

8.4.1 ATOMIC STRUCTURE^{M37}

8.4.1.1 Early History

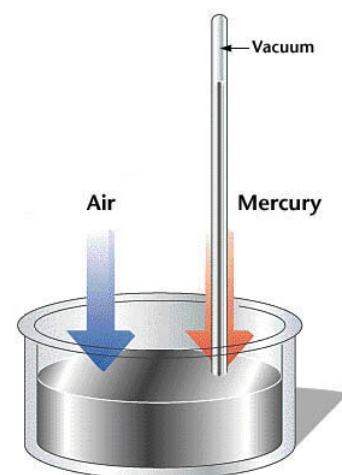
As we noted in our discussion on The Elements, the Greek philosopher Empedocles (492–432 BC) believed that there were just four elements—air, fire, water and earth. Empedocles' theory was quite popular, but it had a number of problems. For example, no matter how many times you break a stone in half, the pieces never resemble any of the core elements of fire, air, water, or earth.

A few decades after Empedocles, another Greek philosopher, Democritus (460–370 BC), developed a new theory of matter that attempted to overcome the problems inherent in Empedocles' model. Democritus' ideas were based on reasoning rather than science. He knew that if you took a stone and cut it in half, each half had the same properties as the original stone. He reasoned that if you continued to cut the stone into smaller and smaller pieces, at some point you would reach a piece so tiny that it could no longer be divided. Democritus called these infinitesimally small pieces of matter **atomos**, meaning *indivisible*. He suggested that atomos were eternal and could not be destroyed. He theorised that atomos were specific to the material that they made up, meaning that the atomos of stone were unique to stone and different from the atomos of other materials, such as fur. This was a remarkable theory that attempted to explain the whole physical world in terms of a small number of ideas.



Ultimately, though, Plato (427–347 BC) and Aristotle (384–322 BC), two of the best-known philosophers of Ancient Greece, rejected the theories of Democritus. Aristotle accepted the theory of Empedocles, adding his own (incorrect) idea that the four core elements could be transformed into one another. Because of Aristotle's great influence, Democritus's theory, and science itself, would be set back almost 2,000 years.

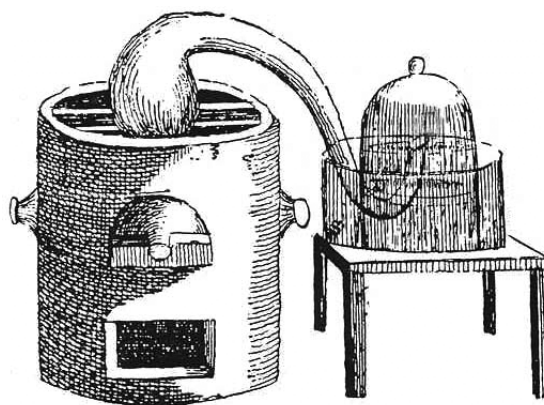
In the seventeenth and eighteenth centuries, several key events helped revive the theory that matter was made of small, indivisible particles. In 1643, Evangelista Torricelli (1608–1647), an Italian mathematician and pupil of Galileo (1564–1642), showed that *air had weight* and was capable of pushing a column of liquid mercury up a glass tube (thus inventing the barometer). This was a startling finding. If air—this substance that we could not see, feel, or smell—had weight, it must be made of something physical. But how could something have a physical presence, yet not respond to human touch or sight? The Swiss mathematician Daniel Bernoulli (1700–1782) proposed an answer. He developed a theory that air and other gases consist of tiny particles that are too small to be seen, and are loosely packed in an empty volume of space. The particles could not be felt because, unlike a solid stone wall that does not move, the tiny particles move aside when a human hand or body moves through them. Bernoulli reasoned that if these particles were not in constant motion they would settle to the ground like dust particles, and he therefore pictured air and other gases as loose collections of tiny billiard-ball-like particles that are continuously moving around and bouncing off one another.



Many scientists were busy studying the natural world at this time. In 1667, the German chemist J.J. Becher (1635–1682) had proposed that materials burned because they contained a substance called **phlogiston** (from the Greek for *set fire*), a proposition later popularised by one of his students G.E. Stahl (1660–1734). As a material burns, he suggested, it gives off phlogiston as visible fire. Stahl also showed that the corrosion of metals is merely a slow process of burning, and further that, while metal will corrode (*i.e.* will burn), the corrosion product (rust) will not. He suggested that this was due to the fact that the metal had released all its phlogiston in turning to rust. Rust thus had no phlogiston left and so could not burn. Air became an important part of this process by acting as a phlogiston receiver.

Shortly after Bernoulli proposed his particle theory, in 1773 the English chemist Joseph Priestley (1733–1804) began to experiment with red mercury calx. Mercury calx, a red solid stone, had been known and coveted for thousands of years because when it is heated, it appears to turn into mercury, a silver liquid metal. Priestley had observed that it does not just turn into mercury; it actually breaks down into two substances when it is heated—liquid mercury and a strange gas. Priestley carefully collected this gas in glass jars and studied it. After many long days and nights in the laboratory, Priestley said of the strange gas, “*what surprised me more than I can well express was that a candle burned in this air with a remarkably vigorous flame.*” Not only did flames burn strongly in this gas, but a mouse placed in a sealed container of this gas lived for a longer period of time than a mouse placed in a sealed container of ordinary air. Priestley’s discovery revealed that substances could combine together or break apart to form new substances with different properties. For example, a colourless, odourless gas could combine with mercury, a silver metal, to form mercury calx, a red mineral.

