Fundamentals of Electric Theory and Circuits

by

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Determining the Atomic Number and Avogadro's Number

Number references (superscript) are listed at the end of the article.

How did scientists determine the number of conduction band electrons in a metal ? In a semiconductor or in doped silicon ? It would be impossible to count these manually !

Scientists could in an era, when the atomic structure was unknown, by studying the properties of elements and using their imagination, conceive a table, the Periodic Table. It was first made by assigning to Hydrogen, the atomic mass of '1'.

The discovery of "elements" (they were not known as pure substances initially) goes back thousands of years and began with Copper which was probably the first metal mined and crafted by humans. It was originally obtained as a native metal and later from the smelting of ores. Earliest estimates of the discovery of copper suggest around 9000 BCE in the Middle East. Those were the times when substances were considered to be metals, salts and acids.

The idea of *element*, which cannot be separated into a simpler substance, occurred in the 19th century (1799 to 1900).

The first scientific discovery of an element (though that was not the term used then) occurred in 1649 when Hennig Brand discovered phosphorous[1].

Lavoisier (1743 – 1794), together with other scientists submitted a program for the reforms of chemical nomenclature to the French Academy of Sciences in 1787. The Classical elements of earth, air, fire, and water (earlier listed by scientists) were discarded, and instead some 55 substances which could not be decomposed into simpler substances by any known chemical means were provisionally listed as *elements*. The elements included light; calorie (matter of heat); the principles of oxygen, hydrogen, and azote (nitrogen); carbon; sulfur; phosphorus; the yet unknown "radicals" of muriatic acid (hydrochloric acid), boric acid, and "fluoric" acid; 17 metals; 5 earths (mainly oxides of yet unknown metals such as magnesia, barite, and strontia); three alkalies (potash, soda, and ammonia); and the "radicals" of 19 organic acids[2].

The structure of the atom was not known then.

By 1869, a total of 63 elements had been discovered. As the number of known elements grew, scientists began to recognize patterns in their properties and began to develop classification schemes.

Most of the literature related to the discovery of elements in the period and the development of the periodic table by Dmitri Mendeleev (1834-1907) before 1911 (when the Rutherford-Bohr model for the atom was proposed), refers to the *properties* of the elements without references to atomic structure and atomic number.

This article makes an attempt to trace the experimental work of scientists (physicists and chemists) when they were formalizing the structure of the periodic table and how their thinking led to linking the table with the atomic structure of elements.

Avogadro's number was initially defined by Jean Baptiste Perrin (1870 – 1942) around 1909 as the number of atoms in one gram-molecule of atomic hydrogen, meaning one gram of hydrogen. A derivation made by Loschmidt to estimate the number of particles in one cubic centimeter of gas at standard conditions is followed by a brief on Millikan's experiment which enabled scientists to fix the value of Avogadro's number more accurately.

Later in this article we will answer the questions:

What's the difference between mass number and atomic weight?
Can atomic mass and atomic weight ever be the same?
Why is the atomic mass of an element a decimal number?

Atomic Number

Henry Moseley finds a link to atomic number

By 1907, when Mendeleev (1834-1907) died, chemists were sure that iodine followed tellurium in the Periodic Table and that there was something odd about their relative atomic masses[3].

However no one was able to *measure* atomic number; it was just the position of an element in the Periodic Table sequence. For example lithium was known to be the third element but this number three was only because its properties meant that it slotted in between helium and beryllium.

