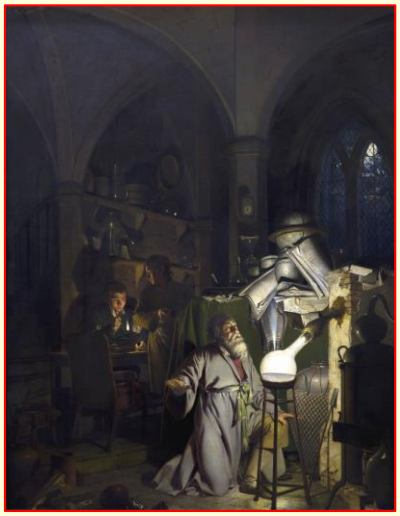


## Chemistry

*The Alchymist*, 1771
Joseph Wright of Derby

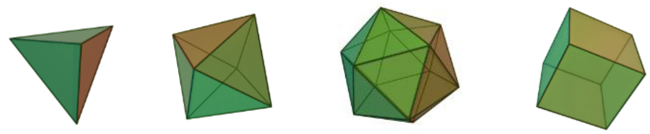
The full title of the painting is
*The Alchymist, In Search of the Philosopher's Stone, Discovers Phosphorus, and prays for the successful Conclusion of his operation, as was the custom of the Ancient Chymical Astrologers*

The painting likely refers to the discovery of phosphorus by the Hamburg alchemist Hennig Brandt in 1669. He heated urine residues to high temperatures. This was a really stinky endeavor but nothing stops the dedicated alchemist. He found that the retort slowly filled with glowing fumes and a burning liquid bubbled out. This solidified but still glowed. He called it phosphorus – light-bearer. He had hoped that he would find the philosopher's stone, something that would change base metals into gold. He had been intrigued by the golden yellow color of the urine.

The chemical reactions in this process were very complicated. Basically various phosphates (ammonium and sodium phosphates) in the urine reacted with carbon with the release of carbon monoxide and phosphorus. and other phosphorus compounds (such as ammonium sodium hydrogen phosphate - $(NH_4)NaHPO_4$
Robert Boyle found that the reaction could be facilitated by adding sand (silicon dioxide):
$4\ NaPO_3 + 2\ SiO_2 + 10\ C \rightarrow 2\ Na_2SiO_3 + 10\ CO + P_4$

Phosphorus is an essential element in fertilizer. More efficient sources of phosphorus than concentrated urine were bird guano or bones. Modern phosphorus is obtained from rocks with high concentrations of calcium phosphate.

## The Classical Elements



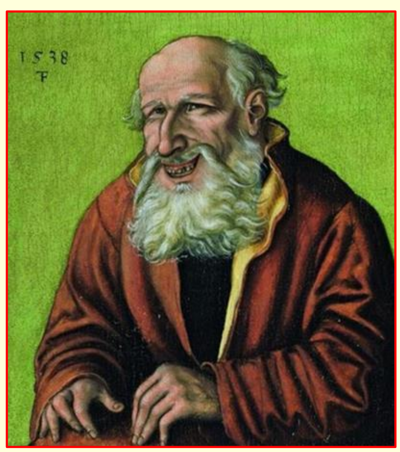

**Empedocles** (490-430 BCE) formally proposed the four basic elements ("roots"), but these derived from earlier ideas and reflected more states of matter (energy, gas, liquid, solid) than building blocks. Other pre-Socratic philosophers claimed one of these four as the primary element. **Plato** (428-348 BCE) attributed the four basic elements to their ideal geometries (illustrated). **Aristotle** (384-322 BCE) added a fifth element (aether). He considered things to be a combination of matter and form (purpose).

According to Plato, fire was a tetrahedron (pyramid), air was an octahedron (diamond), water was an icosahedron (20 sides) and earth was a hexahedron (cube).

Aristotle's theory of being was called "hylomorphism" (*hyle,* wood /matter + *morphe*, form). Another aspect of Aristotle's philosophy was that things combined substance (what it is made of) and attributes (how it is perceived). This was important to the Roman Catholic idea of "transubstantiation" which described the change in the substance of the wine to the blood of Christ without any change in its perceived attributes.

## Democritus (460-370 BCE)

Democritus proposed that there is nothing but matter and the void. Neither gods nor souls exist. All matter is composed of tiny indivisible "atoms." Different atoms can exist by themselves or combine with other atoms. Atoms come together during birth and growth and fall apart during death and decay. Democritus promoted "euthymia" (cheerfulness), and is often known as the laughing philosopher (as opposed to the tearful Heraclitus).




Imaginary portrait of Democritus
Franz Timmerman, 1538

Only fragments of Democritus' writings are available. Democritus was supposedly taught by Leucippus but it is unclear whether his teacher was factual or imaginary. Democritus' materialistic philosophy was taken up by Epicurus (341-270 BCE), and then explained in the poetic exposition of Epicureanism *De Rerum Naturae* by the Roman Titus Lucretius (99-55 BCE).

A quotation from Book I of the poem (translated by C. H. Sisson) can easily be related to modern ideas (inserted in square brackets):

The bodies themselves are of two kinds: the particles [atoms?]
And complex bodies [molecules?] constructed of many of these

The atoms of Democritus were of a finite number of kinds. Each type of atom had a specific shape and size. They could combine together using various hooks and clasps.

The Greek word *atomon* means "uncuttable." Atoms were thought of as fundamental – there was nothing smaller. Modern physics has shown that atoms are composed of even smaller particles – protons, neutrons and electrons. Atoms were considered indivisible until modern physics demonstrated that they could be split.

**Metals of Antiquity**

| | Symbol | Astrology | Alchemy | Melting Point (°C) | Discovery (BCE) |
|---|---|---|---|---|---|
| **Copper** | Cu (cuprum) | Venus | ♀ | 1084 | 9000 (Anatolia) |
| **Lead** | Pb (plumbum) | Saturn | ♄ | 327 | 7000 (Egypt) |
| **Gold** | Au (aurum) | Sun | ☉ | 1064 | 6000 (Europe) |
| **Silver** | Ag (argentum) | Moon | ☾ | 961 | 5000 (Egypt) |
| **Iron** | Fe (ferrum) | Mars | ♂ | 1538 | 4000 (Egypt) |
| **Tin** | Sn (Stannium) | Jupiter | ♃ | 231 | 3500 (Europe) |
| **Mercury** | Hg (Hydrargyrum) | Mercury | ☿ | -38 | 2000 (China/Egypt) |

Philosophy often does not keep up with technology. By the time of the Greek philosophers, miners and smelters had discovered numerous different metallic elements. As well as the metals, human beings had found sulfur (brimstone) and carbon (charcoal). Yet the philosophers did not really consider the nature of these different substances.

Gold, Silver and some Copper can be found in the elemental state. Otherwise the metals have to be extracted from ores. Malachite was used to obtain copper. Cinnabar was the main source of mercury.

The Greek name for Mercury Hydrargyrum combines water (liquid) and silver. It is also known as "quicksilver."

**Cement and Concrete**

One of the great contributions of the Romans was the production of cement and concrete. First lime (calcium oxide) was produced by heating limestone or chalk to high temperature ("calcination"). Lime mixed ("slaked") with water gave a mortar that could be used to bind bricks together. Lime with the addition of other minerals – silicates and aluminates – gave cement which could bind sand and/or gravel to form a concrete. Roman concrete, such as that used to form the dome of the Pantheon (126 CE), has lasted for centuries.

As well as analysis, chemistry is concerned with synthesis. One of the most important compounds to be synthesized was cement.

The main chemical equations for these processes are

Calcination
$CaCO_3 \rightarrow CaO + CO_2$

Slaking
$CaO + H_2O \rightarrow Ca(OH)_2$

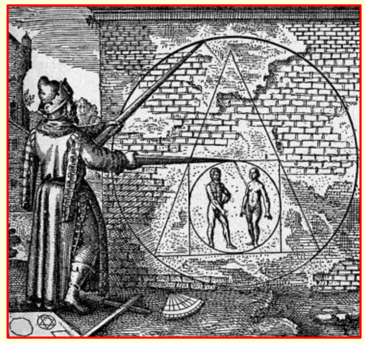
Setting
$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$

The additives (silicates and oxides) that are added to the mixture are often called pozzolans. These were the volcanic ashes that could be mined in Pozzuoli near Naples. These chemicals react with the calcium hydroxide to form compounds such as calcium silicate hydrate and calcium aluminate hydrate. The fact that they take up the water molecules produced in the setting reaction means that the cement or concrete can set under water – hydraulic cement.

