Chronology of Discoveries in Atomic Structure

c. 430 B.C. Leucippus and his pupil, Democritus (c. 460-371 B.C.) of Adbera develop the materialistic philosophical concept of atoms (from atomos, atomos, “uncuttable”). Matter did not form a continuium, but consisted of atoms which are 1) solid, 2) impenetrably hard (or cannot be divided), 3) eternal, 4) homogeneous and identical in substance, and 5) there are a finite number of kinds. Motion is inherent in the atoms (which move in a void) and they differ in their geometrical and mechanical properties. From these qualities of size, shape, and motion our world appears by collision and conglomeration, just as a book arises from different shaped letters and different ordering of the letters.

Atomism did enjoy some success among followers of Epicuris (c. 341-270 B.C.), but it was soon pushed aside (especially by Plato and Aristotle) and did not receive serious consideration until the seventeenth century. Both Aristotle and Plato rejected the idea of a vacuum or void and the concept of self-moving bodies. However, Aristotle did admit to there being a practical lower limit to a substance being subdivided. He called this *minima naturalis*.

Examples of Democritus’ atoms

1417 Rediscovery of the poem *De Rerum Natura* (On The Nature of Things), written by Lucretius (c. 95 - 55 B.C.). This long poem was based on atomistic teachings and explained much of its philosophy. To this day, very little of Lecuippus’ and Democritus’ writings remain.

1660 Pierre Gassendi succeeds in freeing atomic theory from godlessness. Because of its athestic basis as compared to Christianized Aristotle, atomism had only appealed to a few radical philosophers. The general philosophical problem remained, how can it be proved that matter is particulate in nature. The general notion of explaining phenomena in terms of particles begins to arise through the efforts of Issac Newton and Robert Boyle.

1666 Boyle, although not a chemical atomist, did think of matter in finite, ultimate particles too small to be individually perceptible to the senses.

1687 Newton shows that Boyle’s Law (pressure of a gas is inversely proportional to its volume) follows if a gas is made up of mutually repulsive particles, with the forces inversely proportional to their distances apart. This assumption is incorrect, but it is historically important for being among the first uses of atoms or particles in an explanation. Dalton thought Newton had proved the gas molecules are mutually repelling, but was still able to develop much that was correct in his atomic theory.

1704 Newton wrote, “It seems probable to me that God formed matter in solid, massy, hard, impenetrable, movable particles.... God is able to create particles of matter of several sizes and figures....”

1738 Daniel Bernoulli uses the atom idea to correctly account for Boyle’s Law.

1803 John Dalton postulates the existence of atoms and publishes the first table of atomic weights. This hypothesis enables him to explain many features of chemistry on a simple basis. Dalton today is known as the "Father of Modern Atomic Theory." Modern scholarship has identified 4 postulates implicit in Dalton's work. They are: 1) Elements are made up of minute, discrete, indivisible, and indestructible particles called atoms. These atoms maintain their identity through all physical and chemical changes. 2) Atoms of the same element have the same properties. Atoms of different elements have different properties. 3) Atoms of the same element can unite in more than one ratio with another element to form more than one compound. 4) Chemical combination between two or more atoms occur in simple, numerical ratios (i.e., 1 to 2; 2 to 3; ec.).

While it becomes clear that atoms must exist, since Dalton's results are explainable only on an atomic basis, there is still no knowledge about what the structure of an atom is or how they can connect (or bond) together. To Dalton, atoms were hard, featureless spheres which must exist, but he had no knowledge of their inner structure.

1833 Michael Faraday discovers quantitative laws of electrochemical deposition. He introduces the terms electrode, cathode, anode, ion, anion, cation, electrolyte. He establishes that a definite quantity of electricity is associated with each atom of matter. The number of atoms that chemically can react is related to the number of electrons available in the system. In other words, Faraday measured and quantized electricity; he identified a special, integral electron-to-atom relationship. He said, "...if we adopt the atomic theory or phraseology, then the atoms of bodies which are equivalent to each other in their ordinary chemical action, have equal quantities of electricity associated with them."

1838 Faraday studies electric discharges in a vacuum and discovers the Faraday dark space near the cathode.

1886 Eugen Goldstein observes that a cathode-ray tube produces, in addition to the cathode ray, radiation that travels in the opposite direction - away from the anode; these rays are called canal rays because of holes (canals) bored in the cathode; later these will be found to be ions that have had electrons stripped in producing the cathode ray.

