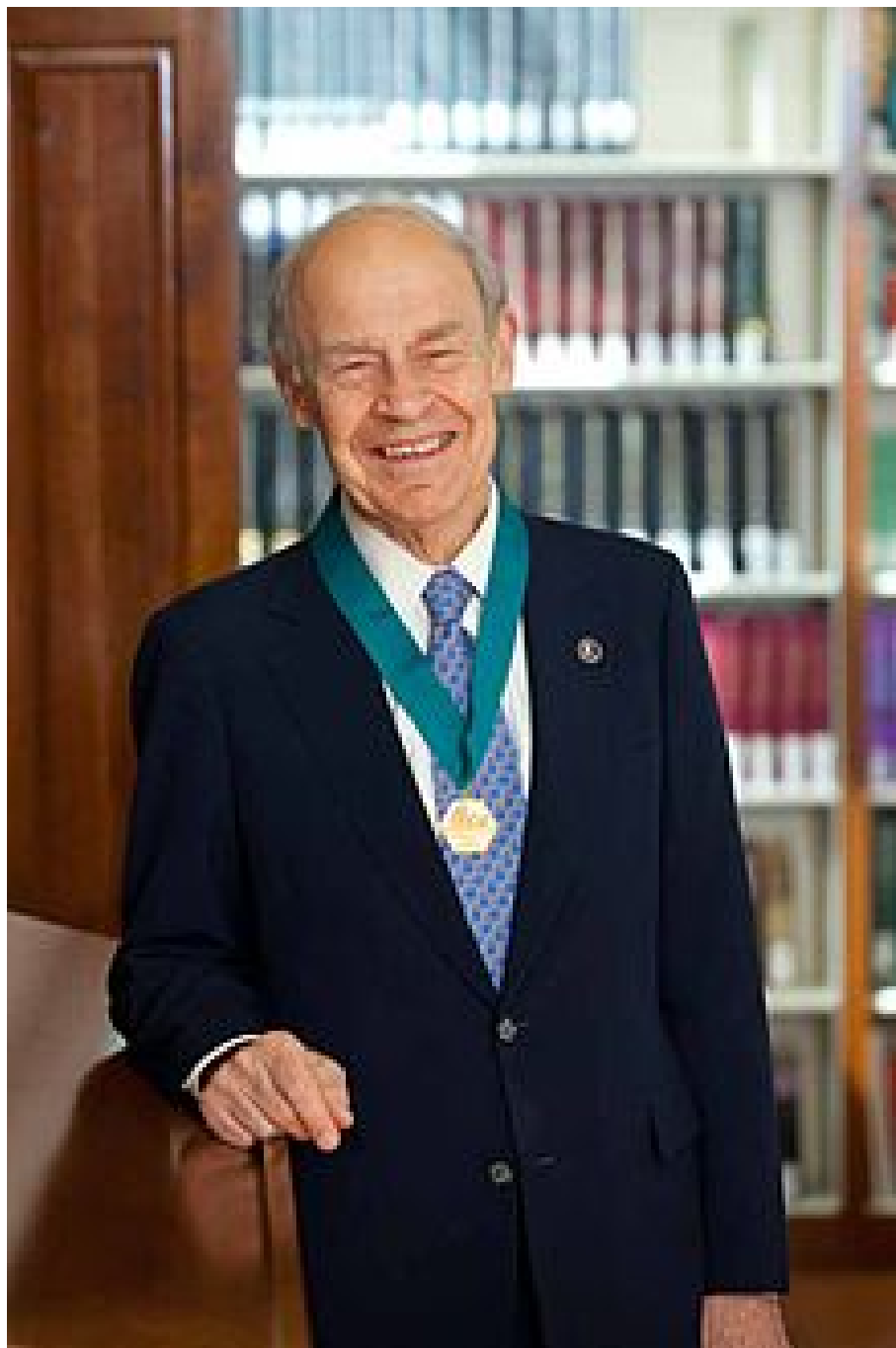


Figure 14.3: Dudley Herschbach accepting the American Institute of Chemistry's gold medal in 2011.



Figure 14.4: Georgene Herschbach, Dudley's wife, was Dean of Students at Harvard until her retirement.



Figure 14.5: **Professor Yuan T. Lee** (born in 1936) shared the 1986 Nobel Prize in Chemistry with Dudley R. Herschbach and John C. Polanyi. He was the first Taiwanese to receive a Nobel Prize.



Figure 14.6: Professor John C. Polanyi (born in 1929). In addition to his scientific research, for which he shared the 1986 Nobel Prize in Chemistry, Prof. Polanyi has also been very active in efforts to reduce the danger of a catastrophic nuclear war. He was the founder of the Canadian national group of Pugwash Conferences on Science and World Affairs, an organization that was awarded the 1995 Nobel Peace Prize.

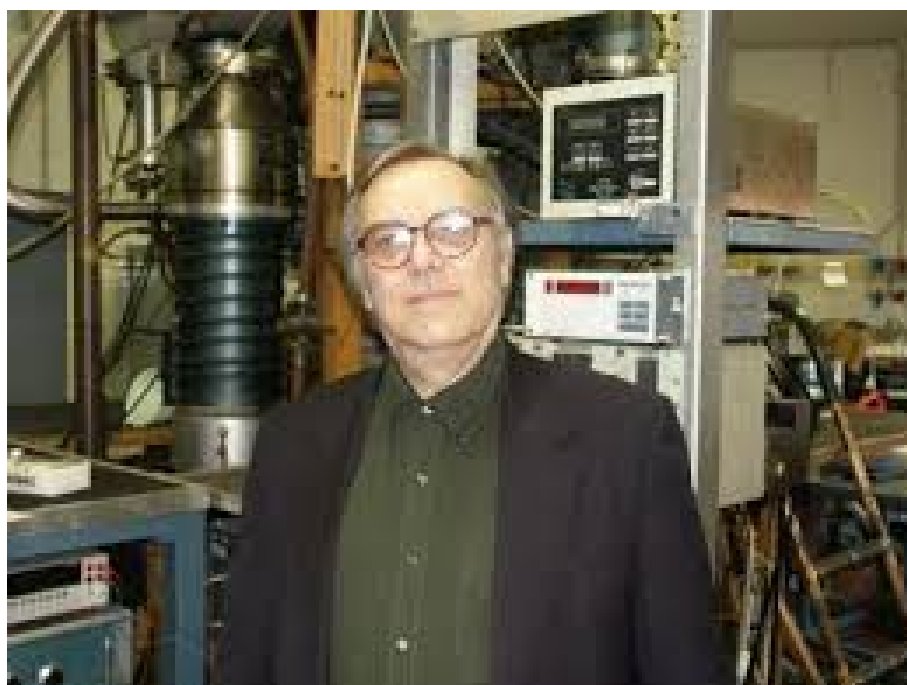


Figure 14.7: Prof. Vincenzo Aquilanti (born in 1939). After working at Harvard with Dudley Herschbach, he returned to Italy, where he became the head of the chemistry department at the University of Perugia. He and his group have done pioneering theoretical and experimental work on the mechanism of chemical reactions, using molecular beam techniques.



Figure 14.8: **Prof. Bretislav Friedrich** (born in 1953). He worked with Dudley Herschbach's Harvard group for 16 years before moving to the Fritz Haber Institute in Germany.

## 14.2 Some excerpts from Dudley Herschbach's Nobel autobiography

I entered Stanford University in 1950 and found a new world with vastly broader intellectual horizons than I'd imagined. Although I gladly played freshman football, I had turned down an athletic scholarship in favor of an academic one. This permitted me to give up varsity football after spring practice, in reaction to a dictum by the head coach that we not take any lab courses during the season. By then the lab and library already were for me much the more exciting playground. My chief mentor at Stanford was Harold Johnston, who imbued me with his passion for chemical kinetics. Many other subjects and professors were also compelling and I took up to ten courses a term. Mathematics was especially appealing; I so admired the teaching of Harold Bacon, George Polya, Gabor Szego, and Bob Weinstock that I simply took all the courses they gave. I received the B.S. in mathematics in 1954 and the M.S. in chemistry in 1955. My Master's thesis, done under the direction of Harold Johnston, was titled: "Theoretical Pre-exponential Factors for Bimolecular Reactions." It employed the transition-state theory of Henry Eyring and Michael Polanyi and treated the proportionality factor in the most venerable formula of chemical kinetics, the Arrhenius equation.

My graduate study continued at Harvard, where again I found an exhilarating academic environment. I received the A.M. in Physics in 1956 and the Ph.D. in Chemical Physics in 1958. My Doctoral Thesis, done under E. Bright Wilson, Jr., was titled: "Internal Rotation and Microwave Spectroscopy". This presented theoretical calculations and experiments dealing with hindered internal rotation of methyl groups. The height of the hindering barrier could be accurately determined because the observed spectra were very sensitive to tunneling between equivalent potential minima. Much that shaped my later research I learned from Bright Wilson and other faculty, especially George Kistiakowsky and Bill Klemperer, or from fellow students, especially Jerry Swalen, Victor Laurie and Larry Krisher. My thesis work also benefited from visits of several months to take spectra at the National Research Council in Ottawa and to compute Mathieu functions at Los Alamos National Laboratory. During 1957-1959, while a Junior Fellow in the Society of Fellows at Harvard, I developed plans for molecular beam studies of elementary chemical reactions.

This work was launched at the University of California at Berkeley, where I was appointed an Assistant Professor of Chemistry in 1959 and became an Associate Professor in 1961. The chief experiments dealt with reactions of alkali atoms with alkyl iodides, systems studied forty years before by Michael Polanyi. Rather simple apparatus sufficed to attain single-collision conditions and revealed that the product molecules emerged with a preferred range of

recoil angle and translational energy. The possibility of resolving such features of reaction dynamics encouraged other workers pursuing kindred experiments and fostered an outburst of new theory. My early work thus interacted particularly with that of Richard Bernstein, Sheldon Datz, Ned Greene, John Polanyi, John Ross, and Peter Toennies.

This new field developed rapidly after I returned to Harvard in 1963 as Professor of Chemistry. We studied a wide range of alkali reactions and found several prototype modes of reaction dynamics which could be correlated with the electronic structure of the target molecule. Processes involving abrupt, impulsive bond exchange or formation of a persistent complex comprise the two major categories. In 1967 Yuan Lee joined our group as a postdoctoral fellow and led the construction of a “supermachine”. This employed greatly augmented differential pumping, sophisticated mass spectroscopy using ion counting techniques adapted from nuclear physics, and supersonic beam sources advocated by enterprising chemical engineers, especially John Fenn and Jim Anderson. The new machine greatly extended the scope of crossed-beam experiments, taking us “beyond the alkali age”. In particular, we were then able to study the same reactions elucidated by John Polanyi with his complementary method of infrared chemiluminescence. This much enhanced the interpretation of reaction dynamics in terms of electronic structure.

### Some personal memories of Prof. Herschbach's group at Harvard

I hope that the reader will forgive me if I add a few personal memories of Prof. Herschbach and his group at Harvard. I visited them a number of times with the help of grants from the Carlsberg Foundation because I was interested in Prof. Herschbach's work with dimensional scaling, and he was interested in my work with hyperspherical harmonics and quantum theory using spaces of high dimension.

Dudley is an incredibly kind and generous person. He is always thinking about things that he can do to make life happier of the young people in his group. This wonderful kindness makes Dudley's team special. When I visited them the group was located in a number of basement rooms in one of the Harvard laboratories. Saturdays, Sundays, late at night, and early in the morning, there were always people working there. No one wanted to be anywhere else. That was where things were happening and that was where the group members were happy. Dudley himself never came to the lab before noon, because he liked to do mathematical work at home in the morning. When he did come in, though, he was available to everyone to discuss the problems on which they were working. Everyone agreed that Dudley was a genius. His extremely strong mathematical background allowed him to solve problems that baffled others. On top of that, his optimism and cheerfulness also overcame every difficulty. Working in his group was a really great experience, which I will always remember.