## The Philosopher's Stone

The main goal of the alchemist was to discover the philosopher's stone. This material could be used to transmute base metal into gold, to cure disease and to provide immortality. The idea of the philosopher's stone likely comes from Greek ideas of a *prima materia*. It was much discussed by Muslim alchemists such as Jabir ibn Hayyan (Geber, 8th Century) who described an *al iksir* (elixir) made from the powdered stone.

In Eastern though, the philosopher's stone may be related to the fabulous jewel *cintamani* that could convey immortality.



"Make of the man and woman a Circle, of that a Quadrangle, of this a Triangle, of the same a Circle and you will have the Stone of the Philosophers." (from *Atalanta Fugiens*, Michael Maier, 1617)

The search for elements and the attempts to change one substance to another was the domain of "alchemy." The word comes from the Arabic (like most words beginning with "al-"), but the origin of the stem "chem" is unknown. It may derive from a Greek word meaning pour (as in the smelting of metals and their alloys) or it may come from an Egyptian word for black (as in the color for earth). The latter perhaps led to the idea that alchemy was "black magic." In French the term "l'oeuvre au noir" (nigredo) refers to the hypothesized first step in the magnum opus – the creation of the philosopher's stone. It also suggests that the alchemists were truly working in the dark.

The illustration is from a book of "emblems" (illustrated allegories, myths, etc), the first of which was about Atalanta, who lost her race with Hippomenes because she paused to pick up the golden apples that he cast in her path.

## Distillation

Jābir ibn Hayyān (Geber) described many techniques for the purification of chemicals in the 8-9tth Century CE. Among these were distillation and crystallization. He also designed equipment to perform these operations. The word alembic is an Arabic derivation from the Greek *ambix*, cup.

The first distillation of alcohol was by Al Kindi in the 9th Century CE. The word alcohol has an Arabic derivation, but there is some dispute as to whether it refers to kohl (black eyeliner) or to bad spirits.

Distillation of perfumes was performed by the ancient Egyptians and Persians, but distilled alcohol was not known until Al Kindi.

Distillation works because alcohol (ethanol) has a lower boiling point than water – $78^0$ rather than $100^0$ C. When distilling one should monitor the temperature of the vapor coming off the liquid. When it increases above $78^0$ the alcohol has all evaporated and now water is being distilled.

The distillation technique spread West from Muslim lands to Europe and East to China and India. The first distillation of vodka was in 1405, of Scotch whisky in 1495, and of cognac in 1549.

Many versions of Islam prohibit alcoholic beverages. However, some Sufis use wine to facilitate mysticism.

Medieval Europe benefited greatly from Islamic science as well as from Arabic translations of classical authors. Many alchemists and physicians travelled to the Middle East to learn their trade. In addition the Islamic lands were a conduit for the transfer of Chinese and Indian knowledge to Europe. Through this connection came gunpowder:

## Gunpowder

Gunpowder – a mixture of charcoal, sulfur and saltpeter (potassium nitrate) – was discovered by Chinese alchemists in the 9th Century as an accidental byproduct in the search for the elixir of life. Its explosive nature led to its use in various weapons. The recipe for gunpowder spread to Europe through Arabic trading routes and was included in the 1300 book *Liber Ignium* (Book of Fires). By 1326 cannon were used in European warfare.

Earliest picture of a European cannon, from *De nobilitatibus sapientii et prudentiis regum*, Walter de Milemete, 1326

The Chinese consider their four most important inventions:
papermaking – 2nd Century
printing - woodblock (8th Century) and movable type (11th Century)
compass - for use in navigation 11th Century
gunpowder – for use as an explosive 11th Century

The ignition of the gunpowder caused a large release of gas (carbon dioxide and nitrogen) which propelled the projectile.
$2\ KNO_3 + S + 3\ C \rightarrow K_2S + N_2 + 3\ CO_2$.

In the beginning ignition was caused by lighting a fuse. Later it was by sparks from a flint. Ultimately it was by exploding a primer sensitive to pressure (cap).

The manufacture of firearms requires a barrel that has to be strong enough to resist the force of the explosion that propels the projectile. Cannons were made with thick iron barrels. Rifles and hand guns require much stronger steel – an alloy of iron and carbon. "Wootz" steel was first produced in Southern India as early as 500 BCE. The technology was copied by the Persians and then by the Arabs, where it was called Damascus steel. This material was forged into swords used by the Saracens and by the Vikings. Modern steel-making using blast furnaces began in the 17th Century.


Copy of lost portrait by Quentin Matsys (1466-1530), Louvre

## Paracelsus (1493-1531)

Theophrastus von Hohenheim called himself "Paracelsus" because he believed he was much further ahead than Celsus who wrote a book *De Medicina* in the 1st century CE. This was one of the early books printed by the new printing presses. Paracelsus rejected the classical ideas of the four elements and the four humors. He focused on the *tria prima*– salt, mercury and sulfur. He suggested that some diseases might be caused by chemical abnormalities and treated by specific chemical medicines. However, other than introducing tincture of opium (laudanum) to Europe, he made no lasting contributions to medicine or chemistry.

Paracelsus was once considered the greatest of the alchemists. However, his contribution to knowledge was much less than his confidence in his own greatness. He did much to overturn the power of the classical authors such as Galen. However, his own system was a meaningless mishmash of astrology and chemistry, bluster and blasphemy.

Paracelsus did discover that opium was far more soluble in alcohol than in water. Opium relieved coughing diarrhea and pain. It is no surprise that it became the most popular of medicines.

Paracelsus did recommend keeping wounds clean to allow them to heal naturally rather than plastering them with the many current treatments of his day (mud, cowdung)

Paracelsus was much concerned with purification and dosage. He stated that some chemicals were beneficial in low dosage though toxic in high. Shades of homeopathy.

Paracelsus has the dubious honor of being the patron saint of alternative medicine – probably because of his truculent attacks on the accepted medicine of his time.

## Robert Boyle (1627-1691)

Boyle was born in Ireland, the seventh son of the richest man in England. After travels in Europe he settled in Oxford, where he conducted experiments. Many were related to Otto von Guericke's air pump. Boyle showed that life could not persist in a vacuum, that sound required air for its transmission, and that volume varied inversely as the pressure (Boyle's Law). He was fascinated by alchemy and wrote *The Skeptical Chemyst* (1661) summarizing alchemical knowledge. He wished to understand the chemistry of such Christian ideas as the resurrection.

Portrait of Boyle by Johann Kerseboom , 16898888

Boyle did propose a remarkably modern idea of the elements and how they combine to form compounds:
I now mean by Elements, as those Chymists that speak plainest do by their Principles, certain Primitive and Simple, or perfectly unmingled bodies; which not being made of any other bodies, or of one another, are the Ingredients of all those call'd perfectly mixt Bodies are immediately compounded, and into which they are ultimately resolved (*The Skeptical Chemyst*, p 350)
However, he had no real understanding – he thought that gold and silver were compounds rather than elements.

He was far more important to physics than to chemistry. Boyle's Law
$PV = k_1$
was later combined with Charles' Law
$V/T = k_2$
and Avogadro's idea of the number (n) of molecules to give the "Ideal Gas Law"
$PV = nRT$
where R is the ideal gas constant. When temperature is in degrees Kelvin, R is 8.3 in the units (meters$^3$ X Pascals)/(temperature X n)

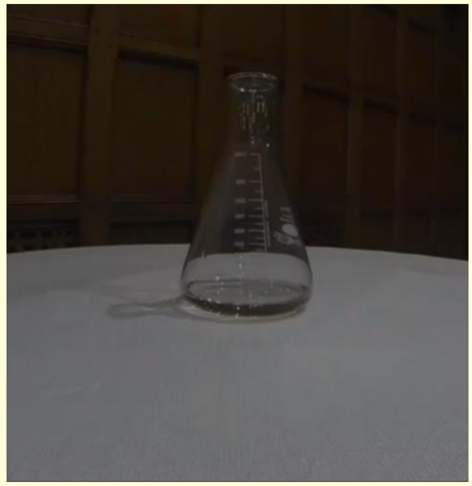
In the end the gas law returned to chemistry and Avogadro's concept of molecules.