1855 German inventor Heinrich Geissler develops mercury pump - produces first good vacuum tubes, these tubes, as modified by Sir William Crookes, become the first to produce cathode rays, leading to the discovery of the electron.

1858 Julius Plucker shows that cathode rays bend under the influence of a magnet suggesting that they are connected with in some way; this leads in 1897 to discovery that cathode rays are composed of electrons.

1865 H. Sprengel improves the Geissler vacuum pump. Pluecker uses Geissler tubes to show that at lower pressure, the Faraday dark space grows larger. He also finds that there is an extended glow on the walls of the tube and that this glow is affected by an external magnetic field.

1869 J.W. Hittorf finds that a solid body put in front of the cathode cuts off the glow from the walls of the tube. Establishes that "rays" from the cathode travel in straight lines.

1871 C.F. Varley is first to publish suggestion that cathode rays are composed of particles. Crookes proposes that they are molecules that have picked up a negative charge from the cathode and are repelled by it.

1874 George Johnstone Stoney estimates the charge of the then unknown electron to be about 10^{-20} coulomb, close to the modern value of 1.6021892 x 10^{-19} coulomb. (He used the Faraday constant (total electric charge per mole of univalent atoms) divided by Avogadro's Number. James Clerk Maxwell had recognized this method soon after Faraday had published, but he did not accept the idea that electricity is composed of particles.) Stoney also proposes the name "electrine" for the unit of charge on a hydrogen ion. In 1891, he changes the name to "electron."

1876 Eugen Goldstein shows that the radiation in a vacuum tube produced when an electric current is forced through the tube starts at the cathode; Goldstein introduces the term cathode ray to describe the light emitted.

1881 Herman Ludwig von Helmholtz shows that the electrical charges in atoms are divided into definite integral portions, suggesting the idea that there is a smallest unit of electricity.

1883 H. Hertz shows that cathode rays are not deflected by electrically charged metal plates, which would seem to indicate that cathode rays cannot be charged particles.

1890 A. Schuster calculates the ratio of charge to mass of the particles making up cathode rays (today known as electrons) by measuring the magnetic deflection of cathode rays.

1892 Heinrich Hertz who has concluded (incorrectly) that cathode rays must be some form of wave, shows that the rays can penetrate thin foils of metal, which he takes to support the wave hypothesis. Philipp von Lenard develops a cathode-ray tube with a thin aluminum window that permits the rays to escape, allow in the rays to be studied in the open air.

1894 Joseph John (J.J.) Thomson announces that he has found that the velocity of cathode rays is much lower than that of light. Stoney introduces the term electron.

1895 Jean-Baptiste Perrin shows that cathode rays deposit a negative electric charge where they impact, refuting Hertz's wave concept and showing that the cathode ray are particles.

1896 Pieter P. Zeeman discovers that spectral lines of gases placed in a magnetic field are split, a phenomenon call the Zeeman effect; H.A. Lorentz explains this effect by assuming that light is produced by the motion of charged particles in the atom. Hendrik Antoon Lorentz uses Zeeman's observations of the behavior of light in magnetic field to calculate the charge to mass ratio of the electron in an atom, a year before electrons are discovered and 15 years before it is known that electron are constituents of atoms.

1897 Walter Kaufmann determines the ratio of the charge to mass for cathode rays in April, about the same time Thomson does, but Kaufmann fails to consider that the rays might be subatomic particles. Thomson discovers the electron, the first known particle that is smaller than the atom, in part because he has better vacuum pumps than were previously available; he, and independently, Emil Weichart, determine the ratio of charge to mass of the particles by deflecting them by electric and magnetic fields. Thomson's work can be divided into three components: 1) he improved J. Perrin's method of collecting charge inside the vacuum tube, showing that a charge was collected only when a magnetic field was used to bend the rays into a path leading to the collector, 2) he showed that the cathode rays are deflected by an electric field. He explained Hertz's results (see 1883 above) by hypothesizing that gas remaining in the tube was ionized, the ions collect on the plate and neutralize the charge on the plates. Using better vacuum pumps avoided this problem. 3) he was able to obtain a good value for the charge to mass ratio in two independent ways – from the temperature rise on the charge collector and by balancing the magnetic and electric deflections of the cathode ray beam.