Priestley called the gas he discovered *dephlogisticated air*, because it was capable, according to Stahl’s proposition, of absorbing more phlogiston (*i.e.* materials burned much more readily) than normal air. In 1778, the French scientist Antoine Lavoisier (1743–1794) conducted many experiments with dephlogisticated air and theorised that the gas made some substances acidic. He renamed Priestley’s gas **oxygen** (from the Greek for *acid maker*). While Lavoisier’s theory about oxygen and acids proved incorrect, the name oxygen has persisted. Lavoisier knew from other chemists before him that acids react with some metals to release another strange and highly inflammable gas, then known as *inflammable air*. Lavoisier mixed the two gases, inflammable air and dephlogisticated air (oxygen), in a closed container and inserted a lighted match. He saw that the inflammable air immediately burned and he observed



droplets of a colourless liquid, identified as water, on the walls of the container. Lavoisier subsequently renamed inflammable air **hydrogen** (from the Greek for *water maker*).

Lavoisier also burned other substances such as phosphorus and sulfur in air, and showed that they combined with air to make new materials. These new materials weighed more than the original substances, and Lavoisier showed that the weight gained by the new materials was lost from the air in which the substances were burned.

8.4.1.1.1 Lavoisier's Law of Conservation of Mass

In 1789, Lavoisier wrote:

"We must lay it down as an incontestable axiom, that in all operations of art and nature, nothing is created, an equal quantity of matter exists both before and after the experiment . . . and nothing takes place beyond changes and modifications in the combination of these elements. Upon this principle the whole art of performing chemical operations depends."

Lavoisier arrived at his conclusions using a balance, so that by "quantity of matter" we may be certain that he meant weight which, in any given place, is proportional to mass so that we may restate his axiom more briefly as:

The mass of an isolated system before a chemical change is equal to its mass after the chemical change.

Thus, if two substances A and B undergo a chemical change becoming C and D, the mass of A and B together before the reaction is equal to the mass of C and D after the reaction:

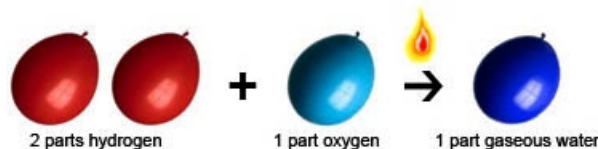
$$\text{Mass}_A + \text{Mass}_B = \text{Mass}_C + \text{Mass}_D$$

8.4.1.1.2 Proust's Law of Definite Proportions

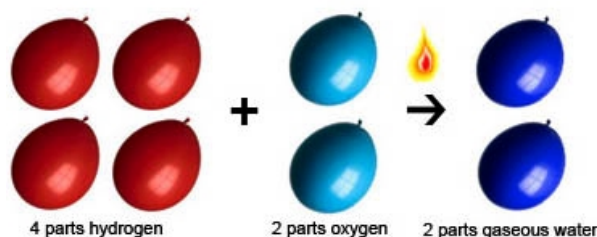
At around the same time, another French chemist, Joseph Louis Proust (1754–1826), performed a number of experiments and observed that no matter how he caused different elements to react with oxygen, they always reacted in defined proportions. He therefore proposed that:

The proportions by mass of the elements in a compound are fixed, and do not depend on its mode of preparation.

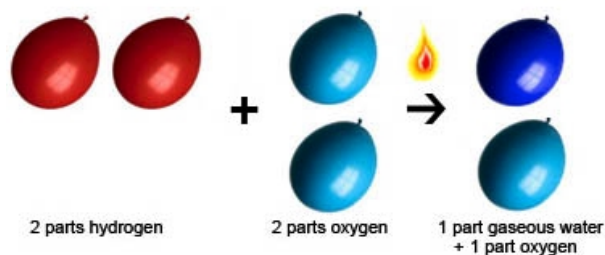
In simple terms, compounds have specific chemical formulae. For example, two parts of hydrogen always reacts with one part oxygen when forming water.



If we begin with twice as much starting material, the reaction simply yields twice as much product.



If one of the starting materials is in excess, the excess will simply remain unchanged after the reaction has occurred.



There are, however, exceptions to the Law of Definite Proportions. An entire class of substances does not follow this rule. The compounds are called non-stoichiometric compounds, or Berthollides¹. The ratio of the elements present in the compound can fluctuate within certain limits, such as in the example of ferrous oxide. The ideal formula is FeO , but due to crystallographic vacancies it is reduced to about $\text{Fe}_{0.95}\text{O}$.

8.4.1.1.3 Dalton's Law of Multiple Proportions

John Dalton (1766–1844) was an English chemist, meteorologist and physicist. In developing his theory on the structure of elements, further to the observations made by Lavoisier and Proust, he noted that, for example, nitrogen and oxygen formed two different compounds that contained different relative amounts of the two elements². In Dalton's own words³:

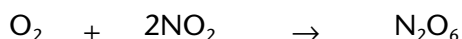
If 100 measures of common air be put to 36 of pure nitrous gas ..., after a few minutes the whole will be reduced to 79 or 80 measures, and exhibit no signs of either oxygenous or nitrous gas. If 100 measures of common air be admitted to 72 of nitrous gas ..., there will, as before, be found 79 or 80 measures of pure azotic gas for a residuum. ... These facts clearly point out the theory of the process: the elements of oxygen may combine with a certain portion of nitrous gas, or with twice that portion, but with no intermediate quantity. ...

Dalton was remarking on the reaction of nitrogen dioxide (*nitrous gas*) with the oxygen that we know to comprise around 21% of the atmosphere (*common air*), noting that the two would combine in ratios of approximately 1:2 or 1:4, but nothing in between. Although we recognise some experimental error in his measurements, we know the reactions Dalton was observing to be:

¹ After Claude Louis Berthollet (1748–1822), who believed that the products of a reaction depended on the ratio of the reactants.