Boyle was the Director of the East India Company. He gathered around himself and supported several other scientists, the most notable of which were Robert Hooke and Thomas Willis. In 1660 just after the restoration of the monarchy under Charles II, Boyle was instrumental in the foundation of the Royal Society in London.

The rich made significant contributions in the early days of science, when there were no research grants. Lord Cavendish – the discoverer of hydrogen – was also immensely rich.

**Resurrection of Camphor**

1. Camphor dissolves into concentrated sulphuric acid and there is no longer any evidence of it (odor, texture, color). The solution becomes yellow.
2. When water is added to the acid, heat and steam are generated. The camphor comes out of solution – it is white, solid and has its characteristic odor.



Camphor is a complex organic molecule obtained from a special tree. It has a strong aroma and is used in creams and in cough suppressant (Vick's vapor rub)

video adapted from
https://www.youtube.com/watch?v=-RvIlNS1kQE

discussion at
https://alexwraggemorley.wordpress.com/2015/01/03/robert-boyles-experimental-proof-of-the-possibility-of-the-resurrection/

text of the essay *Some Physico-Theological Considerations about the Possibility of the Resurrection* (1675)
https://drive.google.com/file/d/0B3GLVQgY9rLMNGRmODllM2UtMDY4Yy00ZWY1LWJhMzktNzI1YWNjOGVhNzE5/view

The section of the essay referring to the camphor experiment:

> If you let a piece of camphire lie a while upon oil of vitriol, shaking them now and then, it will be so corroded by the oil, as totally to dissappear therein, without retaining so much as its smell, or without any manifest sign of there being camphire in that mixture ; yet that a vegetable substance, thus swallow'd up and changed by one of the most fretting and destroying substances known in the world, should not only retain the essential qualities of its nature, but be restorable to its obvious and sensible ones in a minute, and that by so unpromising a medium, as common water, will appear by pouring the solution into a large proportion of that fluid, to whose upper part there will immediately rise white, brittle, strong-scented, and inflammable camphire, as it was before.

The chemical reaction involves the formation of camphorsulfonic acid when the camphor is "dissolved" in the acid. Adding the water creates heat and decreases the concentration of the acid ions. Both these factors drive the equation back to release the camphor

Boyle was very aware of the "resurrection" of Ann Green, who was executed for infanticide in Oxford in 1650. Her body was given to the anatomists for dissection, but she woke up before they could begin.

Soho House in Wandsworth (Birmingham, residence of Matthew Boulton (1728-1809) and principal meeting place of the Lunar Society.

## The Lunaticks

The Lunar Society of Birmingham (1755-1813) was a dinner club and learned society who met monthly (during the full moon) to discuss science. Among the members were Matthew Boulton (manufacturer of metals), James Watt (steam engine), Erasmus Darwin (zoologists and grandfather of Charles), Josiah Wedgewood (manufacturer of pottery), William Withering (botanist and geologist), and Joseph Priestley (chemist). Benjamin Franklin presented his ideas on electricity to the society in 1758.

Holding the meeting during the full moon allowed the attendants to travel home late, there being no street lighting at that time.

Pastel Portrait of Priestley
Ellen Sharples, 1794

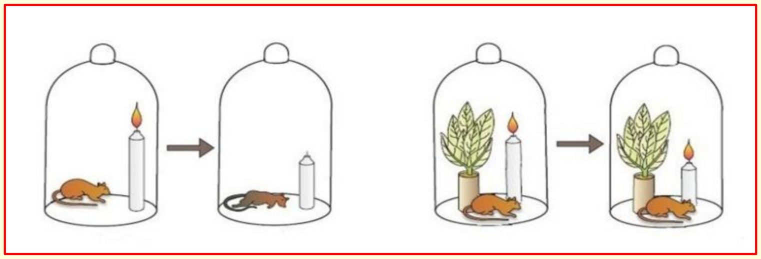
## Joseph Priestley (1733-1804)

Born in Yorkshire to a family of Dissenters (Protestants who disagreed with the Church of England), Priestley initially trained for the ministry. He worked initially as a teacher, publishing the *Rudiments of English Grammar* in 1761. He then became a minister, publishing his *Institutes of Natural and Revealed Religion* in 1774, and becoming a founding member of the Unitarians. He experimented with carbon dioxide ("fixed air") which Joseph Black had made by pouring vitriol over limestone, and invented soda water.

Carbon dioxide had been initially discovered by the Flemish chemist Jan Baptist van Helmont – as the gas released by the burning of charcoal. Joseph Black (1728-1799), a Scottish chemist, produced it in 1754 by pouring sulfuric acid over limestone

$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2$

## Oxygen



Priestley is most famous for his experiments with oxygen. He demonstrated that some part of air is used up by either respiration or a burning flame (left) and that plants in sunlight prolong the life of a breathing rat or a burning candle under a bell jar. In 1774 he produced a gas which he called "dephlogisticated air" by focusing the sun's rays on mercuric oxide. He found that this facilitated the burning of a candle in a closed environment.

The second experiment (illustrated on the right) demonstrated the process of photosynthesis – the conversion of carbon dioxide and water to carbohydrates with the release of oxygen

$$CO_2 + 2H_2O + \text{photons} \rightarrow [CH_2O] + O_2 + H_2O$$

Carbohydrates are molecules that combine carbon, hydrogen and oxygen, e.g. sugars, starches, cellulose.

Carl Wilhelm Scheele (1742-1786), a German-Swedish apothecary, produced oxygen in a similar way to Priestley (heating various oxides including mercuric oxide) in 1772, but he did not publish these findings until 1777. He called the gas *Feuerluft* – fire air. Priestley is therefore usually credited as the discoverer of oxygen and Scheele hardly remembered. However, Scheele did write a letter to Lavoisier telling him of his discovery on September 30, 1774. This precedes Priestley's formal publication of his results in *Philosophical Transactions* in 1975

Priestley interpreted his new gas in terms of phlogiston. This was a fire-like element that was released by burning, the name coming from the Greek *phlox* flame. However, phlogiston was difficult to reconcile with the fact that the combustion (rusting) of metals led to an increase in mass rather than a decrease.

Henry Cavendish (1731-1810) had shown that a gas that he called "flammable air" could be produced by heating iron filings in steam

$$Fe + \quad H_2O \rightarrow FeO + H_2$$

Cavendish also demonstrated that the burning of this gas produced water.
Priestley wondered whether this gas might be phlogiston.

Although Priestley had discovered oxygen, it was left to Lavoisier to demonstrate that it is what combines with matter during combustion and to give it the name "oxygen." However Lavoisier thought that oxygen (Greek for "maker of acid") was a necessary component of all acids.

Hydrochloric acid is an obvious exception to this idea. Lavoisier also named the gas discovered by Cavendish hydrogen (maker of water).

Concerning the question of who discovered oxygen:

> We haven't agreed what "being first" means: is it the initial discovery … the first publication … or full understanding.

(from the 2001 play *Oxygen* by Carl Djerassi (inventor of the contraceptive pill) and Roald Hoffmann (1981 Nobel Prize in Chemistry for his contributions to our understanding of the intermediate steps in chemical reactions)

**Birmingham Riots, 1791**

Priestley moved to Birmingham in 1780, where he became a member of the Lunar Society.

In 1791 a mob of angry rioters attacked the Royal Hotel in Birmingham where a dinner was being held in support of the French Revolution. Although initially supportive of the ideas of the French Revolution, the general feeling in England had changed to support of the French aristocracy who were being guillotined. As well as their anti-French feelings, the mob was also egged on by anger at the Dissenters, who were upsetting the accepted beliefs.