It is important to underscore the fact that the experiment did yield the SAME charge-to-mass ratio (e/m) for every substance tested. Magnets and electrical fields can be used to deflect the cathode ray. The deflection is related to both charge and mass of a particle. Knowing the strengths of the magnetic and electrical fields used allowed Thomson to calculate the e/m ratio, but NOT 'e' or 'm' alone.

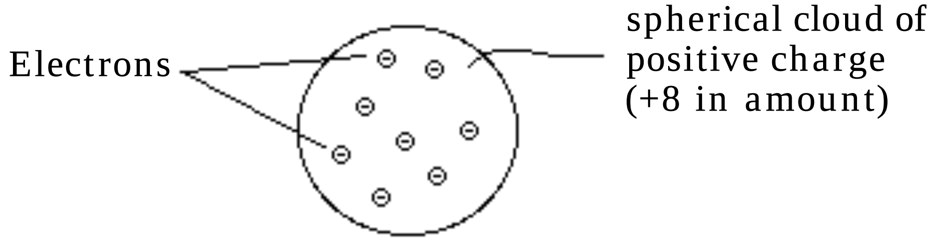
Wilhelm Wein deflects canal rays with magnetic and electrical fields. From the direction and magnitude of the deflection, he concludes that they are positively charged particles with charge-to-mass ratios at least a thousand times greater than Thomson's particles. In fact, the ratios are comparable to e/m ratios of electrically charges atoms, as measured in electrolysis in solutions. He concludes that canal rays are atoms or molecules of gas that have had electrons knocked out of them and thus are attracted to the negative cathode. Most hit the cathode, but some slip through the holes where they can be studied.

Another observation was that most substances tested would release more than one electron as the voltage on the CRT increased. Helium released 1 or 2, lithium up to 3, beryllium up to 4, and so on. Hydrogen, as the exception, never released more than one. Therefore, it was assumed to contain one electron and one proton (the fundamental positive charge)

Since all substances contain electrons, if they are neutral, they must therefore contain positive charges as well. Thomson, in his study of positive canal rays (in the late 1980's and early 1900's), found its e/m value to differ for every substance tested. In that sense, the canal ray tube represented the first mass spectrometer, a device that separates particles of varying mass by differences in deflection when acted upon by a particular magnetic field. Thomson's experiment with canal rays revealed at least two kinds of neon atoms, one with an atomic mass of 20, the other 22. The development work on the mass spectrometer was continued by Francis Ashton, who later won a Nobel Prize for his work. The mass spectrometer is now a fundamental piece of equipment for college-level and above.

1899 Thomson, using Charles Wilson's condensation chamber, proves that cathode particles carry the same amount of charge as hydrogen ions in electrolysis; he measures the charge of the electron and thus completes his discovery of the electron; he also recognizes ionization to be a splitting of atoms and that particles emitted by the photoelectric effect have the same charge to mass ratio as cathode rays.

1902 Lord Kelvin suggests that the positive electricity in an atom is spread in a diffuse, homogeneous manner through out the entire spherical volume. The negative electrons, which are individual particles are embedded in this positive electricity, which is seen as a jelly-like material. The amount of positive electricity is enough to counterbalance the negative, making the atom neutral in charge.



1903-1904 Thomson investigates this model more closely and makes a series of calculations concerning its stability. It comes to be known as the Thomson model. Note, however, that no experiment gave rise to this model, it arose out of a need to satisfy mechanical and electrical stability. It was quickly seen that an analysis of the scattering of alpha particles by a thin piece of metal could serve to test the model for accuracy. Please note also that the sphere of positive charges are not protons. The electrons are seen as hard objects embedded in this cloud of positive charge. Lenard suggests that the positive and negative charges are grouped in pairs.

1904 “Kinetics of a System of Particles Illustrating the Line and Band Spectrum and the Phenomena of Radioactivity” by Hantaro Nagaoka includes his “Saturnian model” of the atom, in which a positive nucleus is surrounded by a ring of thousands of electrons. This model was rejected by Thomson when it was shown to be unstable. Thomson’s “On the Structure of the Atom” proposes the “plum-pudding model” of the atom in which the electrons are embedded in a sphere of diffused positive charge. (The series of publications by Thomson’s group expounding on the model extended over the period 1903-1904)

1906 Ernest Rutherford studies scattering of alpha particles as they pass through mica. Later he uses gold foil. Scattering is a classic technique that is still used in science today. Arthur Compton uses the scattering of electrons and high energy radiation in the 1920s and Robert Hofstadter uses it in the 1950s to study the fine structure of the nuclei and nucleons. J.J. Thomson is awarded the Nobel Prize.