## Suggestions for further reading

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# Chapter 15

## QUANTUM CHEMISTRY

### 15.1 Valence bond theory

#### Lewis structures

In 1916, G.N. Lewis of the University of California, Berkeley, proposed a theory of chemical bonding in which a pair of electrons, one donated by each of the bonding atoms, together form a covalent bond. For example, in the hydrogen molecule,  $\text{H}_2$ , one electron is contributed by each of the two hydrogen atoms. Another example of a Lewis structure is the  $\text{NO}_2^-$  ion shown in Figure 15.2. The outer-shell electrons that do not contribute to bonding are represented by pairs of dots and are called *lone pairs*.

#### Heitler-London theory

The next step in valence bond theory was taken in 1927 by Walter Heitler and Fritz London, who used Erwin Schrödinger's wave equation and Wolfgang Pauli's exclusion principle to study the covalent bonding of the hydrogen molecule.

#### Linus Pauling's contributions

Linus Pauling developed these ideas further by introducing the key concepts of resonance and orbital hybridization. Pauling's two famous books, *Introduction to Quantum Mechanics, With Applications to Chemistry* (with E. Bright Wilson, 1935), and *The Nature of the Chemical Bond* (1939) were extremely important and influential, as was Charles Coulson's *Valence* (1952).

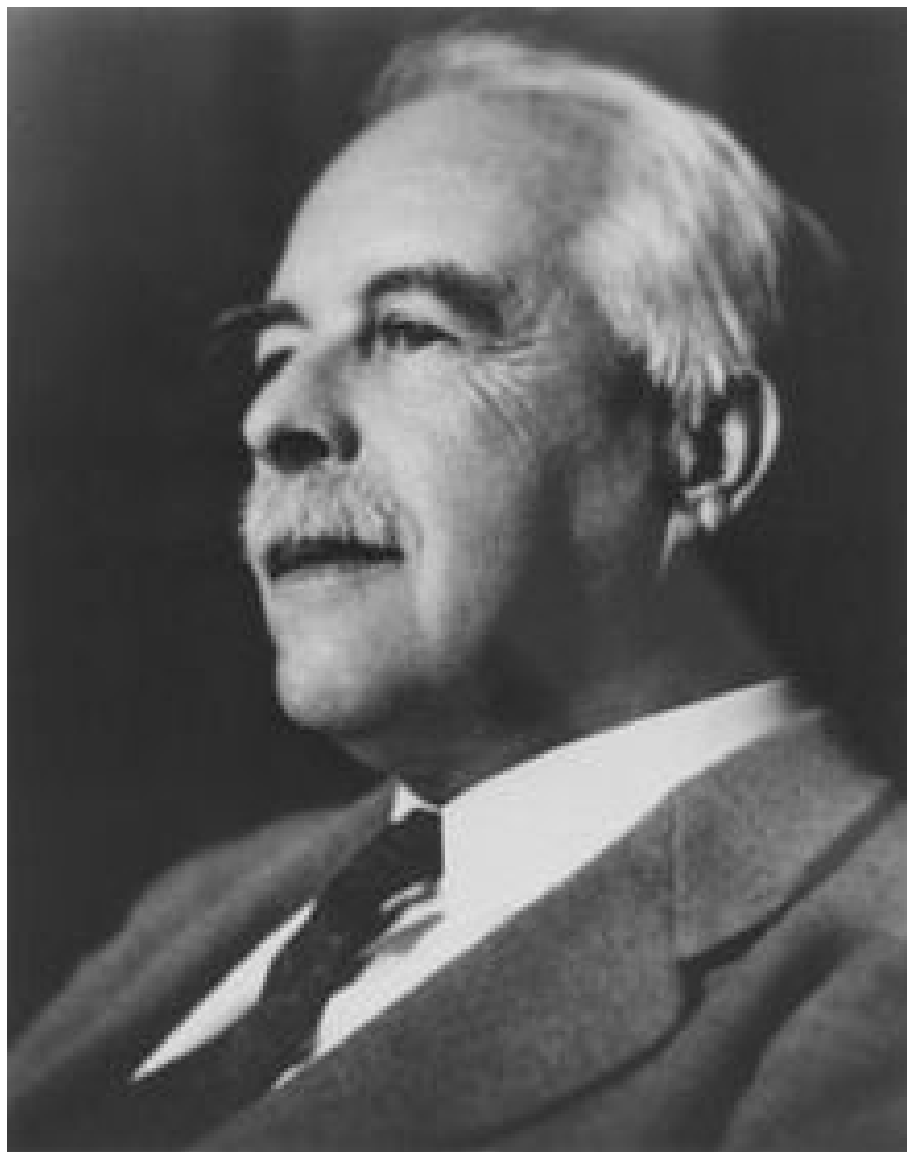


Figure 15.1: Gilbert N. Lewis (1875-1946). He was nominated for the Nobel Prize in Chemistry 41 times, but never won it.

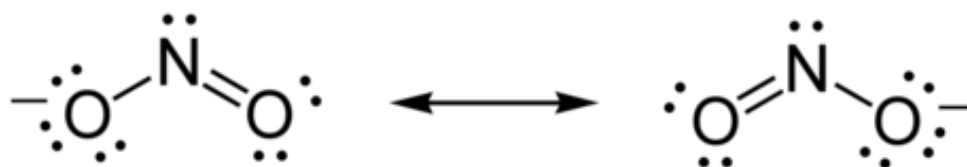


Figure 15.2: The  $\text{NO}_2^-$  ion, an example of a Lewis structure.

## 15.2 Molecular orbital theory

In molecular orbital theory, atomic orbitals shown in Figure 11.6 are used to build up a representation of the orbital of an electron moving in a molecule. For example, Figure 15.3 shows a schematic diagram of the LCAO (Linear Combination of Atomic Orbitals) model of bonding in the  $H_2$  molecule. When two hydrogen atoms approach each other, the two electrons move in an attractive potential produced by both nuclei. Thus the range of their motion is enlarged. According to the Pauli exclusion principle, both electrons are allowed to move in this enlarged region, if they have opposite spins. The electronic wave function in the enlarged region of motion is called a *molecular orbital*.

In the LCAO approximation, molecular orbitals are built up from atomic orbitals centered on the individual atoms of a molecule. For example, suppose that in the  $H_2$  molecule we denote the positions of the two nuclei by  $\mathbf{X}_1$  and  $\mathbf{X}_2$ . Then we can approximate the molecular orbitals  $\phi_\sigma(\mathbf{x})$  and  $\phi_{\sigma^*}(\mathbf{x})$  by symmetric and antisymmetric combinations of the two atomic orbitals,  $\chi_{1s}(\mathbf{x} - \mathbf{X}_1)$  and  $\chi_{1s}(\mathbf{x} - \mathbf{X}_2)$ :

$$\begin{aligned}\phi_\sigma(\mathbf{x}) &= N [\chi_{1s}(\mathbf{x} - \mathbf{X}_1) + \chi_{1s}(\mathbf{x} - \mathbf{X}_2)] \\ \phi_{\sigma^*}(\mathbf{x}) &= N' [\chi_{1s}(\mathbf{x} - \mathbf{X}_1) - \chi_{1s}(\mathbf{x} - \mathbf{X}_2)]\end{aligned}\tag{15.1}$$

where  $N$  and  $N'$  are normalizing constants. The symmetric combination is called a *bonding orbital*, and in the hydrogen molecule ground state it is doubly occupied, the two electrons having opposite spin quantum numbers. In the ground state of  $H_2$ , the antibonding orbital,  $\phi_{\sigma^*}(\mathbf{x})$ , is unoccupied, as is illustrated schematically in Figure 15.3.

### Quantum biochemistry

Erich Hückel devised an extremely simple semiempirical approximation for treating the highest filled and lowest empty molecular orbitals of flat organic molecules such as benzene, naphthalene, pyridine, guanine, cytosine, etc. Solution to Hückel's equations only required the diagonalization of a small matrix, and this could be done even before the advent of electronic computers. During World War II, the French scientist Alberte Pullman sat in a basement room in Paris diagonalizing Hückel matrices with a desk-top mechanical calculator, while her husband Bernard drove a tank for the Free French forces in North Africa. After the war Alberte and Bernard Pullman published a pioneering book entitled *Quantum Biochemistry* (1963), which opened a new field of research.

Meanwhile, the great Hungarian-American biochemist and physiologist Albert Szent-Györgyi, published a book entitled *Introduction to a Submolecular Biology* (1960) in which he explored the biochemical roles of charge donors and charge acceptors. Charge donors are molecules whose highest filled molecular orbitals are relatively high in energy while charge acceptors are molecules are relatively low in energy.

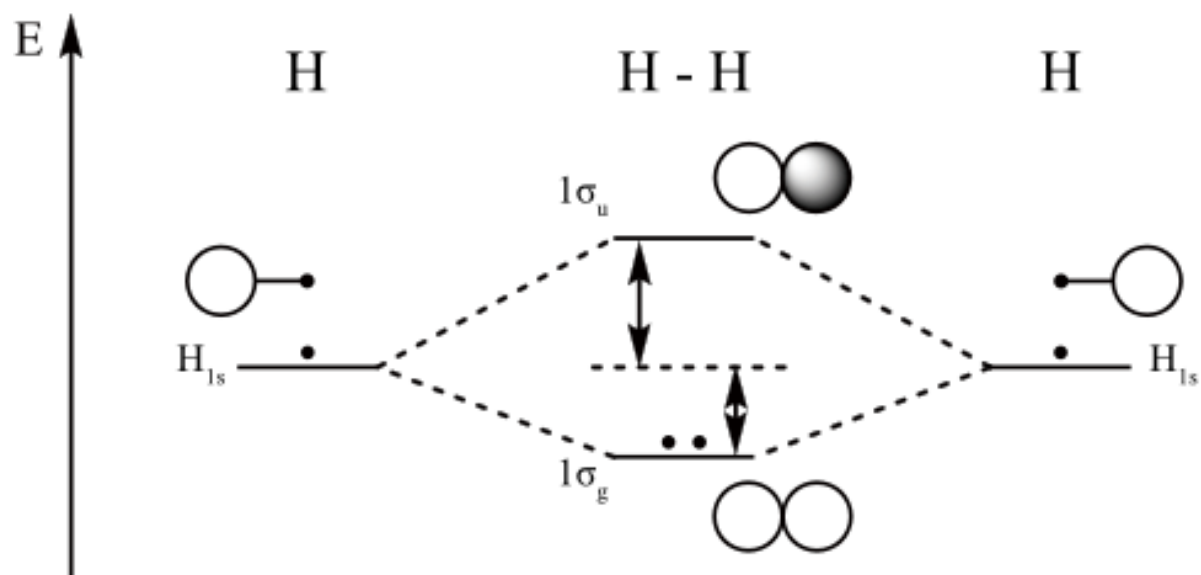


Figure 15.3: A schematic diagram of the LCAO (Linear Combination of Atomic Orbitals) model of bonding in the  $\text{H}_2$  molecule.



Figure 15.4: **Robert Mulliken (1896-1986).** His contributions to molecular orbital theory won him the 1966 Nobel Prize in Chemistry.



Figure 15.5: **Erich Hückel (1896-1980).** He developed a very simple semiempirical approximation for treating the highest filled and lowest empty molecular orbitals of flat organic molecules.