² Note that Proust's Law only states that individual compounds comprise specific combinations of elements. Dalton's Law identifies the way in which some elements can combine in different proportions to form different compounds—the proportions in each case are still specific.

³ John Dalton, "Experimental Enquiry into the Proportion of the Several Gases or Elastic Fluids, Constituting the Atmosphere", *Memoirs of the Literary and Philosophical Society of Manchester* 1, 244-58 (1805)



and



Dalton's Law of Multiple Proportions is more commonly stated as:

When two elements form a series of compounds, the ratios of the masses of the second element that combine with a fixed mass of the first element can always be expressed as the ratio of small whole numbers.

8.4.1.2 Dalton's Atomic Theory

Through his observations of morning fog and other weather patterns, Dalton had noted that water could exist as a gas that mixed with air and occupied the same space as air. In contrast, solids could not occupy the same space as each other; ice, for example, could not mix with air. He was thus led to consider what could allow water to sometimes behave as a gas and sometimes as a solid. Dalton proposed that all matter must be composed of tiny particles. In the gaseous state, those particles float freely around and could mix with other gases, as Bernoulli had proposed. But Dalton extended this idea to apply to all matter—gases, liquids and solids—and in the solid state, he suggested that particles, rather than being free to move about, are fixed in place.

Indeed, Dalton proposed a theory relating to the structure of matter that embraced four fundamental concepts:

- 1. All matter is composed of indivisible particles called atoms.** Bernoulli, Dalton, and others pictured atoms as tiny billiard-ball-like particles in various states of motion. While this concept is useful to help us understand atoms, it is not correct, as we will see as our studies in chemistry progress;
- 2. All atoms of a given element are identical; atoms of different elements have different properties.** Dalton's theory suggested that every single atom of an element such as oxygen is identical to every other oxygen atom; furthermore, atoms of different elements, such as oxygen and mercury, are different from each other. Dalton characterised elements according to their atomic weight, although when isotopes of elements were discovered in the late 1800s this concept changed;
- 3. Chemical reactions involve the combination of atoms, not the destruction of atoms.** Atoms are indestructible and unchangeable, so compounds, such as water and mercury calx, are formed when one atom chemically combines with other atoms. This was an extremely advanced concept for its time—while Dalton's theory implied that atoms bonded together, it would be more than 100 years before scientists began to explain the concept of chemical bonding.
- 4. When elements react to form compounds, they react in defined, whole-number ratios.** The experiments that Dalton and others performed showed that reactions are not random events. Rather, they proceed according to precise and well-defined formulae. This important concept in chemistry will be discussed later in more detail.

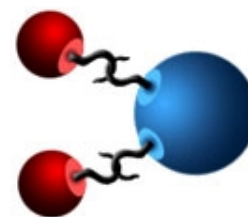
Some of the details of Dalton's atomic theory require more explanation.

Elements As noted when discussing the Chemical Elements (Section 8.1.2), Robert Boyle (1627–1691) recognized that the Greek definition of an element

(earth, fire, air, and water) was not correct. Boyle proposed a new definition of an element as a fundamental substance. Elements are pure substances that form the basis of all of the materials around us;

Atoms A single unit of an element is called an atom. The atom is the most basic unit of the matter that makes up everything in the world around us. Each atom retains all of the chemical and physical properties of its parent element. At the end of the nineteenth century, scientists would show that atoms were actually made up of smaller, *subatomic* particles, and the billiard-ball model of the atom would be replaced by a model that better accounted for these new observations;

Compounds Most of the materials we come into contact with are compounds, substances formed by the chemical combination of two or more atoms of the elements. A single 'particle' of a compound is called a **molecule**. Dalton incorrectly imagined that atoms 'hooked' together to form molecules. However, Dalton correctly realised that compounds have precise formulae. Water, for example, is always made up of two parts hydrogen and one part oxygen. The chemical formula of a compound is written by listing the symbols of the elements together, without any spaces between them. If a molecule contains more than one atom of an element, a number is subscripted after the symbol to show the number of atoms of that element in the molecule. Thus the formula for water is H_2O , never HO or H_2O_2 .

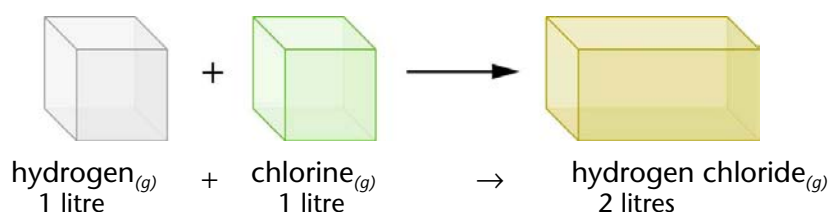


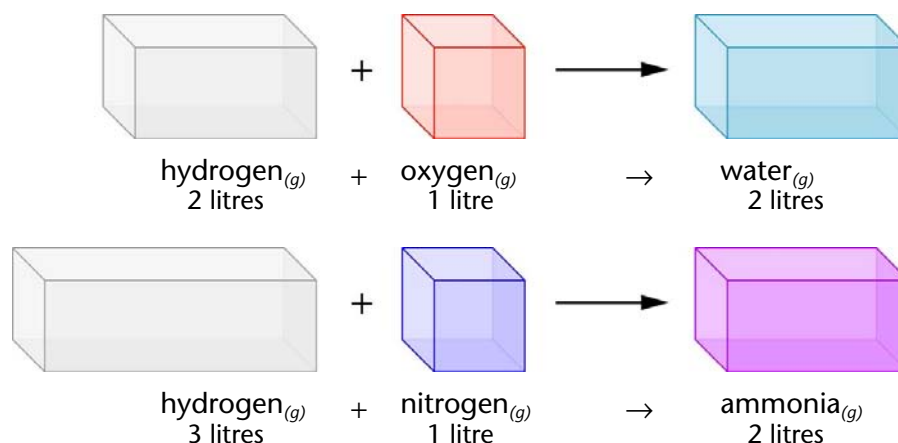
8.4.1.2.1 Gay-Lussac's Law of Combining Gas Volumes