The mob moved on to destroy the houses of Dissenters and members of the Lunar Society. Priestley was a particular target. His house was burned to the ground. (The riots are also called the Priestley Riots). He and his family narrowly escaped and moved to London. In 1794 Priestley emigrated to Pennsylvania.

*Dr. Syntax and the Laughing Gas Party*,
Caricature by William Combe, 1823

Priestley made nitrous oxide in 1775 by wetting iron filings with nitric acid ("aqua fortis" which had been produced by the alchemists) :

$Fe + 4\ HNO_3 \rightarrow Fe(NO_3)_3 + NO + 2\ H_2O$.

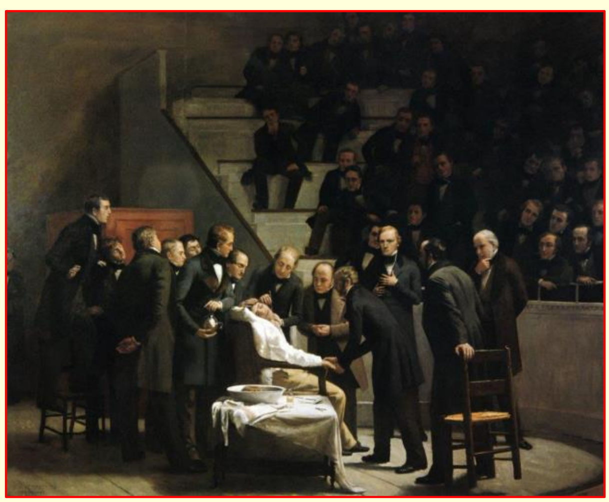
It may have been made earlier by Joseph Black who heated ammonium nitrate

$NH_4NO_3 \rightarrow 2\ H_2O + N_2O$

(This is the present way it is produced industrially though one has to be careful as the process can become explosive)
However, Black did not investigate the gas. Priestley demonstrated its euphoric properties.

Humphrey Davis gave it the name "laughting gas."

## Anesthesia



*First Operation under Ether*, Robert C. Hinckley, 1882 (operation 1846)

Humphrey Davy had noted that nitrous oxide might be useful in surgery in 1800. Nitrous oxide was used in dentistry by Horace Wells in 1844 in Hartford, Connecticut. Nitrous oxide was, however, not powerful enough for major surgery. William Morton was a dentist who was studying to become a medical doctor. He convinced the Boston surgeon John Collins Warren to try ether as an anesthetic. The 1846 operation was to remove a small vascular tumor just below the left mandible.

Ether had been produced by the German chemist August Sigmond Frobenius (1700?-1741) by distilling wine (ethanol) and vitriol (sulfuric acid). He called in "sweet oil of vitriol." Ether had been discovered before but Frobenius produced its first clear description in a 1729 paper.

Several people produced chloroform in the early 1830s by reacting chlorinated lime (sodium hypochlorite, bleach) with ethanol.
It was first used as an anesthetic in 1847 by the Edinburgh obstetrician James Simpson.

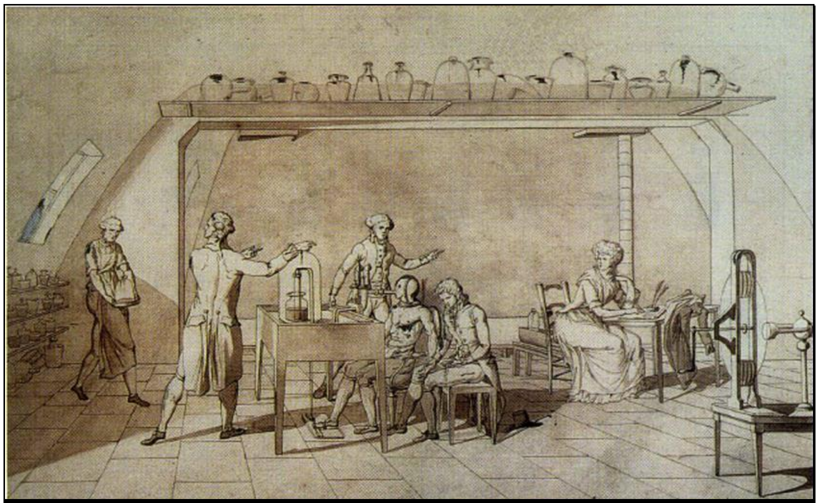
## Antoine Lavoisier (1743-1794)

Born into the nobility, Lavoisier became a shareholder in the hated Ferme Générale, which collected taxes for the government. As part of this he studied how to determine if tobacco had been adulterated with ash. He then began to study chemistry making accurate measurements. He proposed the idea of the conservation of mass – *Rien ne se perd, rien ne se crée, tout se transforme*. His measurements led him to argue convincingly against phlogiston and to name oxygen. During the early days of the French Revolution, Lavoisier was arrested and guillotined for his role in taxation.

Portrait of Lavoisier and his wife
Jacques-Louis David, 1788

Priestley visited Lavoisier in the summer of 1774 and described his experiments on oxygen. Lavoisier confirmed these experiments and those of Cavendish on hydrogen, but did not interpret their results according to the idea of phlogiston. Rather he considered their gases to be elements and named them oxygen (acid maker) and hydrogen (water maker).

Earlier scientists had proposed similar ideas about the conservation of mass, e.g. the Russian Mikhail Lomonosov.
Lavoisier proposed the new terminology of chemistry – e.g. copper sulfate instead of "vitriol of Venus." His *Traité élémentaire de chimie* (Elementary Treatise of Chemistry) was the first textbook of chemistry. More than anyone else he deserves to be known as the father of chemistry.



Experiment to study respiration, watercolor by Madame Lavoisier, ~1780

In this experiment Lavoisier (second from left) is collecting the expired gases from a volunteer. The expired gas is passing through limewater (calcium hydroxide) which combines with the carbon dioxide to give calcium carbonate:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

(This limewater technique was initially used by Joseph Black.)
By weighing the subject and the precipitate calcium carbonate, Lavoisier can prove that respiration involves the production of carbon dioxide from carbon in the body and oxygen in the air. Everything balances: *Rien ne se perd, rien ne se crée, tout se transforme.*

Lavoisier's wife, Marie Anne Pierrette Paulze de Lavoisier (1758-1836) is portrayed on the right of the painting. She illustrated her husband's works with watercolors and engravings. She was young and beautiful. At the time of Priestley's visit to Paris in 1774 she was only 16 years old. She was taught by Jacques-Louis David (who painted the portrait in the previous slide. She translated Priestley's papers on phlogiston for her husband and helped them communicate when Priestley visited Paris. She rescued her husband's papers after his execution and published his memoirs.
Roald Hoffman wrote a paper about Mme Lavoisier
http://www.roaldhoffmann.com/sites/all/files/mme_lavoisier.pdf

## Phlogiston and Oxygen

Johann Joachim Becher (1635-1682), a German alchemist proposed that all combustible materials were made of phlogiston, which was given off when the material was burned, and a dephlogisticated part, which was considered its true form.

Lavoisier pointed out that if phlogiston was released from rusting metals (which gained mass) phlogiston would have negative mass. This was impossible. He therefore called the gas that Priestley and Scheele had discovered "oxygen" rather than "dephlogisticated air."

When wood burns the carbon in it forms carbon dioxide and carbon monoxide, and the other elements form ash – calcium carbonate, potassium carbonate, oxides of iron and other metals. The gases escape and the ash weighs only about 1% than the original. So it was natural to think that something had been released. Scientists then considered the rusting of metals. This seemed to be the same type of process as the burning of wood but much slower. However, rusting metals gain weight. This is due to the formation of metallic oxides.

The gorgeous photograph of rusted iron from Wikipedia
https://upload.wikimedia.org/wikipedia/commons/thumb/a/a4/Rust_on_iron.jpg/1280px-Rust_on_iron.jpg

The discovery of oxygen and the concept of phlogiston are considered in the 2001 play *Oxygen* by Carl Djerassi and Roald Hoffmann.