Figure 15.6: **Alberte Pullman (1920-2011).**



Figure 15.7: **Alberte Pullman with her husband, Bernard.**

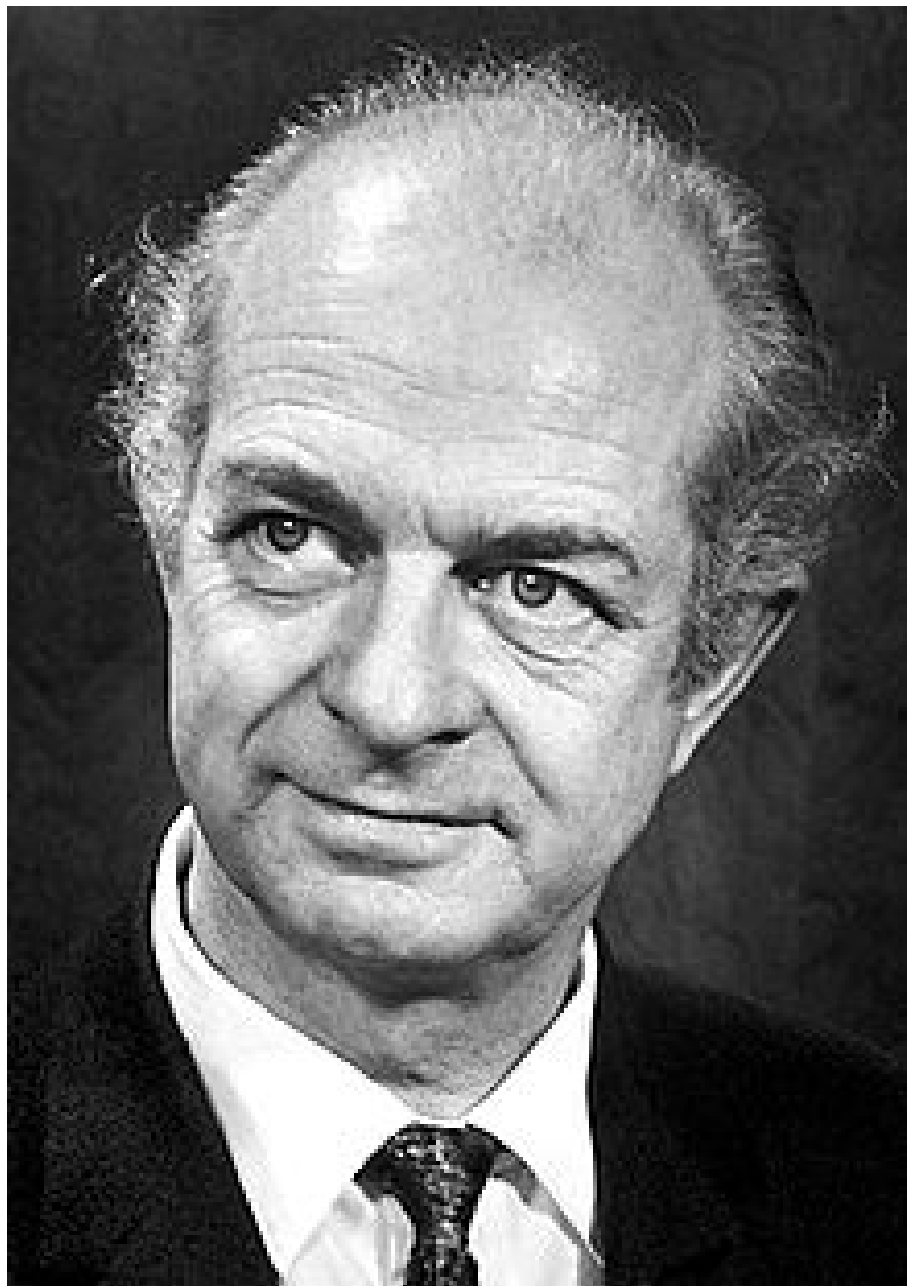


Figure 15.8: Linus Pauling (1901-1994). The New Scientist called him one of the 20 most important scientists in history. He was awarded the Nobel Prize in Chemistry in 1954 and the Nobel Peace Prize in 1962.

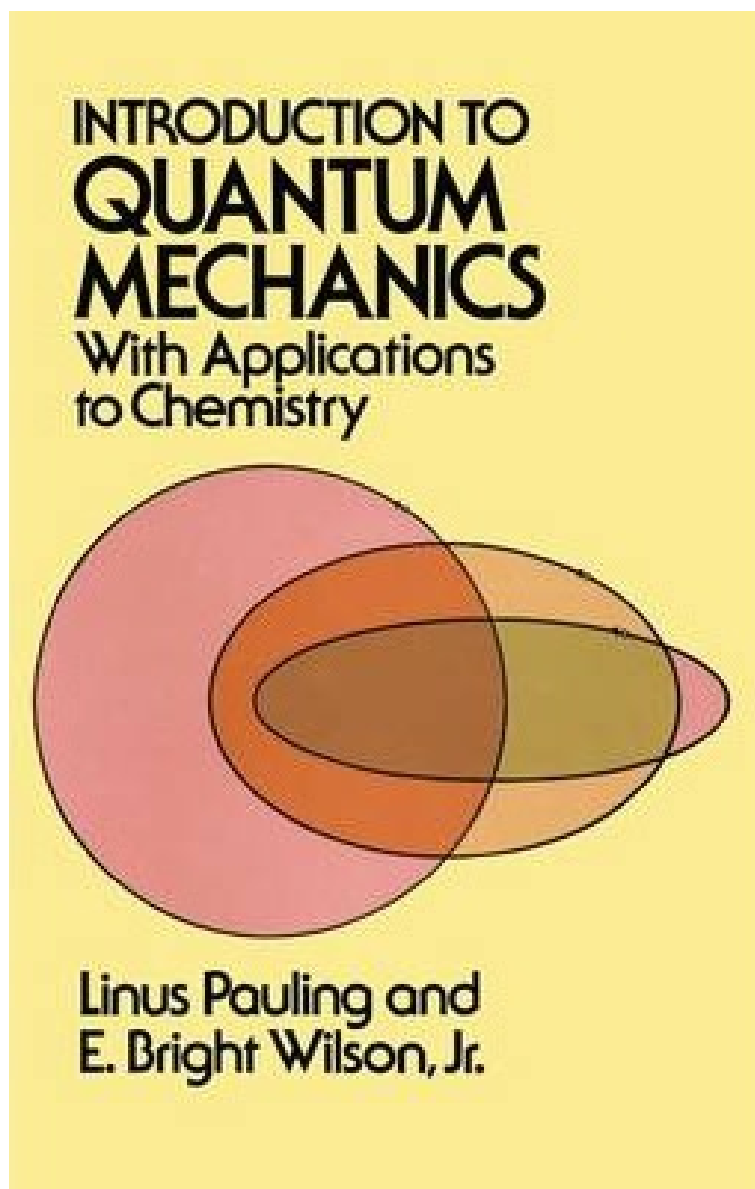


Figure 15.9: Two-time Nobel Prize winner Linus Pauling, Research Professor at the Linus Pauling Institute of Science and Medicine, Palo Alto, California, and E. Bright Wilson, Jr., Professor Emeritus of Chemistry at Harvard University, provide a readily understandable study of “wave mechanics,” discussing the Schrödinger wave equation and the problems which can be solved with it. The book was first published in 1935, and it is still in use today.

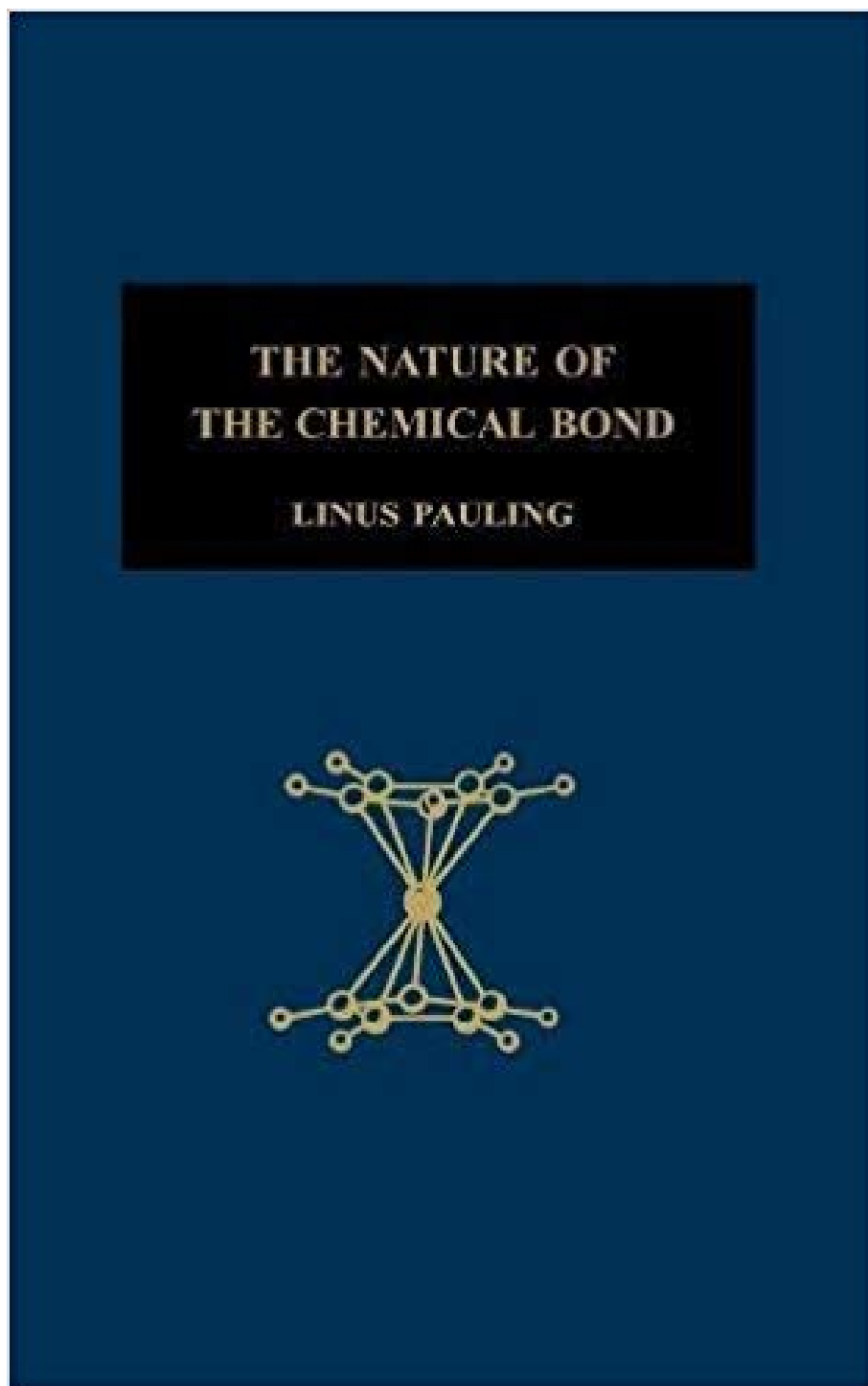


Figure 15.10: Linus Pauling's famous book, *The Nature of the Chemical Bond and the Structure of Molecules and Crystals*. Cornell University Press, 1939.



Figure 15.11: Clemens C.J. Roothaan (1918-2019). His thesis supervisor, Robert Mulliken, said of him, “I tried to induce Roothaan to do his Ph.D. thesis on Hückel-type calculations on substituted benzenes. But after carrying out some very good calculations on these he revolted against the Hückel method, threw his excellent calculations out the window, and for his thesis developed entirely independently his now well known all-electron LCAO SCF self-consistent-field method for the calculation of atomic and molecular wave functions, now appropriately referred to, I believe, as the Hartree-Fock-Roothaan method”.