In 1808 Joseph Louis Gay-Lussac (1778–1850) proposed his Law of Combining Gas Volumes:

Providing comparisons are made under the same conditions of temperature and pressure there is a simple ratio between the volumes of gases that react with one another and the volumes of any gases produced by the reaction.

For example, in the following reactions it is found that:





It is important to realise that:

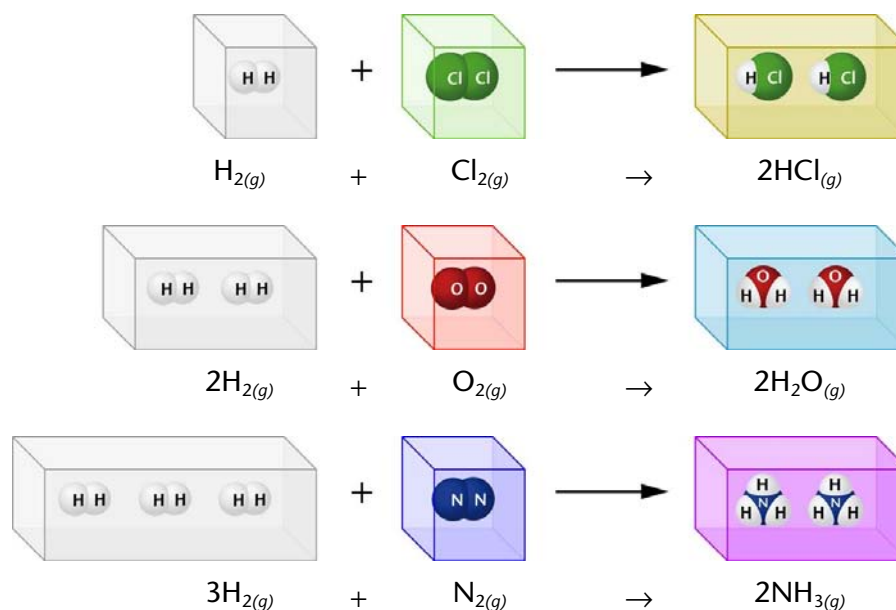
- The volumes before and after the reaction are not equal, although the masses before and after the reaction are;
- There is a simple volume relationship only when gases are involved;
- There is no simple relationship between the volumes of reacting solids and liquids.

Both Dalton and Gay-Lussac attempted to explain the Law of Combining Gas Volumes in terms of the atomic theory, since it was reasonable to expect that a theory which explained mass relationships observed during chemical changes would explain the simple volume relationships observed when gases reacted. They, and the theory, however, failed to do so.

In 1811 Amadeo Avogadro (Conte de Quarengha) (1776–1856), an Italian Professor of Chemistry, suggested a solution to the problem. He pictured, in particular, the particles of hydrogen and chlorine gas as groups of atoms, not single atoms. These groups of atoms he called molecules—little masses of little heaps. He put forward his hypothesis:

At the same temperature and pressure, equal volumes of gases contain the same number of molecules.

These ideas reconciled Gay-Lussac's facts and Dalton's theory, and the examples presented on the previous page could be explained as illustrated:



It was not for some 50 years, however, that Avogadro's hypothesis was accepted. Chemists of the time were unable to reconcile the proposition that identical atoms could combine with one another with Berzelius⁴ suggestion that compounds were produced when different atoms became oppositely charged and attracted one another.

8.4.1.2.2 Molecular Weights of Gases

Using Avogadro's idea that equal volumes of gases under the same conditions contain the same number of molecules, we can find the ratio of the masses of the molecules of two different gases by comparing the masses of the same volumes of the two gases.

$$\frac{\text{Molecular Weight}_A}{\text{Molecular Weight}_B} = \frac{\text{Mass}_{\text{Volume A}}}{\text{Mass}_{\text{Volume B}}}$$

This ratio is the ratio of the densities of the two gases. Originally, hydrogen gas, having the lowest density of all the elements, was used as the standard with which all other gas densities were compared. The mass of one atom of hydrogen was taken to be exactly one unit.

The mass of a molecule *relative* to the mass of an atom of hydrogen was called the relative molecular weight, or simply the **molecular weight**. If the molecular weight and the number of atoms in a molecule of a gaseous element were known, one could obtain the mass of the atom of the element *relative* to the mass of the hydrogen atom—the relative atomic weight of the element, or simply its **atomic weight**.

$$\text{Atomic Weight} = \frac{\text{Molecular Weight}}{\# \text{ Atoms in Molecule}}$$

8.4.1.2.3 Atomic Weights

The determination of the atomic weights of gaseous elements was thus fairly straight forward, but only a few of the elements exist as gases at room temperature. How can we determine the atomic weights of the other elements?

⁴ Jöns Jakob Berzelius (1779–1848), Swedish chemist who is credited with the invention of the modern chemical notation.