Since Carl Wilhelm Scheele is not appropriately recognized, the following is a tangential anecdote related to another of his discoveries.

## Death of Napoleon

Franz Josef Sandmann
*Napoléon à Sainte-Hélène*, 1820

Napoleon was exiled to the Island of Saint Helena in the South Atlantic Ocean in 1815 and died there in 1821 of stomach cancer. Recent evidence has shown that he also suffered from chronic arsenic poisoning. This was probably not part of a conspiracy to murder him, but due to arsenic in the wallpaper. Carl Scheele, the unrecognized discoverer of oxygen, had also invented cupric hydrogen arsenite (CuHAsO3) "Scheele's green" which was used to color wallpaper.

Carl Wilhelm Scheele was a prolific chemist. He discovered many things besides oxygen. He isolated the metals barium, tungsten and molybdenum. Perhaps most importantly in 1774 he isolated chlorine gas by pouring muriatic (hydrochloric) acid over manganese dioxide:

$$MnO_2 + 4\ HCl \rightarrow MnCl_2 + Cl_2 + 2\ H_2O$$

He called it "dephlogisticated muriatic acid."

In 1810 Humphrey Davy produced chlorine by electrolysis of sodium chloride

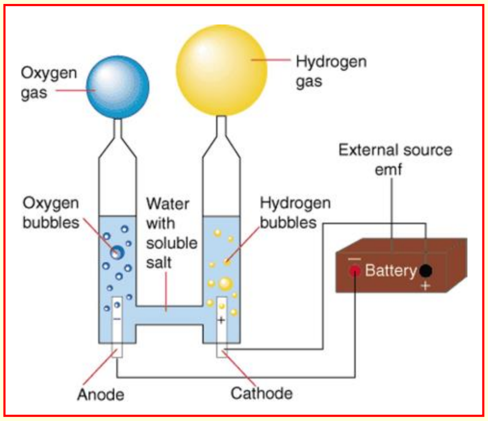
$$2NaCl + 2\ H_2O \rightarrow Cl_2 + H_2 + 2\ NaOH$$

He called it chlorine from the Greek *chloros*, yellow-green

## Electrolysis

Soon after Alessandro Volta invented the voltaic pile in 1800, William Nicholson and Anthony Carlisle used it to convert water into hydrogen and oxygen (illustration).

Humphrey Davy (1778-1829) used electrolysis of various salt solutions to discover the elements sodium, potassium, calcium and magnesium. He also demonstrated that chlorine and iodine were elements.



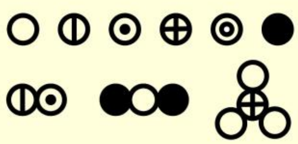

Before he worked on electrolysis. Humphrey Davy and Thomas Beddoes had founded the Pneumatic Institute in Bristol in 1798. They studied the properties of gases such as oxygen and nitrous oxide. Their goal was to treat diseases by the inhalation of gases.

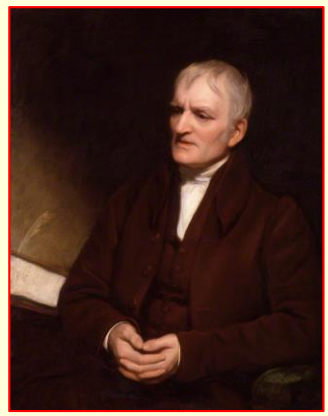
In 1815 Davy invented a safety lamp to be used in mines. The lamp's flame was surrounded by iron mesh to keep it away from any methane in the mine. The flames could not pass through the mesh to ignite methane in the air.

In the diagram it should be noted that the volume of hydrogen collected is twice that of the oxygen.

## John Dalton (1766-1844)

In his *New System of Chemical Philosophy* (1808), Dalton proposed that all elements were composed of indivisible atoms, with all the atoms of one element being the same and different from those of any other element. Atoms combine in simple whole-number rations to form chemical compounds. Chemical reactions can combine, separate or re-arrange these atoms.





Portrait of Dalton
Thomas Phillips, 1835

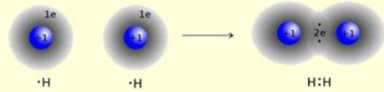
An example of Dalton's "law of multiple proportions" is that the elements of oxygen may combine with a certain amount of nitrous gas nitric oxide – NO) or with twice that amount (nitrous oxide – $N_2O$) but with no intermediate quantity.Dalton's law was anticipated in an 1802 paper by Joseph Proust, a French chemist.

John Dalton was a Quaker. He never married and lived a very modest life. As a dissenter he was unable to have a university position. For much of his life he taught at colleges or as a private tutor. One of his pupils was James Prescott Joule, who contributed to our knowledge of energy.

As well as proposing his new ideas of atomic chemistry, Dalton described color-blindness, which was for a long time called "Daltonism." The unit Dalton (Da) is used to describe the atomic mass relative to 1/12 the mass of carbon (C).

**Amedeo Avogado (1776-1856)**

His major contribution was the idea of "molecules" as distinct from atoms. He proposed that gaseous elements existed as molecules composed of two bonded atoms:




Avogadro's Law states that "equal volumes of all gases, at the same temperature and pressure, have the same number of molecules." This allowed him to decide from the results of water hydrolysis that water was composed of two atoms of hydrogen and one of oxygen. Avogadro could then calculate the relative atomic weights of gases from the weights of equal volumes. Thus oxygen weighed 8 times more than hydrogen. .

Born in Turin and trained in ecclesiastical law, Avogadro soon turned to science.
He is commemorated by Avogadro's number – the number of molecules in 1 gm of hydrogen. Avogadro's number has been altered to Avogadro's constant by basing it on carbon rather than hydrogen. Its value is $6 \times 10^{23}$

The depiction of the hydrogen molecule shows covalent bonding, something that explains Avogadro's idea. However the concept of covalent bonding did not come about until the work of Gilbert Lewis in 1916.

## Photography

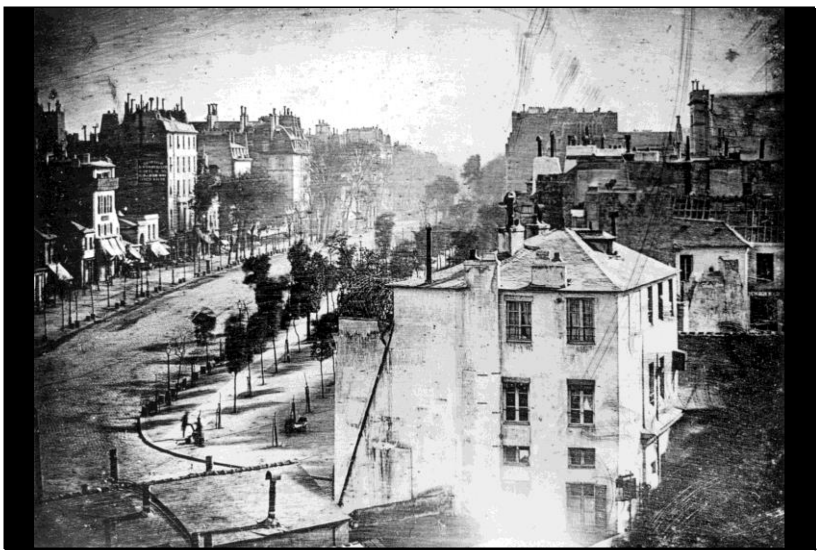
Louis Daguerre (1787-1851)

The first camera photographs were taken by Nicéphore Niépce in the mid 1820s using paper coated with silver chloride. In 1839 Louis Daguerre used a copper plate coated with silver iodide. Light precipitated silver from the coating. The latent image was developed by exposing the plate to mercury vapor. The image was fixed by dissolving the unexposed silver iodide in a salt solution. The silver in the image reflects light. Fox Talbot in 1841 used a different approach, making a negative image that could be used to print multiple photographs.