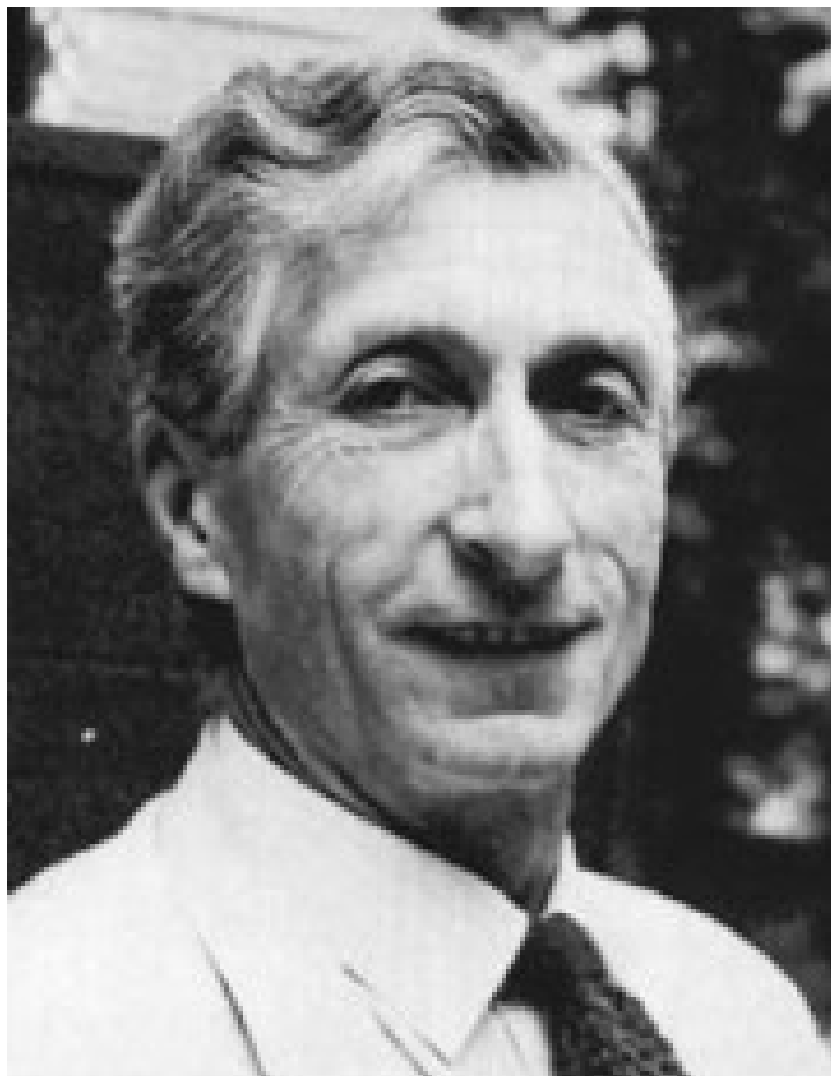


Figure 15.12: Charles Coulson (1910-1974). He was the leader of important quantum chemistry groups, first at Kings College London, and then later at Oxford University. He was a very tall man, and also a religious one, with a strong sense of duty. On the day of his death in 1974, he worked until the last minute. His last words were, “I think I can’t do any more”. His book, *Valence*, greatly influenced the development of quantum chemistry.

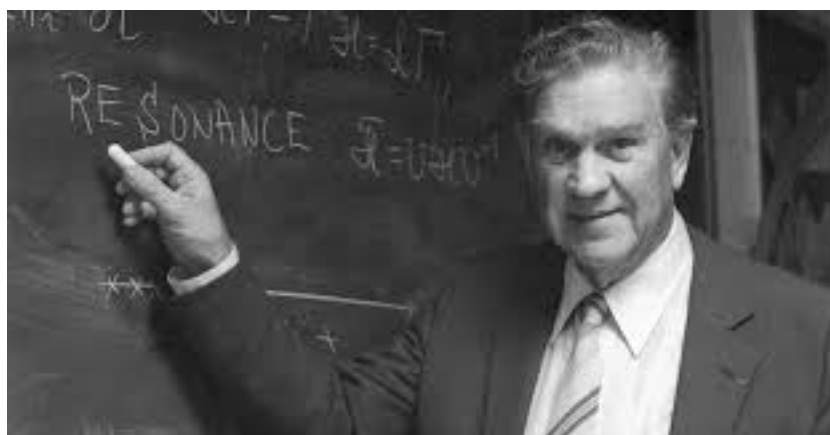


Figure 15.13: Per-Olov Löwdin (1916-2000). Prof. Löwdin founded two important quantum chemistry groups, one at the University of Uppsala in Sweden, and another at the University of Florida in Gainesville. Many scientists were introduced to quantum chemistry at his famous Uppsala summer schools, which often included mountain-climbing expeditions. Prof. Löwdin also founded two important journals, *The International Journal of Quantum Chemistry* and *Advances in Quantum Chemistry*. He invented a number of mathematical techniques much used in the field, for example his method for symmetrical orthogonalization of basis functions.

## 15.3 Quantum chemistry and the development of computers

### Some personal memories of early computers

I hope that readers will forgive me if I tell them of my own personal memories of early computers:

When I arrived at Imperial College (then part of the University of London) in 1962, I worked with a crystallographic group that using the Mercury computer at University College to do the calculations needed to arrive at molecular structures. This gave me the chance to use Mercury to do quantum chemical calculations. I always went over to University College with the crystallographers at night, because time on the computer was so expensive that we could only afford to use it at night. I would make a bed for myself out of three rather hard chairs in a row and would try to sleep. At 3 AM or 4 AM they would wake me up and would say “Now it’s your turn”.

Mercury was as big as a house, but could do far less than a modern laptop. It had 50,000 or so vacuum tubes which required cooling. The cooling system sometimes broke down, and one or another of the vacuum tubes sometimes failed, so one had to be grateful for the periods when Mercury was working. Our programs were written on punched tape in a language called CHLF3. (The letters stood for Cambridge, London, Harwell and Farnborough, the four places that had Mercurys). After we had read the paper tape into the computer, the program was converted into a magnetic form on a rapidly rotating drum, and then checked against the original input. If it did not check, we had a so-called “drum parity”, which meant that we had to stop the computer and restart it by hand, using a bewildering array of manual controls.

After finishing the work on Mercury at 6 AM or so, I would walk home, passing through the almost-deserted streets of Soho, and seeing pale-faced teenagers who had been up all night, high on amphetamines. They were sitting on the pavement near an underground station, waiting for it to open.

After we had used Mercury for two years or so, IBM gave Imperial College one of their early computers. Using this was much better. Programs for the IBM machine were written on punched cards. We just went over to the machine with our punched cards and stood in line to have them read into the computer. Then a few minutes later we were handed a printout of the output.

The IBM was much better than the machines that were available in eastern Europe, and for this reason I was contacted by Janos Ladik and his group at the Hungarian Academy of Science, who proposed a collaboration. We worked together for several years, calculating the electronic structure of a number of polypeptides and polynucleotides.

In 1965, Janos Ladik invited me to attend a meeting of quantum theorists and computer scientists from both East and West, held at a town on the Hungarian Puszta, the great Hungarian plain east of Budapest. Both Charles Coulson and Per-Olov Löwdin were there, as well as many scientists from the eastern side of the Iron Curtain. At the meeting,



Figure 15.14: **Enrico Clementi (born 1931) explained to us that microminiaturization would soon make computers hundreds of times faster, smaller and less expensive. He was completely right.**

Enrico Clementi spoke about computer programs that he had developed for performing *ab-initio*<sup>1</sup> calculation of the electronic structure of molecules. Clementi was an important IBM scientist, and he had his own laboratory with a large computer which he could use as he liked. The programs that he described to us took hundreds of hours to complete an electronic structure calculation on a single molecule.

In the question period after Clementi's lecture, someone from the audience said: "It's all right for you, Clementi. You can use hundreds of hours on a single calculation if you want to, because you are sitting at IBM with your own dedicated computer. But what about the rest of us? What good are these programs to us?"

Clementi answered: "In a few years, computers will be hundreds of times faster, and they will also be cheaper." The audience asked: "And how will this happen?". Clementi answered: "Through microminiaturization." He was completely right. That was exactly what happened.

## The invention of transistors; Microelectronics

The problem of unreliable vacuum tubes was solved in 1948 by John Bardeen, William Shockley and Walter Brattain of the Bell Telephone Laboratories. Application of quantum theory to solids had lead to an understanding of the electrical properties of crystals. Like atoms, crystals were found to have allowed and forbidden energy levels.

The allowed energy levels for an electron in a crystal were known to form bands, i.e., some energy ranges with many allowed states (allowed bands), and other energy ranges

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<sup>1</sup>*ab-initio* is a Latin expression meaning "from the beginning". Such programs are completely free of input parameters based on experiments.

with none (forbidden bands). The lowest allowed bands were occupied by electrons, while higher bands were empty. The highest filled band was called the “valence band”, and the lowest empty band was called the “conduction band”.

According to quantum theory, whenever the valence band of a crystal is only partly filled, the crystal is a conductor of electricity; but if the valence band is completely filled with electrons, the crystal is an electrical insulator. (A completely filled band is analogous to a room so packed with people that none of them can move.)

In addition to conductors and insulators, quantum theory predicted the existence of “semiconductors” - crystals where the valence band is completely filled with electrons, but where the energy gap between the conduction band and the valence band is very small. For example, crystals of the elements silicon and germanium are semiconductors. For such a crystal, thermal energy is sometimes enough to lift an electron from the valence band to the conduction band.

Bardeen, Shockley and Brattain found ways to control the conductivity of germanium crystals by injecting electrons into the conduction band, or alternatively by removing electrons from the valence band. They could do this by “doping” the crystals with appropriate impurities, or by injecting electrons with a special electrode. The semiconducting crystals whose conductivity was controlled in this way could be used as electronic valves, in place of vacuum tubes.

By the 1960's, replacement of vacuum tubes by transistors in electronic computers had led not only to an enormous increase in reliability and a great reduction in cost, but also to an enormous increase in speed. It was found that the limiting factor in computer speed was the time needed for an electrical signal to propagate from one part of the central processing unit to another. Since electrical impulses propagate with the speed of light, this time is extremely small; but nevertheless, it is the limiting factor in the speed of electronic computers.

## Integrated circuits

In order to reduce the propagation time, computer designers tried to make the central processing units very small; and the result was the development of integrated circuits and microelectronics. (Another motive for miniaturization of electronics came from the requirements of space exploration.)

Integrated circuits were developed in which single circuit elements were not manufactured separately. Instead, the whole circuit was made at one time. An integrated circuit is a sandwich-like structure, with conducting, resisting and insulating layers interspersed with layers of germanium or silicon, “doped ” with appropriate impurities. At the start of the manufacturing process, an engineer makes a large drawing of each layer. For example, the drawing of a conducting layer would contain pathways which fill the role played by wires in a conventional circuit, while the remainder of the layer would consist of areas destined to be etched away by acid.

The next step is to reduce the size of the drawing and to multiply it photographically. The pattern of the layer is thus repeated many times, like the design on a piece of wallpaper.

The multiplied and reduced drawing is then focused through a reversed microscope onto the surface to be etched.

Successive layers are built up by evaporating or depositing thin films of the appropriate substances onto the surface of a silicon or germanium wafer. If the layer being made is to be conducting, the surface would consist of an extremely thin layer of copper, covered with a photosensitive layer called a “photoresist”. On those portions of the surface receiving light from the pattern, the photoresist becomes insoluble, while on those areas not receiving light, the photoresist can be washed away.

The surface is then etched with acid, which removes the copper from those areas not protected by photoresist. Each successive layer of a wafer is made in this way, and finally the wafer is cut into tiny “chips”, each of which corresponds to one unit of the wallpaper-like pattern.

Although the area of a chip may be much smaller than a square centimeter, the chip can contain an extremely complex circuit. A typical programmable minicomputer or “microprocessor”, manufactured during the 1970’s, could have 30,000 circuit elements, all of which were contained on a single chip. By 1986, more than a million transistors were being placed on a single chip.

As a result of miniaturization, the speed of computers rose steadily. In 1960, the fastest computers could perform a hundred thousand elementary operations in a second. By 1970, the fastest computers took less than a second to perform a million such operations. In 1987, a computer called GF11 was designed to perform 11 billion floating-point operations (flops) per second.

GF11 (Gigaflop 11) is a scientific parallel-processing machine constructed by IBM. Approximately ten floating-point operations are needed for each machine instruction. Thus GF11 runs at the rate of approximately a thousand million instructions per second (1,100 MIPS). The high speed achieved by parallel-processing machines results from dividing a job into many sub-jobs on which a large number of processing units can work simultaneously.