The general method used was to note the amount of oxygen consumed in the generation of the oxide of the element in question. With a knowledge of the composition of the product, and the atomic weight of oxygen, the atomic weight of the element could be deduced. For example, by measuring the amount of oxygen consumed by a given amount of mercury in forming mercury oxide (mercury calx), and noting the weight of the mercury oxide produced, the atomic weight of mercury could be determined (assuming that mercury and oxygen combined in a simple 1:1 ratio!):



Thus, if the oxidation of 100.00 g of mercury produces 107.98 g of mercury oxide, 7.98 g of oxygen must have been consumed. Given the atomic weight of oxygen as 16.00, the atomic weight of mercury could be determined:

$$\begin{aligned} \frac{\text{Atomic Weight}_{\text{Hg}}}{100.00 \text{ g}} &= \frac{\text{Atomic Weight}_{\text{O}}}{\text{Weight}_{\text{O}}} = \frac{\text{Atomic Weight}_{\text{O}}}{\text{Weight}_{\text{HgO}} - \text{Weight}_{\text{Hg}}} \\ \therefore \text{Atomic Weight}_{\text{Hg}} &= 100.00 \times \frac{\text{Atomic Weight}_{\text{O}}}{\text{Weight}_{\text{HgO}} - \text{Weight}_{\text{Hg}}} \\ &= 100.00 \times \frac{16.00}{7.98} = 200.59 \end{aligned}$$

The greatest problem that faced the nineteenth century chemists was the determination of the ratio of the number of atoms of each element in a compound, because most compounds *do not* actually form with a simple 1:1 ratio of constituents.

Following from the determination of atomic weights, however, the molecular weight of any substance could be calculated by simply adding together the atomic weights of the constituent atoms.

In 1960, the carbon-12 atom (the nucleus of which contains 6 protons and 6 neutrons) was adopted as the standard against which atomic weights are determined. On this scale, the carbon-12 atom is given the atomic weight of 12.0000 Unified Atomic Mass Units (**u**) and all other atomic weights are obtained using this as the reference weight. On this new scale, the mass of a single hydrogen atom is 1.008 **u**, the difference (from the original value of 1.000 **u**) being accounted for by the binding energy (according to Einstein's famous equation $E = mc^2$) associated with the nuclides in the carbon atom.

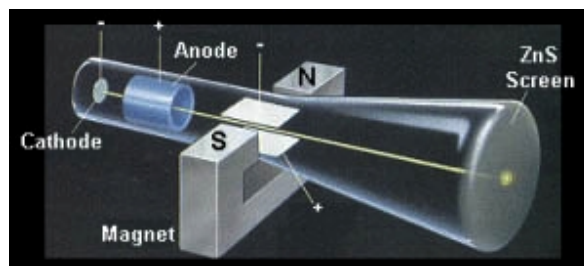
It should be emphasised that the term atomic or molecular weight is actually a misnomer. It is not really a weight at all, rather a relative number, the ratio of two weights and hence a pure number. Nonetheless, the Unified Atomic Mass Unit, or Dalton (**Da**), is used as the unit of atomic or molecular mass.

8.4.1.3 Post-Dalton Refinement of the Atomic Theory⁵

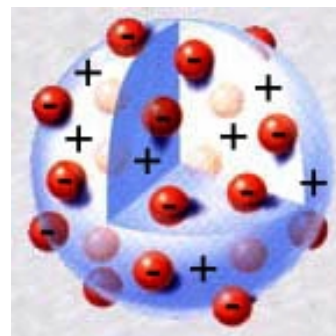
Until the final years of the nineteenth century, the accepted model of the atom resembled that of a billiard ball—a small, solid sphere. In 1897, the British physicist J.J. Thomson (1856–1940) dramatically changed the modern view of the atom with his discovery of the **electron**. Thomson's work suggested that the atom was not an *indivisible* particle as Dalton had suggested, but a jigsaw puzzle made of smaller pieces.

⁵ http://www.visionlearning.com/library/module_viewer.php?mid=50

Thomson's notion of the electron came from his work with a nineteenth century scientific curiosity: the cathode ray tube. For years scientists had known that if an electric current was passed through a vacuum tube, a stream of glowing material could be seen; however, no one could explain why. Thomson found that the mysterious glowing stream would bend toward a positively charged electric plate. Thomson theorised, and was later proven correct, that the stream was in fact made up of small particles, pieces of atoms that carried a negative charge. These particles were later named electrons.

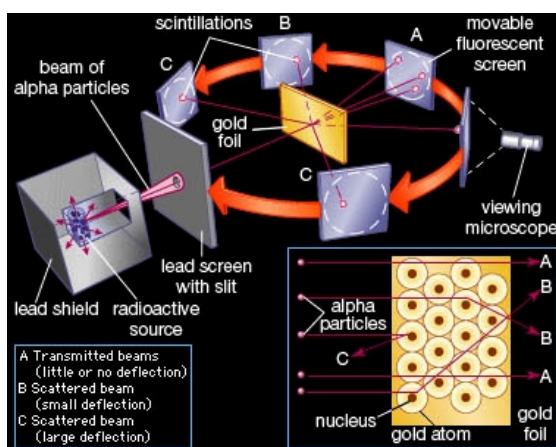


In 1886, Eugen Goldstein (1850–1930) discovered that atoms had positive charges. Thomson subsequently imagined that atoms looked like pieces of raisin bread, a structure in which clumps of small, negatively charged electrons (the "raisins") were scattered inside a smear of positive charges.



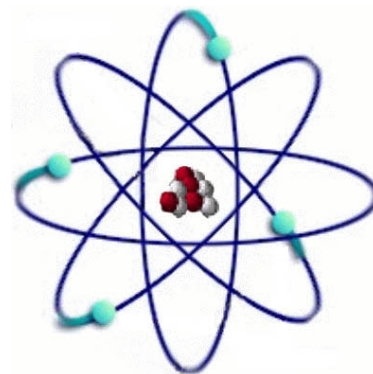
In 1908, however, New Zealand physicist Ernest Rutherford (1871–1937), a former student of Thomson's, proved Thomson's raisin bread structure incorrect.