1907 Hans Geiger begins a program of research on the scattering of alpha particles as they pass through thin metal foils. Alpha particle scattering had been discovered in 1903 by Rutherford and had initially been seen as a problem plaguing his research, so Geiger's measurements would help to remove its influence in calculations.

1908 Geiger reports that the number of scattered particles decreases rapidly with increased scattering angle and that no alpha particles were observed to be scattered by more than a few degrees. Charles G. Barkla discovers that each element has a characteristic X-ray, produced by scattering of X-ray beams; this is the key discovery that eventually leads to the concept of atomic number.

1909 Ernest Marsden, under the direction of Geiger and Rutherford, determines that some alpha particles bounce back from a thin gold foil. Many years later Rutherford recalls the events:

> One day, Geiger came to me and said, “Don't you think that young Marsden, whom I am training in radioactive methods, ought to begin a small research?” Now I had thought that too, so I said, “Why not let him see if any alpha particles can be scattered through a large angle?” I may tell you in confidence that I did not believe that there would be, since we knew that the alpha particle was a very fast massive particle, with a great deal of energy, and you could show that if the scattering was due to the accumulated effect of a number of small scatterings the chance of an alpha particle being scattered backwards was very small. Then I remember two or three days later Geiger coming to me in great excitement and saying, “We have been able to get some of the alpha particles coming backwards…” It was quite the most incredible event that has ever happened to me in my life. It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you.

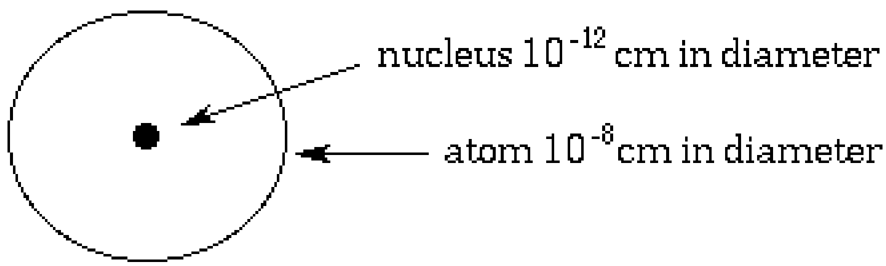
Geiger found that the most probable scattering angle is 0.87 degrees, but about 1 alpha particle in 8,000 is scattered through an angle greater than 90 degrees. This result is not in accord with Thomson’s model of 1904. As the alpha particle approached the center of the atom, it would be in a region of average zero electric charge and could not be deflected. The same would apply if it went too far from the center.

1911 Rutherford, presents his theory of the atom, consisting of a charged, small, dense nucleus, to the Manchester Literary and Philsophical society on March 7. Hans Geiger recalled many years later how he found out Rutherford's theory:

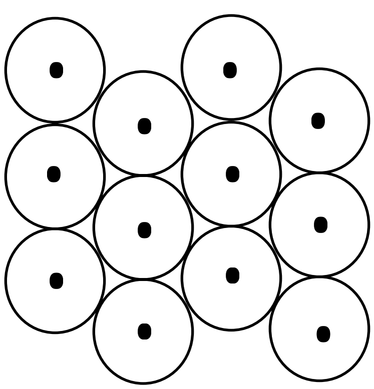
"...one day, Rutherford, obviously in the best of spirits, came into my room and told me that he now knew what the atom looked like and how to explain the large deflections of alpha particles."

Only an abstract of that early March talk survives, but later in the year he published a long article explaining his ideas. Interestingly, the alpha particle deflections observed would have been the same if the nucleus had been either positively of negatively charged. In fact, Rutherford wrote, "The main deductions from the theory are independent of whether the central charge is supposed to be positive or negative." He finally used the velocities of alpha particle emission by radioactive elements to eliminate the negative charge. (Replication of the Rutherford experiment in a world of antimatter would yield the same results found in our world of matter.) One problem of the model had to do with the orbiting electrons. James Clerk Maxwell had shown that moving electric charges (i.e. electrons in this case) give off energy and should spiral into the nucleus. They do not. Hence, how to explain this. Geiger and Marsden start a program of carefully measuring the fraction of alpha particles scattered by various angles. In 1913 they report that their experimental results are in good agreement with Rutherford's calculations. Thus they establish that Rutherford's picture of an atomic nucleus surrounded by electrons is correct. Rutherford also concludes that nuclear charge is about half the atomic weight. Charles Barkla reaches the same conclusion from x-ray scattering experiments.