Computer memories have also undergone a remarkable development. In 1987, the magnetic disc memories being produced could store 20 million bits of information per square inch; and even higher densities could be achieved by optical storage devices. (A “bit” is the unit of information. For example, the number 25, written in the binary system, is 11001. To specify this 5-digit binary number requires 5 bits of information. To specify an  $n$ -digit binary number requires  $n$  bits of information. Eight bits make a “byte”.)

In the 1970’s and 1980’s, computer networks were set up linking machines in various parts of the world. It became possible (for example) for a scientist in Europe to perform a calculation interactively on a computer in the United States just as though the distant machine were in the same room; and two or more computers could be linked for performing large calculations. It also became possible to exchange programs, data, letters and manuscripts very rapidly through the computer networks.

## Moore's law

In 1965, only four years after the first integrated circuits had been produced, Dr. Gordon E. Moore, one of the founders of Intel, made a famous prediction which has come to be known as "Moore's Law". He predicted that the number of transistors per integrated circuit would double every two years, and that this trend would continue through 1975. In fact, the general trend predicted by Moore has continued for a much longer time. Although the number of transistors per unit area has not continued to double every two years, the logic density (bits per unit area) has done so, and thus a modified version of Moore's law still holds today. How much longer the trend can continue remains to be seen. Physical limits to miniaturization of transistors of the present type will soon be reached; but there is hope that further miniaturization can be achieved through "quantum dot" technology, molecular switches, and autoassembly.

A typical programmable minicomputer or "microprocessor", manufactured in the 1970's, could have 30,000 circuit elements, all of which were contained on a single chip. By 1989, more than a million transistors were being placed on a single chip; and by 2000, the number reached 42,000,000.

As a result of miniaturization and parallelization, the speed of computers rose exponentially. In 1960, the fastest computers could perform a hundred thousand elementary operations in a second. By 1970, the fastest computers took less than a second to perform a million such operations. In 1987, a massively parallel computer, with 566 parallel processors, called GFll was designed to perform 11 billion floating-point operations per second (flops). By 2002 the fastest computer performed 40 at teraflops, making use of 5120 parallel CPU's.

Computer disk storage has also undergone a remarkable development. In 1987, the magnetic disk storage being produced could store 20 million bits of information per square inch; and even higher densities could be achieved by optical storage devices. Storage density has until followed a law similar to Moore's law.

In the 1970's and 1980's, computer networks were set up linking machines in various parts of the world. It became possible (for example) for a scientist in Europe to perform a calculation interactively on a computer in the United States just as though the distant machine were in the same room; and two or more computers could be linked for performing large calculations. It also became possible to exchange programs, data, letters and manuscripts very rapidly through the computer networks.

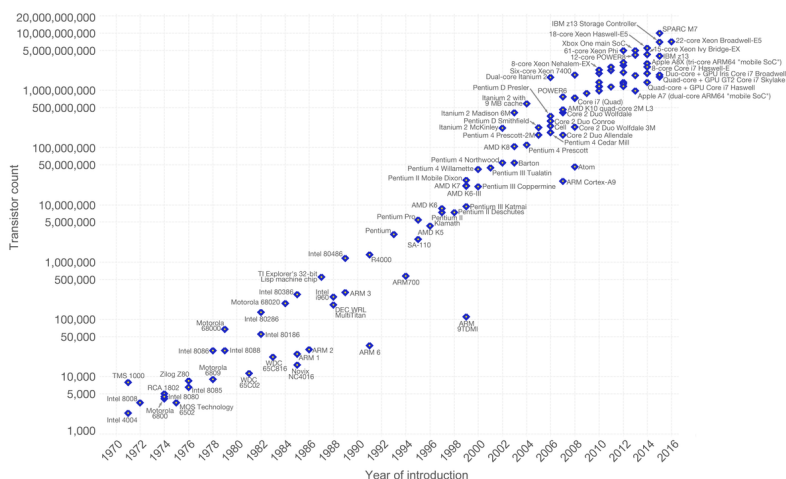
The exchange of large quantities of information through computer networks was made easier by the introduction of fiber optics cables. By 1986, 250,000 miles of such cables had been installed in the United States. If a ray of light, propagating in a medium with a large refractive index, strikes the surface of the medium at a grazing angle, then the ray undergoes total internal reflection. This phenomenon is utilized in fiber optics: A light signal can propagate through a long, hairlike glass fiber, following the bends of the fiber without losing intensity because of total internal reflection. However, before fiber optics could be used for information transmission over long distances, a technological breakthrough in glass manufacture was needed, since the clearest glass available in 1940 was opaque in lengths



Figure 15.15: Gordon E. Moore (born 1929), a founder of Intel and the author of Moore's Law. In 1965 he predicted that the number of components in integrated circuits would double every year for the next 10 years". In 1975 he predicted the this doubling would continue, but revised the doubling rate to "every two years. Astonishingly, Moore's Law has held much longer than he, or anyone else, anticipated.



Moore's Law – The number of transistors on integrated circuit chips (1971-2016) OurWorld



The data visualization is available at [OurWorldinData.org](https://ourworldindata.org). There you find more visualizations and research on this topic.

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Figure 15.17: Amazingly, Moore's Law has held much longer than he, or anyone else, anticipated. Perhaps quantum dot technologies can extend its validity even longer.

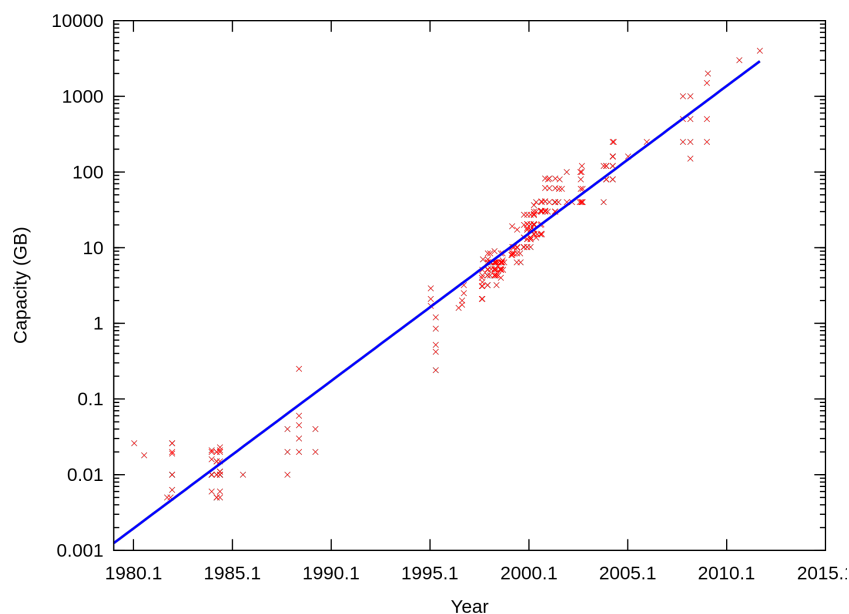


Figure 15.18: **A logarithmic plot of the increase in PC hard-drive capacity in gigabytes. An extrapolation of the rate of increase predicts that the individual capacity of a commercially available PC will reach 10,000 gigabytes by 2015, i.e. 10,000,000,000,000 bytes. (After Hankwang and Rentar, Wikimedia Commons)**

more than 10 m. Through studies of the microscopic properties of glasses, the problem of absorption was overcome. By 1987, devices were being manufactured commercially that were capable of transmitting information through fiber-optic cables at the rate of 1.7 billion bits per second.

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# Chapter 16

## NANOSCIENCE

### 16.1 Quantum dots

One of the main goals of nanoscience is to drastically increase the speed of computers by carrying microminiaturization to its ultimate limit, where the size of the components is in the nanometer range, i.e. of the order of magnitude  $10^{-9}$  m. or  $10^{-7}$  cm. For systems of this size quantum mechanical effects become dominant. Therefore the scientists who visualize computers based on nanoscale components have named these components *quantum dots*.

As is well known, atoms have a ground state and a number of discrete excited states. Similarly, the quantum dots created by workers in the field of nanoscience have ground states and discrete excited states. Thus quantum dots are closely analogous to atoms with respect to their absorption and emission of light, and they are sometimes even described as “artificial atoms”.

It is possible that the dream of achieving a workable ultra-high-speed computer based on quantum dots may soon be achieved. Scientists working at Google Research Laboratories have very recently announced progress towards this goal. Here are some quotations from an article by John Mecklin, published in the Bulletin of the Atomic Scientists on October 24, 2019:

**In a development at the edge of scientific advance and journalistic descriptive capabilities, a group of Google researchers say they have achieved the science fiction-sounding feat known as “quantum supremacy.” In a paper published in Nature, members of Google’s AI Quantum team describe their successful efforts to create a computer that capitalizes on the laws of physics most obviously in play at the subatomic realm. That quantum computer, named Sycamore, “performed the target computation in 200 seconds, and from measurements in our experiment we determined that it would take the world’s fastest supercomputer 10,000 years to produce a similar output,” two scientists involved in the experiment - John Martinis, chief scientist quantum hardware,**

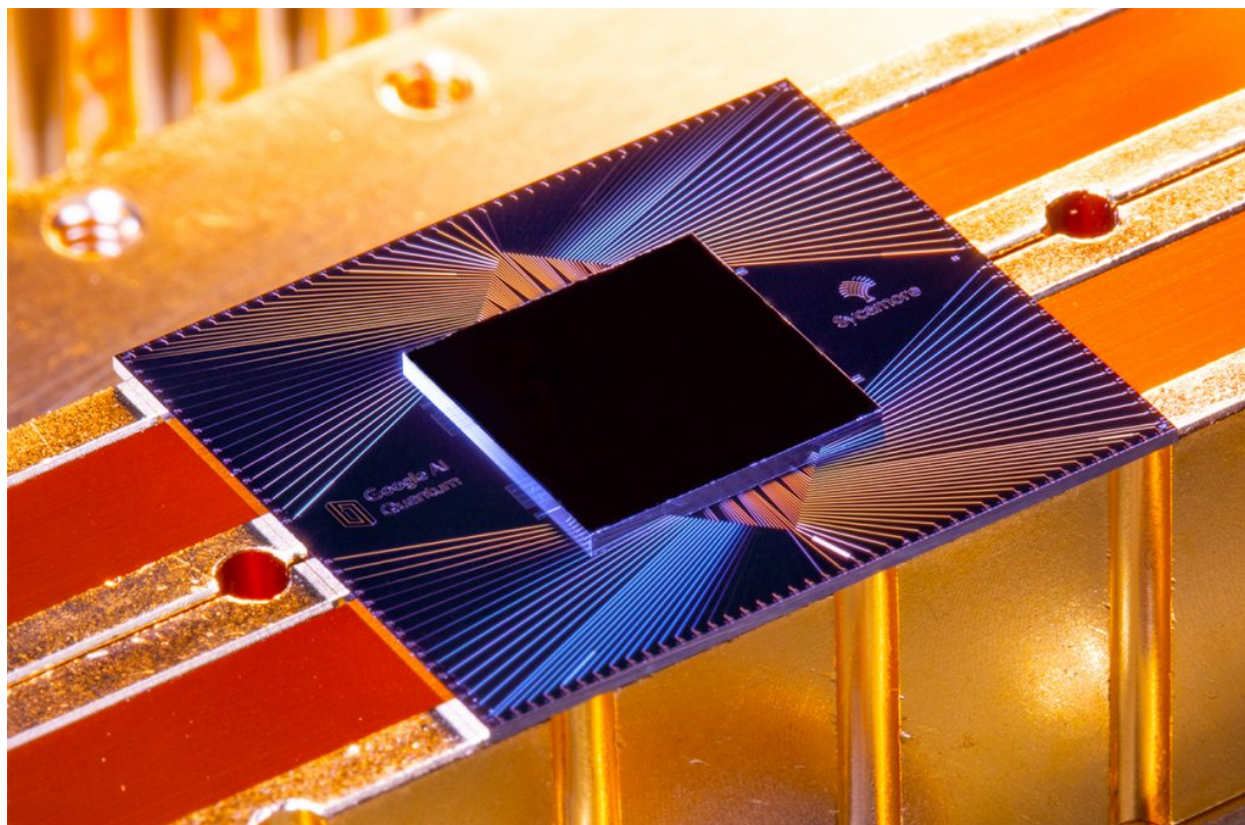


Figure 16.1: The Sycamore quantum processor. Photo credit: Erik Lucero, research scientist and lead production quantum hardware.

and Sergio Boixo, chief scientist quantum computing theory - wrote on the Google AI Blog.