Rutherford performed a series of experiments with radioactive alpha particles. While it was unclear at the time what the alpha particle was, it was known to be very tiny. Rutherford fired tiny alpha particles at solid objects such as gold foil. He found that while most of the alpha particles passed right through the gold foil, a small number of alpha particles passed through at an angle (as if they had bumped up against something) and some bounced straight back like a tennis ball hitting a wall. Rutherford's experiments suggested that gold foil, and matter in general, had holes in it! These holes allowed most of the alpha particles to pass directly through, while a small number ricocheted off or bounced straight back because they hit a solid object.



In 1911, Rutherford proposed a revolutionary view of the atom. He suggested that the atom consisted of a small, dense core of positively charged particles in the centre (or **nucleus**) of the atom, surrounded by a swirling ring of electrons. The nucleus was so dense that the alpha particles would bounce off of it, but the electrons were so tiny,

and spread out at such great distances, that the alpha particles would pass right through this area of the atom. Rutherford's atom resembled a tiny solar system with the positively charged nucleus always at the centre and the electrons revolving around the nucleus.



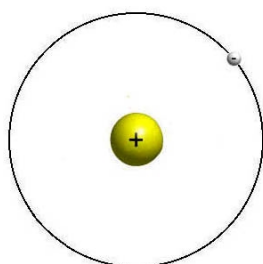
The positively charged particles in the nucleus of the atom were called **protons**. Protons carry an equal, but opposite, charge to electrons, but protons are much larger and heavier than electrons.

In 1932, James Chadwick (1891–1974) discovered a third type of subatomic particle that he named the **neutron**. Neutrons help stabilise the protons in the atom's nucleus. Because the nucleus is so tightly packed together, the positively charged protons would tend to repel each other normally. Neutrons help to reduce the repulsion between protons and stabilise the atom's nucleus. Neutrons always reside in the nucleus of atoms and they are about the same size as protons. However, neutrons do not have any electrical charge—they are electrically neutral.

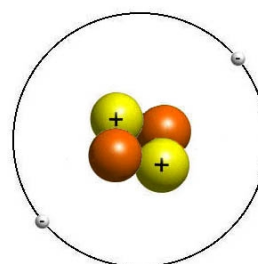
Atoms are electrically neutral because the number of protons (+ charges) is equal to the number of electrons (– charges) and thus the two cancel out. As atoms get larger, the number of protons (and usually also neutrons) in the nucleus increases, and so does the number of electrons (in the neutral state of the atom).

Atoms are extremely small. One hydrogen atom (the smallest atom known) is approximately 5×10^{-8} mm (0.5 Å) in diameter. To put that in perspective, it would take almost 20 million hydrogen atoms to make a line as long as this dash -. Most of the space taken up by an atom is actually empty because the electron spins at a relatively large distance from the nucleus. For example, if we were to draw a hydrogen atom to scale and used a 1 cm proton, the atom's electron would spin at a distance of ~0.5 km from the nucleus—the atom would be larger than a football field!

Atoms of different elements are distinguished from each other by their number of protons (the number of protons is constant for all atoms of a single element; the number of neutrons and electrons can vary under some circumstances). To identify this important characteristic of atoms, the term **atomic number (z)** is used to describe the number of protons in an atom. For example, $z = 1$ for hydrogen and $z = 2$ for helium.



Hydrogen atom (${}^1_1\text{H}$)
Atomic Number = 1
Atomic Weight \approx 1



Helium atom (${}^4_2\text{He}$)
Atomic Number = 2
Atomic Weight \approx 4

The atomic weight (as defined above, in Section 8.4.2.1.4) of an atom can be approximated by simply adding up the number of protons and neutrons in the atom. While protons and neutrons are about the same size, the electron is more than 1,800 times smaller than the two. Thus the electrons' weight is inconsequential in

determining the weight of an atom—it's like comparing the weight of a flea to the weight of an elephant. Refer to the illustration above to see how the number of protons plus neutrons in the hydrogen and helium atoms corresponds to the atomic mass.

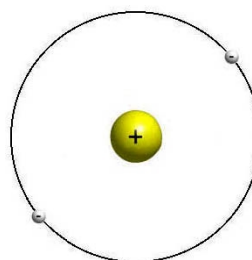
Normally, atoms contain equal numbers of protons and electrons. Because the positive and negative charges cancel each other out, atoms are normally electrically neutral. But, while the number of protons is always constant in any atom of a given element, the number of electrons can vary.

8.4.1.3.1 Ions

When the number of electrons changes in an atom, the electrical charge changes. If an atom gains electrons, it picks up an imbalance of negatively charged particles and therefore becomes negative. If an atom loses electrons, the balance between positive and negative charges is shifted in the opposite direction and the atom becomes positive. In either case, the magnitude (+1, +2, -1, -2, etc.) of the electrical charge will correspond to the number of electrons gained or lost. Atoms that carry electrical charges are called **ions** (regardless of whether they are positive or negative). For example, the following illustration shows a positive hydrogen ion (which has lost an electron) and a negative hydrogen ion (which has gained an extra electron). The electrical charge on the ion is always written as a superscript after the atom's symbol.