The main process underlying the photosensivity was
$2Ag^{+} + 2X^{-} \rightarrow 2Ag + X^{2}$
where X is a halogen – chlorine, bromine, iodine.
The mercury vapor would react with the released halogen, leaving the silver as a precipitate

Talbot used paper negatives. The next development was to use glass negatives. Ultimately the silver halides (bromide, iodide) were embedded in a collodion film.

Color photography requires three separate color sensitive images. This was initially proposed by James Clerk Maxwell in 1855 and the first color photograph was produced by Thomas Sutton in 1861. It was not until 1935 that Eastman Kodak produce a film which integrated three layers of photosensitive material – Kodachrome.



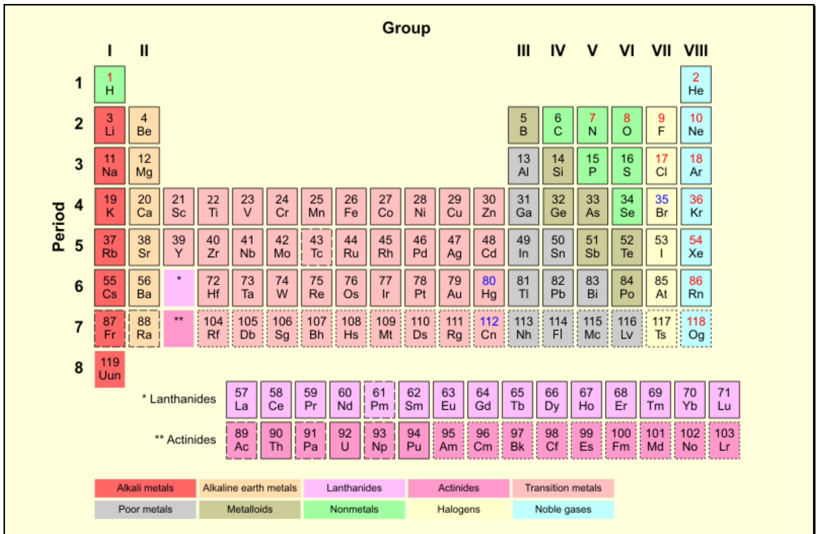
This is Daguerre's 1839 photograph of the Boulevard du Temple in Paris. This is considered the first photograph to include people. The many people walking along the street are not seen because they were blurred out by the passage of time required to take the photograph. In the lower right a man has his boots shined. Since he and the shoeshine boy did not move very much during the exposure, they are recorded.

## Dmitri Ivanovich Mendeleev (1834-1907)

Mendeleev became a professor of chemistry at the Technological Institute of Saint Petersburg in 1864. While preparing his textbook of chemistry, he realized that the elements arranged in order of their relative atomic weights exhibited a periodicity at multiples of 8. This ordering fit with the different valences of the elements. Mendeleev presented his table at the meeting of the Russian Chemical Society in 1869.

Mendeleev wearing his Edinburgh University robes, Ilya Repin, 1885

Other scientists had noted the periodicity but Mendeleev was the first to present a table of the elements. Why the elements were periodic at intervals of 8 is related to the fact that elements strive to have 8 electrons in their outermost shell (2 electrons for hydrogen and helium). This concept did not come about until the 20th Century theories of the atom.

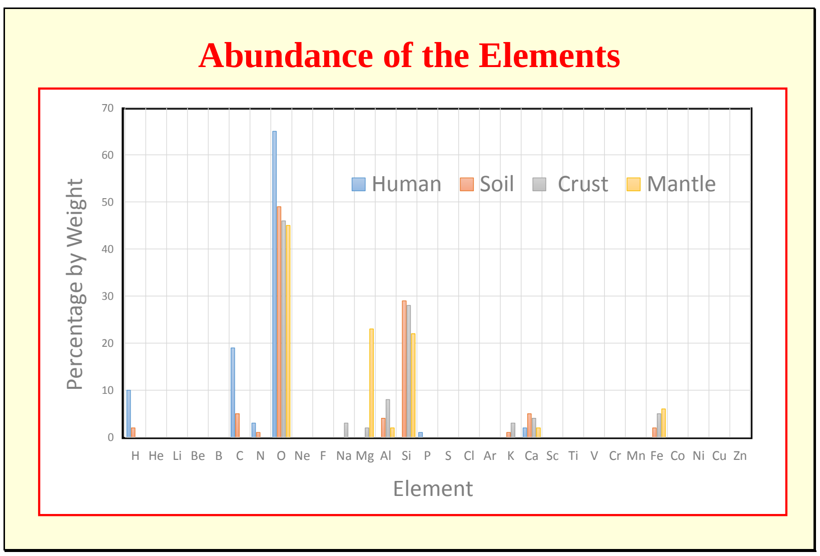



The color of the atomic number indicates the state of the element at standard temperature and pressure: solid (black), liquid (blue) or gas (red).
The complete outline means primordial elements (older than the earth), the dashed outline means resulting from the decay of another element (e.g. promethium) and dotted outline means synthetic.
Atoms of metals readily lose their outer shell electrons, and thus are able to conduct electricity. The alkali metals are named after the Arabic word for soda ash (sodium carbonate). The halogens are those elements that react with metals to produce salts (Greek *als,* salt + *genein*, beget). The

lanthanides together with scandium (Sc) and yttrium (Y) are sometimes called the "rare earths" (lathanide comes from the Greek *lanthanein* 'escape notice.' The name actinide derives from the Greek *aktin*, ray.

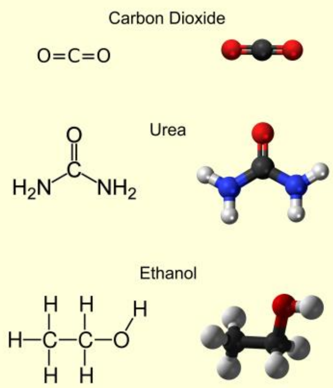
Mendeleev's table was missing several elements. These were later discovered and fitted into the table. In particular he had no knowledge of the noble gases – Helium, Neon, Argon, Krypton, etc. These elements were "inert." They tend not to react with other elements because their outer shell of electrons contained 8 and was therefore "full." Lord Rayleigh and William Ramsay identified argon in 1895 for which they received the 1904 Nobel Prize in Physics.

Mendeleev was recommended for the Nobel Prize in 1906 and in 1907 but he was adamantly opposed by one member of the Swedish Academy, whom Mendeleev had once criticized. So in the end he never received the prize.




The human body is made up mainly of oxygen, carbon and hydrogen.
The earth has much more silicon than carbon, though there is carbon in the soil.
The amount of iron increases as one goes more deeply into the Earth. This is likely because the heavier elements slowly sink through the lighter elements under the influence of gravity. The Earth's core is 80% iron and 20% nickel.

## Organic Chemistry




In the early 1800s, many supposed that certain compounds could only be produced by living organism – “vitalism.” In 1828 Friedrich Wöhler refuted this theory by accidentally synthesizing urea from exposing cyanates to ammonia. This led to the field of organic chemistry - the science of carbon compounds.

In 1858 both August Kekulé and Archibald Couper proposed the idea of tetravalent carbon atoms that could link together with themselves and other elements in interesting ways.

Wöhler’s process was complicated. First ammonium cyanate was formed by mixing a cyanate (e.g. lead cyanate) with ammonia and water:

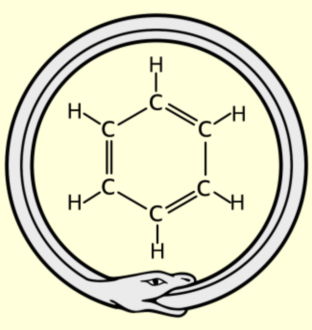
$$Pb(OCN)_2 + 2NH_3 + H_2O \rightarrow PbO + 2NH_4^+ + 2OCN^-$$

The excess water, in which the ammonium cyanate was dissolved, was then evaporated to cause the formation of urea:

$$NH_4^+ + OCN^- \rightarrow H_2NCONH_2$$

The structural formula shown on the left derive from the work of August Kekulé in 1858. The ball-and-stick models were first used by August Wilhelm von Hofmann in 1865.