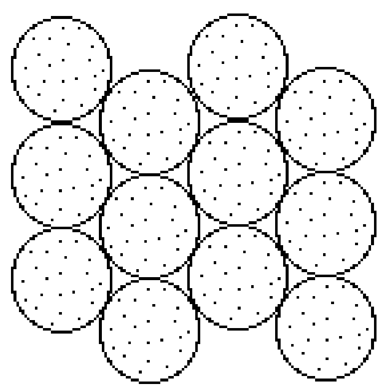
The Rutherford Model



Rutherford's Model of a thin gold foil might look like this:



Thomson's Model might be pictured this way



The nucleus dots are way, way out of scale (as in way, way too big) in the Rutherford Model. The nucleus was so tiny (10^{-12} cm in diameter), that the atom (10^{-8} cm in diameter) was 99.99% empty space.

In the Rutherford Model, the alpha particles mostly went through empty space, but once in a while one came close to the nucleus (Rutheford's "charge concentration") and was deflected strongly (more than 90°). The Thomson Model has no such possibility because the charges were equally spread throughout the atom.

1912 Neils Bohr visits Rutherford and seizes on the problem of explaining the behavior of the electrons in their orbits around the nucleus. He also identifies atomic number (up to this time simply the numerical order of the elements in the periodic table) with the nuclear charge.

1913 Antonius van der Broeck, notes that atomic mass and the number of electrons in an atom are independent. He also suggests, independent of Bohr, that the nuclear charge is exactly equal to the “atomic number” used to order the elements in the periodic table. Bohr publishes a formula which gives the length of the radiation (usually X-rays) given off when an electron enters one of the innermost orbits of the atom in terms of the electrical charge on the nucleus. Henry Gwyn-Jeffries Moseley, deduces the place of elements in the periodic table from their X-ray spectra and formulates his law of numbers of electrons; an element has the same number of electrons as its atomic number. Before this time, the elements had been put in order (with a few exceptions) by increasing atomic mass. Moseley comfirms Bohr’s prediction and associates this order with an increase in the nuclear charge that increases in whole number multiples of the electron charge. (The only difference being the nuclear charge is positive and the charge on the electron negative.)

1913 Rutherford, from continued scattering experiments, concludes that “the hydrogen atom has the simplest possible structure of a nucleus with one unit charge.”

1914 Robert A. Millikan measures the charge on the electron directly. His work shows that the electric charge always comes in integer multiples of 1.592×10^{-19} coulomb. This is less than 1% from the currently accepted value of $1.60217733(49) \times 10^{-19}$ coulomb. The 49 refers to the plus/minus error in the last two digits (the 33).

1915 Moseley is killed in battle.

1919 Rutherford carries out the first artifical nuclear reaction. In the decay products are nuclei of hydrogen (what we now call protons). He recognizes this particle as being truly elementary, on a par with the electron.

1920 Rutherford proposes the name “proton” for the fundamental particle which makes up the hydrogen nucleus. The word proton had been used from about 1908 as a general term for a building block from which all elements are built. He also proposes the existence of the neutron, an uncharged particle that is part of the nucleus. He sees it as a combination of an electron and a proton. He says, “... it may be possible for an electron to combine much more closely with the H nucleus, forming a kind of nuclear doublet. Such an atom would have very novel properties.” Today we see it as a particle in and of itself, not a combination (although, see quarks). He also proposed the name proton for the nucleus of the hydrogen atom. Interestingly, he also proposes the existence of a hydrogen isotope with mass two. Today it is called deuterium.

1921 William Draper Harkins introduces the term neutron: “... a term representing one negative electron and one hydrogen nucleus.”

1932 James Chadwick discovers the neutron. Harold Urey discovers deuterium.

1950 - 1957 Robert Hofstadter uses the scattering of electrons by the nucleus to study the detailed structure of the nucleus, protons, and neutrons.

1964 Richard Feynman and George Zweig independently propose the parton model for the structure of protons and neutrons. Partons come to be known as quarks.

And study continues to this day.