For those who know some physics and are up for the challenge, the Nature paper is an enticing forest of quantum concepts - from qubits to cross-entropy benchmarking and beyond - that explains precisely how the quantum supremacy experiment was carried out and why it is of inestimable import. If you go the Nature route, you will encounter fascinating sentences such as these:

“In a superconducting circuit, conduction electrons condense into a macroscopic quantum state, such that currents and voltages behave quantum mechanically. Our processor uses transmon qubits, which can be thought of as nonlinear superconducting resonators at 5-7 GHz. The qubit is encoded as the two lowest quantum eigenstates of the resonant circuit.”

For those who don't know quantum eigenstates from *The Eiger Sanction* (and might, therefore, wonder whether quantum supremacy were a new Jason Bourne movie), both the Washington Post and New York Times offer engaging layman's explanations of the import of the quantum supremacy achievement.

## 16.2 Fullerenes

Fullerenes are large symmetrical molecules consisting of pure carbon. They take their name from the American architect, Buckminster Fuller (1895-1983), who popularized the geodesic dome, a construction that has the same geometry as the molecule  $C_{60}$ .

Fullerenes were discovered in England at the University of Sussex, by a team headed by Harry Kroto, and also in Texas at Rice University by Richard Smalley, Robert Curl, and their team. The fullerenes were found in the residue created by vaporizing carbon in a helium atmosphere. Kroto, Smalley and Curl shared the 1996 Nobel Prize for Chemistry.

Many types of fullerenes have been discovered, including those of spheroidal and ellipsoidal shapes as well as carbon nanotubes. They have found applications in medicine and biology, textiles, springs, alloys, coatings, transistors, thermal management, solar cells, hydrogen storage, energy storage, electrical cables, supercapacitors, and water treatment.

The graphite plane shown in Figure 16.5 has the fullerene structure of fullerenes, but the plane can be very large in size. A crystal of graphite consists of tightly-bonded planes such as that shown in the figure, stacked with other similar planes, the bonding between planes being only through van der Waals forces and thus very weak. Correspondingly, the conductivity of graphite is high in directions parallel to the planes, but low in directions perpendicular to them.

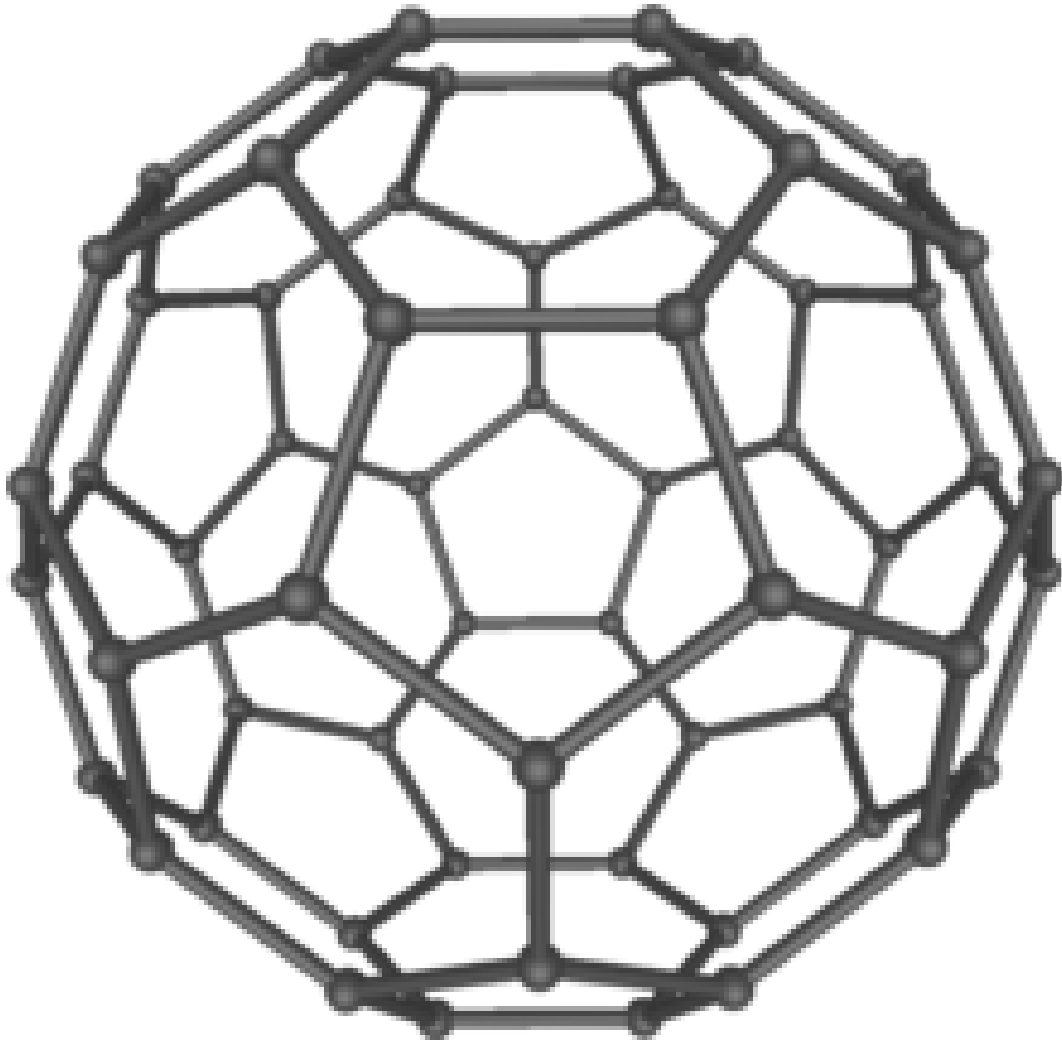


Figure 16.2: Model of the C<sub>60</sub> fullerene.

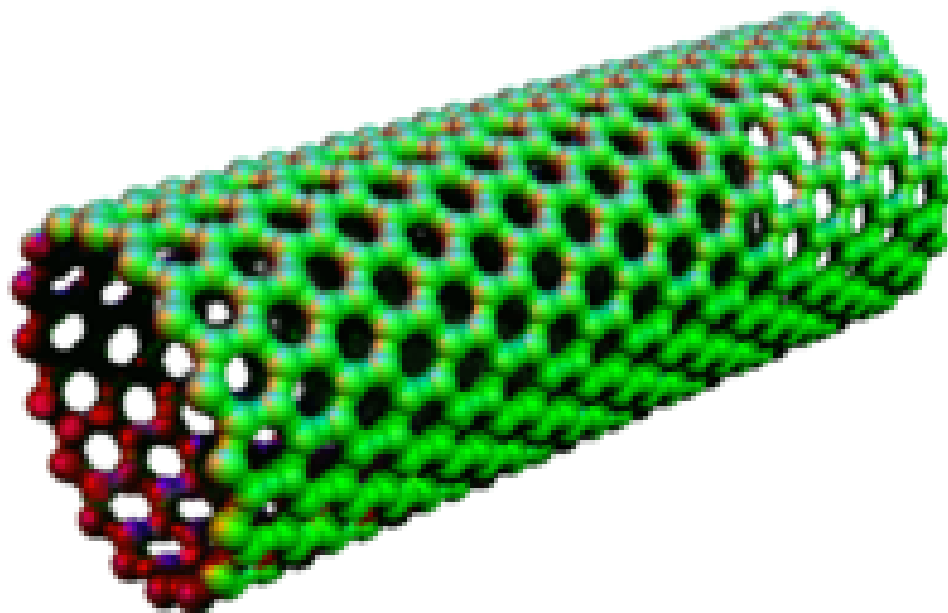


Figure 16.3: Model of a carbon nanotube.

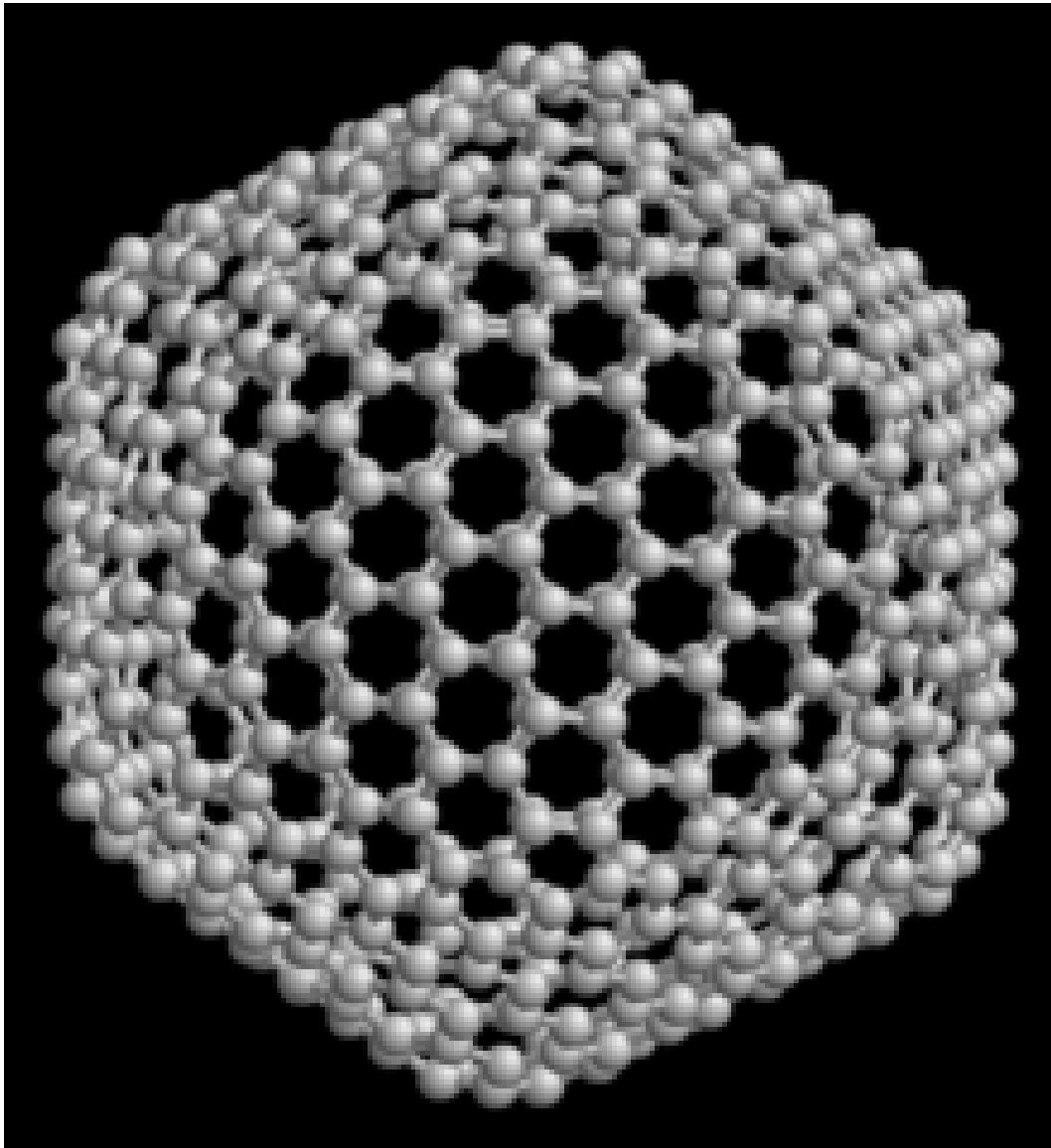


Figure 16.4: The icosahedral fullerene C<sub>540</sub>.