## Kekulé’s Dream

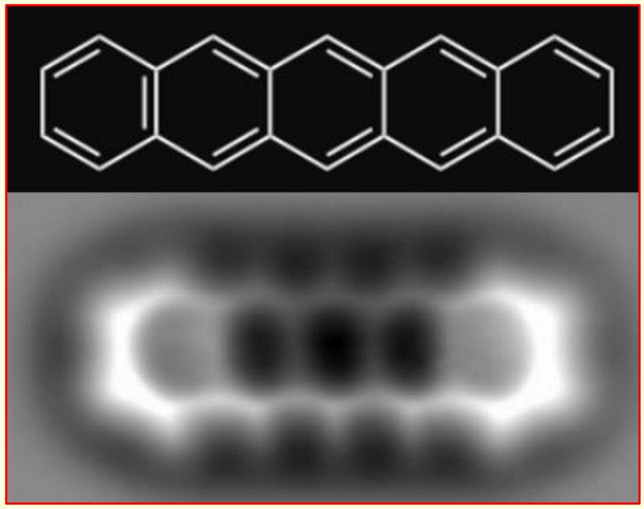


The ouroboros (Greek: *oura*, tail + *bora*, food) structure of the benzene ring.

I turned my chair to the fire and dozed. Again the atoms were gamboling before my eyes. This time the smaller groups kept modestly in the background. My mental eye, rendered more acute by the repeated visions of the kind, could now distinguish larger structures of manifold conformation; long rows sometimes more closely fitted together all twining and twisting in snake-like motion. But look! What was that? One of the snakes had seized hold of its own tail, and the form whirled mockingly before my eyes. As if by a flash of lightning I awoke; and this time also I spent the rest of the night in working out the consequences of the hypothesis.

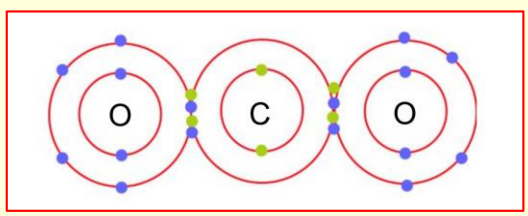
August Kekulé (1829-1896) was a German chemist. He studied the way that carbon reacted with other elements. He proposed that each element had a “valence” which determined the amounts in which it reacted. In 1865 he had a dream that led him to the idea that benzene was a hexagonal ring of carbon atoms.

Molecule of Pentacene (a linear polymer of 5 benzene rings) as viewed using atomic force microscopy.

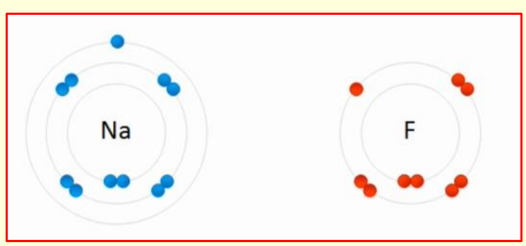


The structure of molecules cannot be viewed by light or electron microscopy However, a recent technique which measures the forces around atoms can show molecular structure. In this picture we actually “see” the benzene rings that Kekulé dreamed of.

**Covalent Bond**




**Ionic Bond**



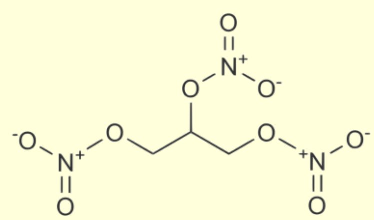

It was not until the 20th Century that the idea of chemical bonds was formulated. Two main types of bonds were ionic and covalent. In an ionic bond one element donates one or more electrons to another. In a covalent bond two elements share electrons. Metals form ionic bonds. Carbon forms covalent bonds.

The concept of valence and the periodic table of the elements were combined in the idea that elements had electrons in shells around their nucleus and that they tended either by donation or sharing to get a set of 8 electrons in their outer shell.

Linus Pauling (1901-1994) was able to explain how these bonds formed on the basis of the new quantum physics which defined how electrons are arranged in orbitals around their atoms and how these orbitals can interact between separate atoms. In 1939 he published the first edition of his book *The Nature of the Chemical Bond*. He received the Nobel Prize in Chemistry in 1954 and the Nobel Peace Prize in 1962.

**Nitroglycerin**

In 1847 Ascanio Sobrero (1812-1888), an Italian chemist, synthesized nitroglycerin from glycerol and nitric acid. His face was badly scarred in an explosion and he warned about the dangers of this compound. The compound explodes with small changes in pressure to release large volumes of gas.



$$4C_3H_5N_3O_9 \rightarrow 6N_2 + 12CO + 10H_2O + 7O_2$$

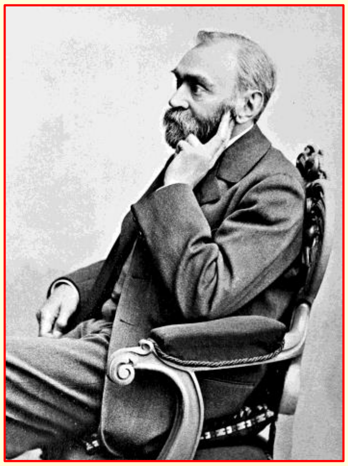
Another problem with nitroglycerin was that it could cause severe headaches by acing as a vasodilator. In 1879 William Murrell a British physician reported that dilute doses of nitroglycerin could be used to relieve angina pectoris, a disorder caused by decreased blood flow (ischemia) to the heart, manifesting as severe pain and pressure in the chest.

Angina Pectoris comes from the Latin *angere* ("to strangle") and *pectus* ("chest").

The explosion of nitroglycerin is triggered by a mechanical pressure change (detonation) rather than by ignition (deflagration). Once the explosion begins a pressure wave moves rapidly though the rest of the explosive material causing it all to explode almost simultaneously. This is much more powerful than an explosion that works by ignition, such as that of a petrol bomb.

## Alfred Nobel (1833-1896)

Born into a Swedish family that owned the Bofors armament factory, Nobel became fascinated by the possibility of making a safe version of nitroglycerin to use in mining and construction. After much experimentation he found that he could stabilize the compound by mixing it with diatomaceous earths. In 1867 he patented this invention as "dynamite." Dynamite could then be "detonated" with a blasting cap. Dynamite made the Nobel family very rich. Alfred Nobel left most of his estate to fund the Nobel Prizes, the first of which were awarded in 1901.



Portrait by Gösta Florman

Dynamite comes from the Greek *dynamis*, power or force.

The blasting cap contained a small amount of explosive such as Mercury fulminate. The blasting cap was activated by lighting a fuse made of hemp soaked in potassium nitrate. Modern blasting caps are detonated with an electric current.

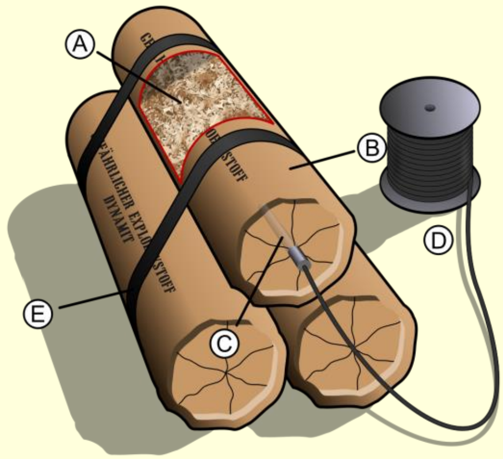
Nobel also patented other explosives such as gelignite.

Dynamite was not used as much in warfare as other explosive chemicals such as TNT. Nevertheless the Bofors company continued to manufacture armaments, and this caused Nobel, who was a pacifist, to worry about his legacy. A French newspaper mistakenly published a premature obituary in 1888 under the headline *Le Marchand de la mort est mort* (The merchant of death has died). This upset Nobel, who wished to be remembered differently.

Bofors continued to manufacture armaments. The Bofors gun, an anti-aircraft cannon, was designed in the 1930s.

Alfred Nobel was prescribed Nitroglycerin for chest pain near the end of his life.