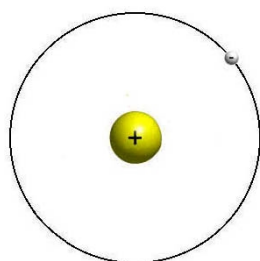
H⁺ ion



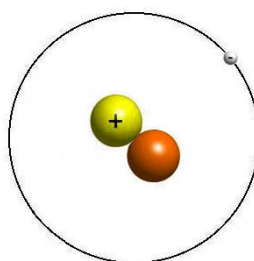
H⁻ ion

8.4.1.3.2 Isotopes

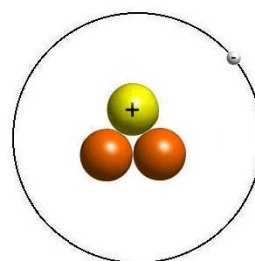
The number of neutrons in an atom can also vary. Two atoms of the same element that contain different numbers of neutrons are called **isotopes**. For example, normally hydrogen contains no neutrons. Isotopes of hydrogen, however, that contain one neutron (deuterium) or two (tritium) also exist. The atomic number (**z**) is the same in each isotope. The atomic mass, however, increases by one in deuterium and two in tritium, as the respective atoms are made heavier by the addition of one or two neutrons.



Hydrogen (${}^1_1\text{H}$)
Atomic Number = 1
Atomic Weight \approx 1



Deuterium (${}^2_1\text{H}$)
Atomic Number = 1
Atomic Weight \approx 2



Tritium (${}^3_1\text{H}$)
Atomic Number = 1
Atomic Weight \approx 3

8.4.1.3.3 Electron Shells

Ernest Rutherford's view of the atom consisted of a dense nucleus surrounded by freely spinning electrons. In 1913, the Danish physicist Niels Bohr (1885–1962) proposed yet another modification to the theory of atomic structure based on a curious phenomenon called **line spectra**.

When matter is heated, it gives off light. For example, turning on an ordinary light bulb causes an electric current to flow through a metal filament that heats the filament and produces light. The electrical energy absorbed by the filament excites the atoms' electrons, causing them to "wiggle". This absorbed energy is eventually released from the atoms in the form of light.

When normal white light, such as that from the sun, is passed through a prism, the light separates into a continuous spectrum of colours:



Bohr knew that when pure elements were excited by heat or electricity, they gave off distinct colours rather than white light. This phenomenon is most commonly seen in modern-day neon lights, tubes filled with gaseous elements (most commonly neon). When an electric current is passed through the gas, a distinct colour (most commonly red) is given off by the element. When light from an excited element is passed through a prism, only specific lines (or wavelengths) of light can be seen. These lines of light are called line spectra. For example, when hydrogen is heated and the light is passed through a prism, the following line spectra can be seen:



Each element has its own distinct line spectra. For example:



Helium Line Spectra



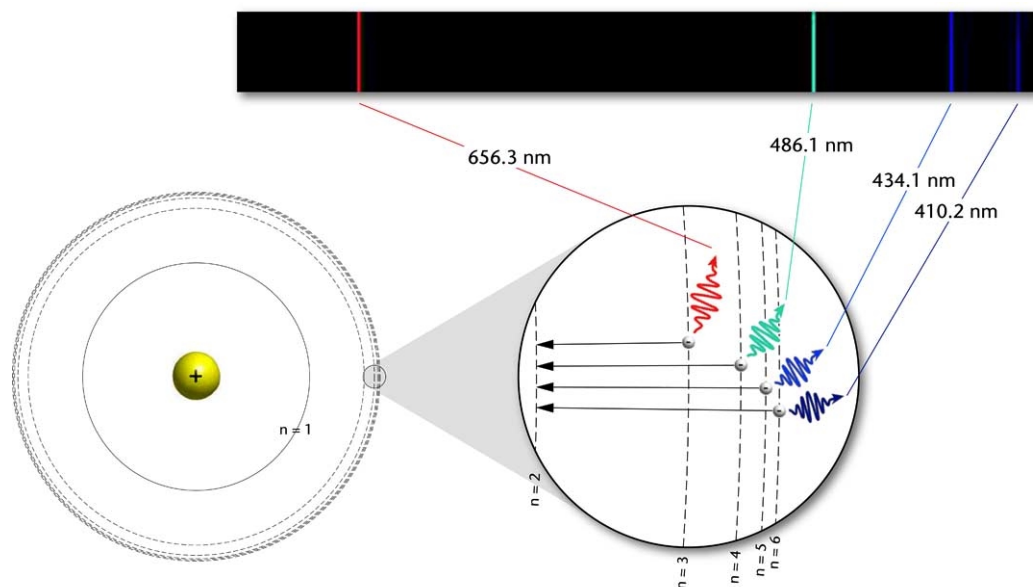
Neon Line Spectra

To Bohr, the line spectra phenomenon showed that atoms could not emit energy continuously, but only in very precise quantities (he described the energy emitted as quantised). Because the emitted light was due to the movement of electrons, Bohr suggested that electrons could not move continuously in the atom (as Rutherford had suggested) but only in precise steps. Bohr hypothesised that electrons occupy specific energy levels. When an atom is excited, such as during heating, electrons can jump to higher levels. When the electrons fall back to lower energy levels, precise quanta of energy are released as specific wavelengths (lines) of light.

Under Bohr's theory, an electron's energy levels (also called electron **shells**) can be imagined as concentric circles around the nucleus. Normally, electrons exist in the

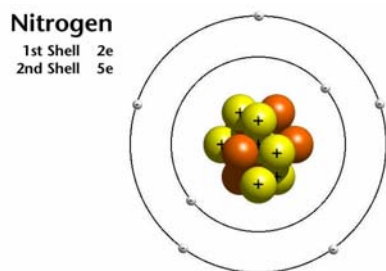
ground state, meaning they occupy the lowest energy level possible (the electron shell closest to the nucleus). When an electron is excited by adding energy to an atom (for example, when it is heated), the electron will absorb energy, and *jump* to a higher energy level (a shell further away from the nucleus). After a short time, this electron will spontaneously *fall* back to a lower energy level, giving off a photon of light energy. Key to Bohr's theory was the fact that an electron could only *jump* and *fall* to precise energy levels, thus emitting a limited spectrum of light.