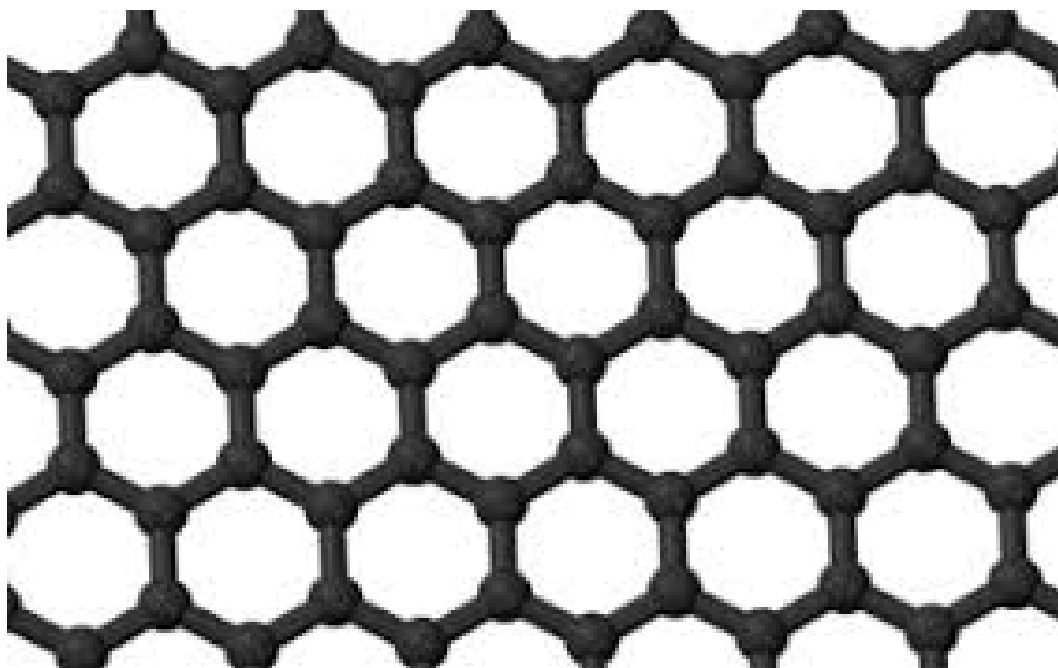


Figure 16.5: The structure of a plane of graphite.

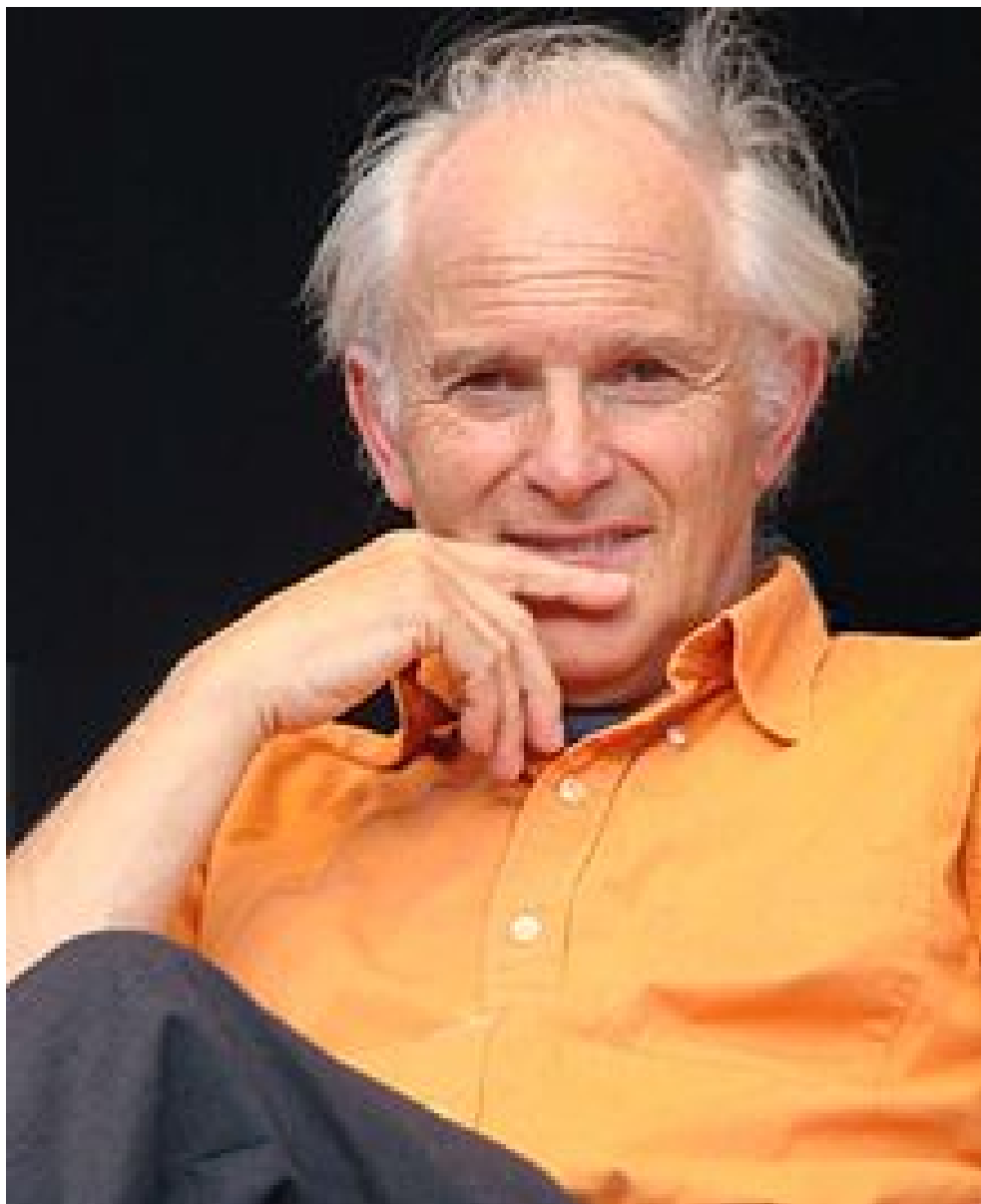


Figure 16.6: Sir Harry Kroto (1939-2016). He shared the 1996 Nobel Prize in Chemistry with Robert Curl and Richard Smalley for their discovery of fullerenes.

## 16.3 Jean-Marie Lehn's supramolecular chemistry

### Autoassembly in biology

Biological molecules have physical shapes and patterns of excess charge<sup>1</sup> which are recognized by complementary molecules because they fit together, just as a key fits the shape of a lock. Examples of biological "lock and key" fitting are the fit between the substrate of an enzyme and the enzyme's active site, the recognition of an antigen by its specific antibody, the specificity of base pairs in DNA and RNA, and the autoassembly of structures such as viruses and subcellular organelles.

One of the best studied examples of autoassembly through the mechanism of molecular complementarity is the tobacco mosaic virus. The assembled virus has a cylindrical form about 300 nm long (1 nm = 1 nanometer =  $10^{-9}$  meters = 10 Ångstroms), with a width of 18 nm. The cylindrically shaped virus is formed from about 2000 identical protein molecules. These form a package around an RNA molecule with a length of approximately 6400 nucleotides. The tobacco mosaic virus can be decomposed into its constituent molecules in vitro, and the protein and RNA can be separated and put into separate bottles.

If, at a later time, one mixes the protein and RNA molecules together in solution, they spontaneously assemble themselves into new infective tobacco mosaic virus particles. The mechanism for this spontaneous autoassembly is a random motion of the molecules through the solvent until they approach each other in such a way that a fit is formed. When two molecules fit closely together, with their physical contours matching, and with complementary patterns of excess charge also matching, the Gibbs free energy of the total system is minimized. Thus the self-assembly of matching components proceeds spontaneously, just as every other chemical reaction proceeds spontaneously when the difference in Gibbs free energy between the products and reactants is negative. The process of autoassembly is analogous to crystallization, except that the structure formed is more complex than an ordinary crystal.

A second very well-studied example of biological autoassembly is the spontaneous formation of bilayer membranes when phospholipid molecules are shaken together in water. Each phospholipid molecule has a small polar (hydrophilic) head, and a long nonpolar (hydrophobic) tail. The polar head is hydrophilic - water-loving - because it has large excess charges with which water can form hydrogen bonds. By contrast, the non-polar tail of a phospholipid molecule has no appreciable excess charges. The tail is hydrophobic - it hates water - because to fit into the water structure it has to break many hydrogen bonds to make a hole for itself, but it cannot pay for these broken bonds by forming new hydrogen bonds with water.

There is a special configuration of the system of water and phospholipid molecules which has a very low Gibbs free energy - the lipid bilayer. In this configuration, all the hydrophilic polar heads are in contact with water, while the hydrophobic nonpolar tails are in the interior of the double membrane, away from the water, and in close contact

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<sup>1</sup> They also have patterns of polarizable groups and reactive groups, and these patterns can also play a role in recognition.

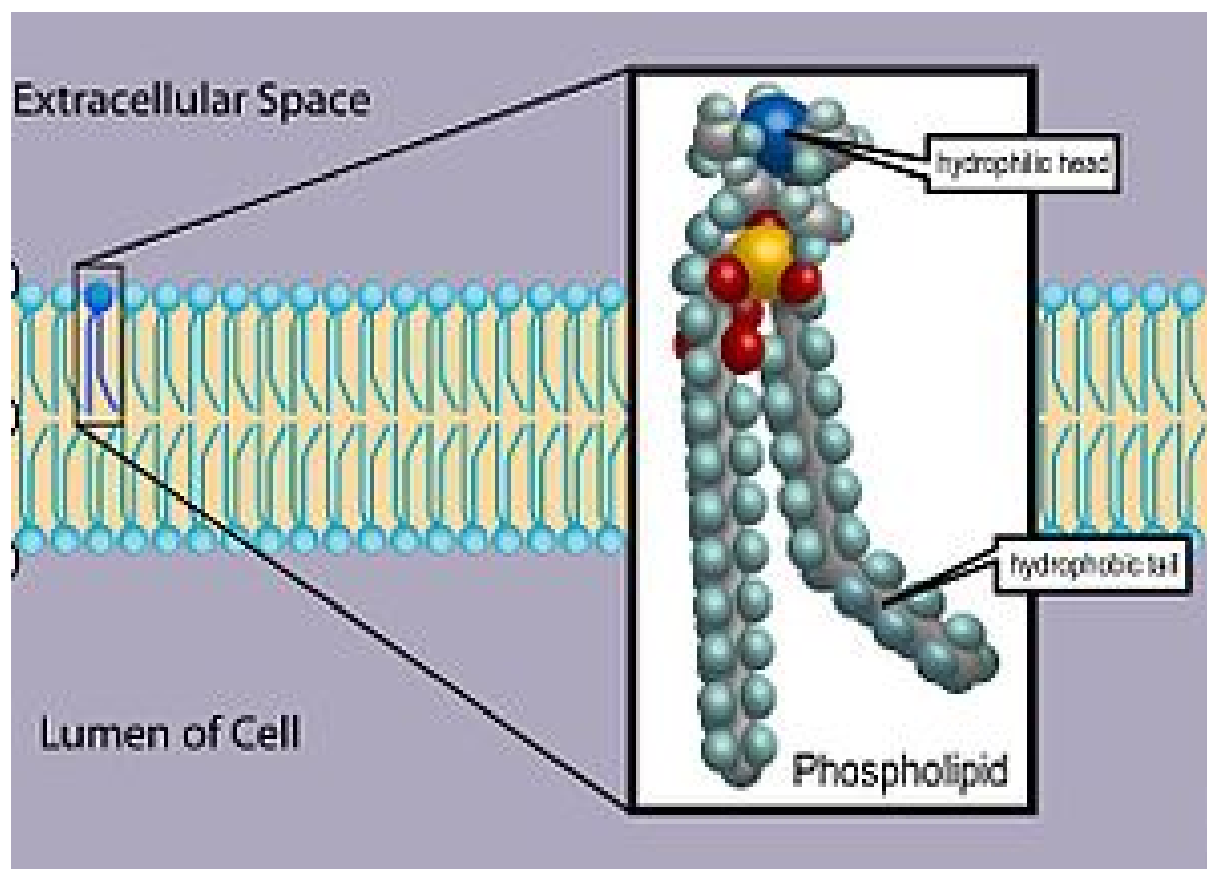


Figure 16.7: When phospholipids are placed in water and shaken, membranes identical to those of living organisms assemble themselves spontaneously. The hydrophilic (“water-loving”) head of the phospholipic molecules forms hydrogen bonds with water, while the two hydrophobic (“water-fearing”) tails are in the interior of the membrane. Autoassembly is a universal mechanism in living organisms, and researchers in nanoscience also try to use autoassembly to create the structures that they design.

with each other, thus maximizing their mutual Van der Waals attractions. (The basic structure of biological membranes is the lipid bilayer just described, but there are also other components, such as membrane-bound proteins, caveolae, and ion pores.)