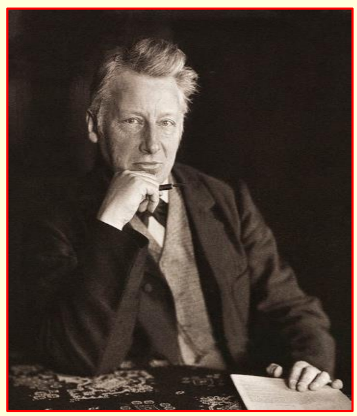
## Dynamite




A. Nitroglycerin mixed with sawdust
B. Protective coating
C. Blasting cap
D. Electric wire
E. Tape to hold sticks together

## Chemical Reactions

In the latter half of the 19th Century, chemist began to study the dynamics of chemical reactions. What made chemical reactions proceed? What determined the rate of reaction? A Dutch chemist, Jacobus Van't Hoff, published a very influential book *Études de Dynamique chimique* (Studies in Chemical Dynamics) in 1884. This described the effects of reactant concentration, pressure, temperature, and catalysts. These effects were interpreted in terms of the new science of thermodynamics. He received the first Nobel Prize in Chemistry in 1901.



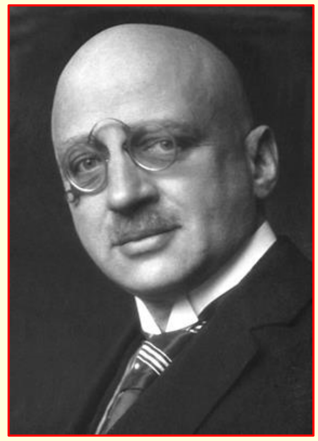
Jacobus Henricus van 't Hoff (1852-1911) portrait by Nicola Perscheid, 1904

The text in English (1896) of Van't Hoff's book is available at
https://archive.org/details/studiesinchemica00hoffrich

Using these principles, Fritz Haber was able to synthesize ammonia from nitrogen and hydrogen.

## *Brot aus Luft*

The main requirements for fertilizer are accessible phosphorus and nitrogen, both of which are essential to plant metabolism. Phosphorus was initially obtained from bird guano or bone ash. In the 19th Century it was obtained from phosphorus minerals under high temperature. It was not until 1909 that Fritz Haber discovered a way to produce ammonium from the nitrogen in the air using high temperature and pressure, and a metal catalyst. This allowed the economical production of ammonium compounds for fertilizer. His technique was scaled up from the laboratory to industry by Carl Bosch.



Fritz Haber (1868-1934)
Nobel Prize Photograph, 1918

We began this session with phosphorus and its use in fertilizer. The other main ingredient was nitrogen. Even though this gas makes up 80% of the Earth's atmosphere, it cannot be used by plants unless it is in some compound form ("fixed").

*Brot aus Luft* – bread from air.

The equation for the Haber-Bosch process was
$N_2 + 3H_2 \rightarrow 2NH_3$
Various metal catalysts could be used. A catalyst is something that facilitates a chemical reaction but remains unchanged during the reaction. The etymology is from Greek *cata*/down and *lysein*/loosen.

The ammonium could be combined with phosphoric acid to produce di-ammonium phosphate, which is a major ingredient of fertilizers.

Haber's discovery was immensely significant. It allowed land that had been exhausted to become fertile again. It has saved billions of people from starvation.

As well as the production of fertilizer, ammonium could be used in the manufacture of explosives. The Haber-Bosch process was therefore essential to the German war effort in World War I, since German had difficulty importing nitrates because of the English blockade.

***Tod aus Luft***

Fritz Haber converted from Judaism to Christianity as a young man, probably in an enthusiasm of German patriotism. During the Great War he supervised the German poison-gas program. This program came to be known as *Tod aus Luft* – death from the air. The first gas used was chlorine. Later gases were phosgene and mustard gas.

Australian Infantry
with Gas Masks
Battle of Ypres, 1917

Haber's first wife Clara had obtained her Ph.D. in chemistry. She was an activist for women's rights and a pacifist. She committed suicide in 1915. Her depression may have been related to her loss of her scientific career after marriage or to her opposition to her husband's work in chemical warfare.

After the war Haber directed the Kaiser Wilhelm Institute in Berlin. There he continued his work on chemical warfare, tried to obtain gold from sea water and supervised research on pesticides. The latter work ultimately led to the development of the poison gas Zyklon-B used in the Nazi death camps. In 1933 he was forced to resign by the new Nazi regulations limiting Jews from work in German universities. He died in 1934 in Switzerland.

The following is a 1999 poem by Roald Hoffman, who won the 1981 Nobel Prize for Chemistry:

**Fritz Haber**

invented a catalyst to mine cubic miles
of nitrogen from air. He fixed the gas
with iron chips; German factories coming
on stream, pouring out tons of ammonia,

fertilizers, months before the sea lines
to Chilean saltpeter and guano were cut,
just in time to stock powder, explosives
for the Great War. Haber knew how catalysts

work, that a catalyst is not innocent, but
joins in to carve off the top or undermine
some critical hill, or reaching molecular

arms for the partners in the most difficult

stage of reaction, brings them near, eases
the desired making and breaking of bonds.
The catalyst reborn rises to its match—
making again; a cheap pound of Haber's

primped iron could make a million pounds
of ammonia.  Geheimrat Haber of the Kaiser
Wilhelm Institute thought himself a catalyst
for ending the War; his chemical weapons

would bring victory in the trenches; burns
and lung cankers were better than a dum-dum
bullet, shrapnel.  When his men unscrewed
the chlorine tank caps and green gas spilled

over the dawn field an Ypres he carefully
took notes, forgot his wife's sad letters.
After the War Fritz Haber dreamed in Berlin
of mercury and sulfur, the alchemists' work

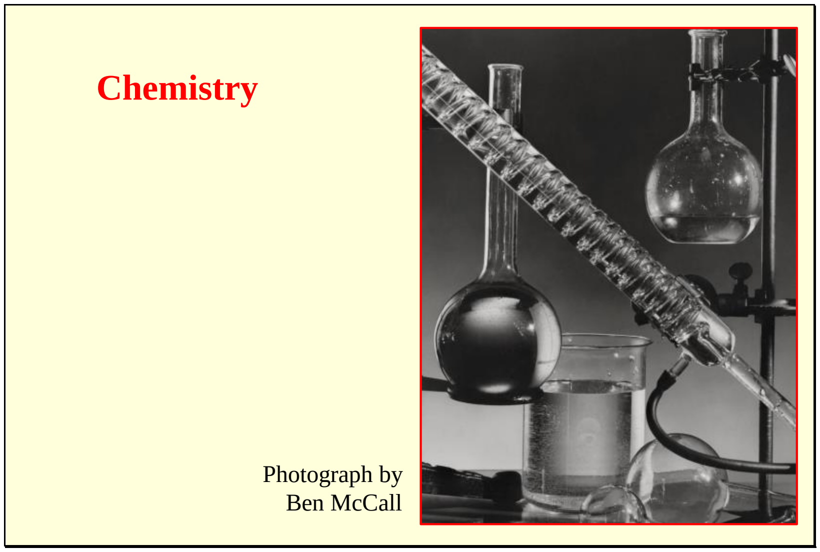
hastening the world, changing themselves.
He wondered how he could extract the millions
of atoms of gold in every liter of water,
transmuting the sea to the stacked bullion

of the German war debt. And the world, well,
it *was* changing;  in Munich one could hear
the boots of brown-shirted troopers, one paid
a billion marks for lunch. A catalyst again

that's what he would find, and found – himself,
in Basel, the foreign town on the banks of his
Rhine, there he found himself, the Protestant
Geheimrat Haber, now the Jew Haber, in the city
of wily Paracelsus, a changed and dying man.

Geheimrat – privy councilor (term also used for an eminent professor)

Slide 40




And so we come to the end of our review of chemistry's history.
Chemistry has benefited humanity immensely. The slogan "Better Living though Chemistry" is true in many, many ways.
However, like all science, chemistry can be used for ill as well as good. Poisons can be made specifically to kill or can be the inadvertent byproducts of other chemical procedures.