The line spectra for an excited hydrogen atom, for example, comprise only those wavelengths that correspond to the energy difference between two electron shells in the hydrogen atom. The transitions that generate lines in the visible part of the electromagnetic spectrum are those that involve electrons falling back from higher shells ($n > 2$) to the second electron shell ($n = 2$). This series of transitions is known as the Balmer Series, after the Swiss mathematician Johann Balmer (1825–1898) who developed who developed an empirical formula to predict the location of these spectral lines. The Lyman Series, after the American physicist Theodore Lyman (1874–1954) who first observed them, comprises lines associated with electrons falling back to the Ground State ($n = 1$), but these are all in the (higher energy) ultra violet region and are not visible.



Balmer Series electronic transitions leading to the visible hydrogen line spectra

Not only did Bohr predict that electrons would occupy specific energy levels, he also predicted that those levels had limits to the number of electrons each could hold.



Bohr model of a nitrogen atom ($^{14}_7\text{N}$)

Shell #	Electrons
1	2
2	8
3	18
4	32

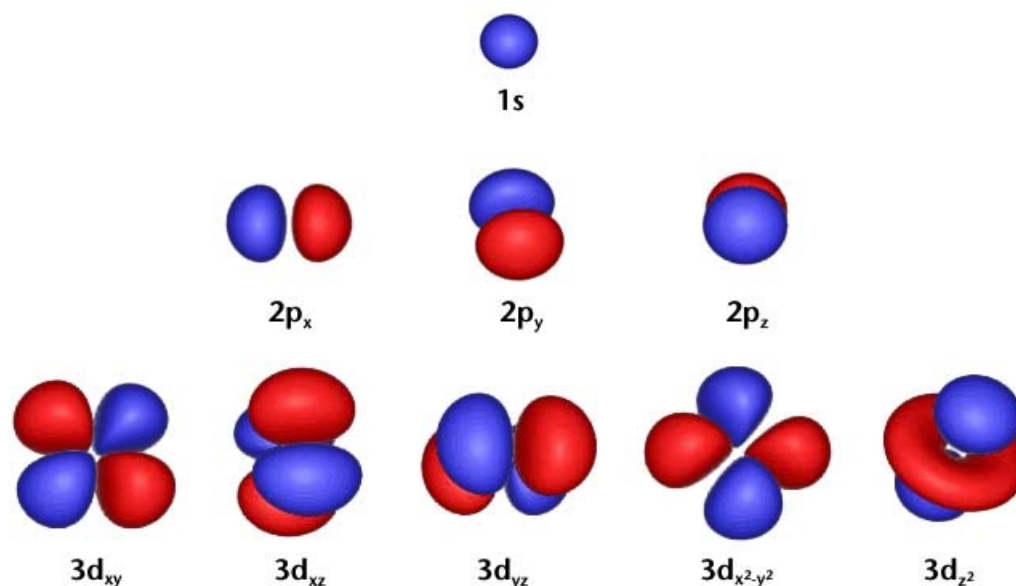
Bohr electron shell capacities

Under Bohr's theory, the maximum capacity of the first (or innermost) electron shell is two electrons. For any element with more than two electrons, the extra electrons will

reside in additional electron shells. For example, in the ground state configuration of nitrogen (which has seven electrons) two electrons occupy the first shell and five electrons occupy the second shell.

8.4.1.3.4 Atomic Orbitals

The development of quantum mechanics, the field itself arising out of initial mathematical models proposed by German physicist Werner Heisenberg (1901–1976) and Austrian-Irish physicist Erwin Schrodinger (1887–1961), led to further refinements of the atomic model through the 20th century. While consistent with the Bohr Model, the atomic model defined by quantum mechanics is largely mathematical (it is not easy to draw a picture of an atom as defined by quantum mechanics). Rather than orbiting the nucleus like planets around a sun, quantum theory proposes that the location of electrons is defined by a wave function that is dependent on the values of various quantum numbers. Rather than defining orbits for electrons, this mathematical function defines a 3-dimensional *orbital* within which an individual electron may be located. As atoms become larger, orbital structures become more complex. As an example, the illustration below shows the shapes of the $1s$, $2p$ and $3d$ orbitals⁶, according to modern quantum mechanics.



Atomic $1s$ (sharp), $2p$ (principle) and $3d$ (diffuse) orbitals⁷
The nucleus is located at the centre of the orbital (for s -orbitals)
or at the central point between the orbital lobes (for p - & d -orbitals)

The story of the development of modern atomic theory is one in which scientists built upon the work of others to produce a more accurate explanation of the world around them. This process is common in science, and even incorrect theories can contribute to important scientific discoveries. Dalton, Priestley, and others laid the foundation of atomic theory, and many of their hypotheses are still useful. In the decades that followed, however, other scientists would show that atoms are not solid, like billiard balls, but complex systems of particles.

⁶ Note that these are just some examples of atomic orbitals. For example, there are also $2s$ and $3s$ orbitals (which look similar to the $1s$ orbital), and $3p$ orbitals (which look similar to the $2p$ orbitals). There are also additional orbitals in the 4th (fundamental), 5th (**g**), 6th (**h**) etc. shells.

⁷ <http://www.chemcomp.com/journal/molorb.htm>

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