The mechanism of self-organization of supramolecular structures is one of the most important universal mechanisms of biology. Chemical reactions take place spontaneously when the change in Gibbs free energy produced by the reaction is negative, i.e., chemical reactions take place in such a direction that the entropy of the universe increases. When spontaneous chemical reactions take place, the universe moves from a less probable configuration to a more probable one. The same principle controls the motion of larger systems, where molecules arrange themselves spontaneously to form supramolecular structures. Self-assembling collections of molecules move in such a way as to minimize their Gibbs free energy, thus maximizing the entropy of the universe.

Biological structures of all kinds are formed spontaneously from their components because assembly information is written onto their joining surfaces in the form of complementary surface contours and complementary patterns of excess charge<sup>2</sup>. Matching pieces fit together, and the Gibbs free energy of the system is minimized. Virtually every structure observed in biology is formed in this way - by a process analogous to crystallization, except that biological structures can be far more complex than ordinary crystals.

Researchers in microelectronics, inspired by the self-assembly of biological structures, dream of using the same principles to generate self-organizing integrated circuits with features so small as to approach molecular dimensions. As we mentioned in Chapter 15, the speed of a computing operation is limited by the time that it takes an electrical signal (moving at approximately the speed of light) to traverse a processing unit. The desire to produce ever greater computation speeds as well as ever greater memory densities, motivates the computer industry's drive towards ultraminiaturization.

Currently the fineness of detail in integrated circuits is limited by diffraction effects caused by the finite wavelength of the light used to project an image of the circuit onto a layer of photoresist covering the chip where the circuit is being built up. For this reason, there is now very active research on photolithography using light sources with extremely short wavelengths, in the deep ultraviolet, or even X-ray sources, synchrotron radiation, or electron beams. The aim of this research is to produce integrated circuits whose feature size is in the nanometer range - smaller than 100 nm. In addition to these efforts to create nanocircuits by "top down" methods, intensive research is also being conducted on "bottom up" synthesis, using principles inspired by biological self-assembly. The hope to make use of "the spontaneous association of molecules, under equilibrium conditions, into stable, structurally well-defined aggregates, joined by non-covalent bonds"<sup>3</sup>



Figure 16.8: **Jean-Marie Lehn** (born in 1939).

## Supramolecular chemistry

The Nobel Laureate Belgian chemist J.-M. Lehn pioneered the field of supramolecular chemistry by showing that it is possible to build nanoscale structures of his own design. Lehn and his coworkers at the University of Strasbourg used positively-charged metal ions as a kind of glue to join larger structural units at points where the large units exhibited excess negative charges. Lehn predicts that the supramolecular chemistry of the future will follow the same principles of self-organization which underlie the growth of biological structures, but with a greatly expanded repertoire, making use of elements (such as silicon) that are not common in carbon-based biological systems.

Other workers in nanotechnology have concentrated on the self-assembly of two-dimensional structures at water-air interfaces. For example, Thomas Bjørnholm, working at the University of Copenhagen, has shown that a nanoscale wire can be assembled spontaneously at a water-air interface, using metal atoms complexed with DNA and a DNA template. The use of a two-dimensional template to reproduce a nanostructure can be thought of as “microprinting”. One can also think of self-assembly at surfaces as the two-dimensional version of the one-dimensional copying process by which a new DNA or RNA strand assembles itself spontaneously, guided by the complementary strand.

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<sup>2</sup> Patterns of reactive or polarizable groups also play a role.

<sup>3</sup> G.M. Whiteside et al., *Science*, **254**, 1312-1314, (1991).

## 16.4 The scanning tunneling microscope

In 1981, Gerd Binnig and Heinrich Rohrer of IBM's Research Center in Switzerland announced their invention of the scanning tunneling microscope. The new microscope's resolution was so great that single atoms could be observed. The scanning tunneling microscope consists of a supersharp conducting tip, which is brought near enough to a surface so that quantum mechanical tunneling of electrons can take place between tip and surface when a small voltage is applied. The distance between the supersharp tip and the surface is controlled by means of a piezoelectric crystal. As the tip is moved along the surface, its distance from the surface (and hence the tunneling current) is kept constant by applying a voltage to the piezoelectric crystal, and this voltage as a function of position gives an image of the surface.

Variations on the scanning tunneling microscope allow single atoms to be deposited or manipulated on a surface. Thus there is a hope that nanoscale circuit templates can be constructed by direct manipulation of atoms and molecules, and that the circuits can afterwards be reproduced using autoassembly mechanisms.

The scanning tunneling microscope makes use of a quantum mechanical effect: Electrons exhibit wavelike properties, and can tunnel small distances into regions of negative kinetic energy - regions which would be forbidden to them by classical mechanics. In general it is true that for circuit elements with feature sizes in the nanometer range, quantum effects become important. For conventional integrated circuits, the quantum effects which are associated with this size-range would be a nuisance, but workers in nanotechnology hope to design integrated circuits which specifically make use of these quantum effects.

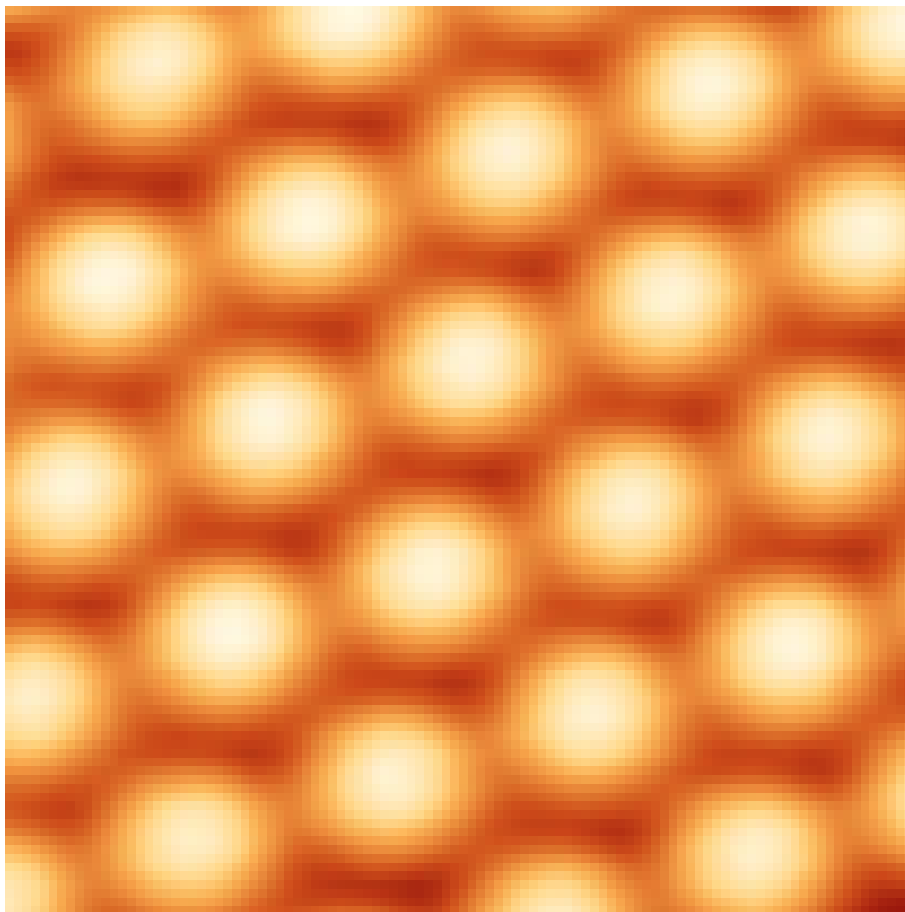


Figure 16.9: The silicon atoms on the surface of a crystal of silicon carbide.

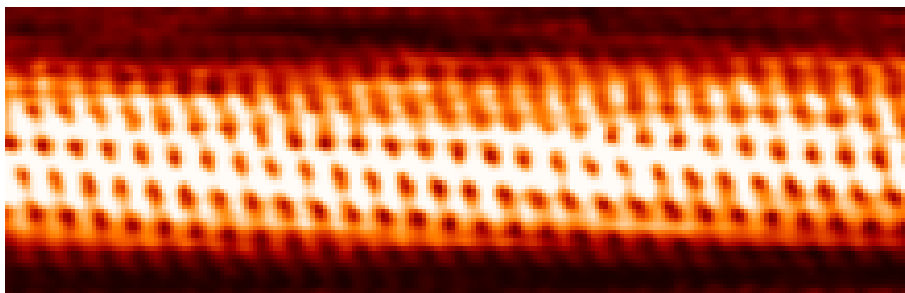


Figure 16.10: An STM image of a single-walled carbon nanotube.

## 16.5 Anita Goel: biomedical applications of nanoscience

One of the world's top science and technology innovators, Dr. Anita Goel showcased nanotechnology-enabled solutions that she and Nanobiosym are developing to address some of the most pressing global challenges. A Harvard-MIT trained physicist and physician, and an internationally recognized nanotechnology expert and entrepreneur, Dr. Goel unveiled some of Nanobiosym's breakthrough technologies like Gene-RADAR, a nanotechnology device platform that reduces the infrastructure required for diagnosing diseases from a centralized pathology lab to a mobile device much like a cellphone. She invited the audience to join the Nanobiosym Global Innovation Ecosystem to help scale up these game-changing technologies and collectively tackle the largest problems facing our planet today. "I believe that science and technology alone, no matter how game-changing, are not enough. We need to raise the consciousness with which we deploy these technologies across the globe." She also outlined a roadmap to harness nanotechnology to drive the new global economy defining key leadership roles that Europe and the United States, as well as emerging economies can play.

Inspired by the underlying unity of nature, Dr. Goel embarked upon a quest over 15 years ago to bring the worlds of physics and biomedicine together using nanotechnology - the ability to probe and control nature at very small scales - less than a billionth of a meter. "We already have the tools within science and technology to address many of the world's problems today such as access to healthcare, sustainable supplies of energy, food and water." Dr. Goel urged the need for a more holistic approach that transcends the conventional boundaries between various fields of science, technology, industries and geopolitics, enabling new quantum leaps in how we solve global problems.



Figure 16.11: Nanobiosym Chairman and CEO Dr. Anita Goel, MD, PhD and Former UK Prime Minister Tony Blair delivered keynote addresses at the annual Novartis Forum for Excellence in Spain on June 2, 2011. Mr. Blair outlined five key challenges facing our planet today, while Dr. Goel unveiled game-changing nanotechnology solutions in development by Nanobiosym to address the most pressing global challenges in healthcare, energy and the environment.

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