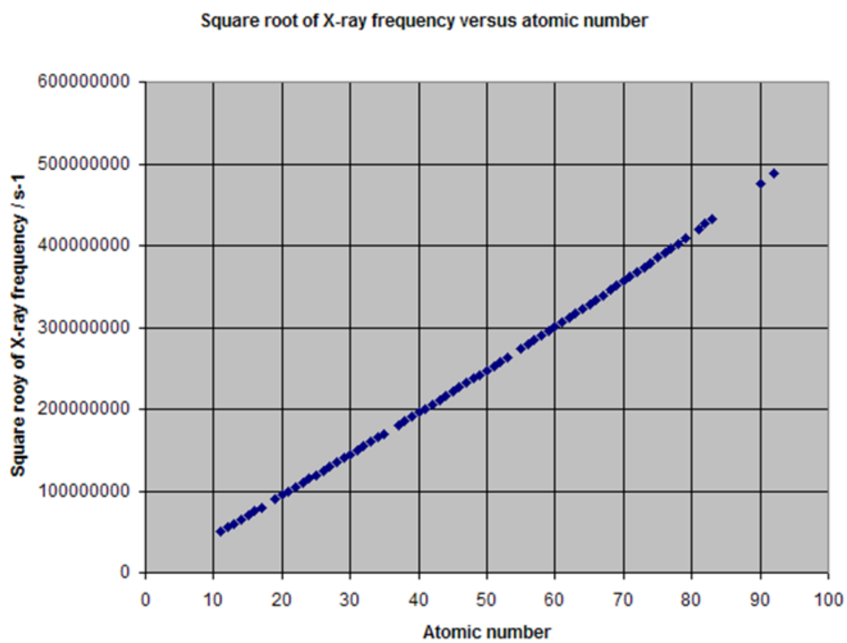
Henry Moseley (1887 – 1915) found and measured a property linked to Periodic Table position.

Henry Moseley

Since then the atomic number became more meaningful and the three pairs of elements that seemed to be in the wrong order could be explained.

Moseley used what was then brand-new technology in his experiments. A device now called an electron gun had just been developed. He used this to fire a stream of electrons (like machine gun bullets) at samples of different elements[4]. He found that the elements gave off X-rays. (This is how the X-rays used in hospitals are produced.)

Moseley measured the frequency of the X-rays given off by different elements. Each element gave a different frequency and he found that this frequency was mathematically related to the position of the element in the Periodic Table, and in a sense, he could actually measure atomic number.



You can see that the graph relating frequency to atomic number is a very good straight line while that relating frequency to relative atomic mass is not so good (not shown here but available in the link[5]).

The relationship is actually quite complicated. In fact Moseley plotted the *square root* of the X-ray frequency against atomic number, but do not let this detail obscure how important this result was.

Notice that there are some gaps in the graph where X-ray data are missing – there were more of these in Moseley's time. Some of them were because it was not easy to fire an electron beam at some elements. Others were because there were still several elements undiscovered when Moseley made his measurements in 1913.

Activity 1

Suggest what sort of elements it might not be easy to fire a beam of electrons at. These would be the elements for which X-ray data was missing.

Activity 2

Use the **After** function of the **interactive Periodic Table** to find out how many elements that are now known were undiscovered in 1913.

The periodic table and a natural number for each element

Russian chemist Dmitri Mendeleev (shown in the photograph) created a periodic table of the elements that ordered them numerically by atomic weight, yet occasionally used chemical properties in contradiction to weight[6].

Loosely speaking, the existence or construction of a periodic table of elements creates an ordering of the elements, and so they can be numbered in order.

Dmitri Mendeleev claimed that he arranged his first periodic tables in order of atomic weight ("Atomgewicht"). However, in consideration of the elements' observed chemical properties, he changed the order slightly and placed tellurium (atomic weight 127.6) ahead of iodine (atomic weight 126.9). This placement is consistent with the modern practice of ordering the elements by proton number, *Z*, but that number was not known or suspected at the time.

A simple numbering based on periodic table position was never entirely satisfactory, however. Besides the case of iodine and tellurium, later several other pairs of elements (such as argon and potassium, cobalt and nickel) were known to have nearly identical or reversed atomic weights, thus requiring their placement in the periodic table to be determined by their chemical properties.

However the gradual identification of more and more chemically similar lanthanide elements, whose atomic number was not obvious, led to inconsistency and uncertainty in the periodic numbering of elements at least from lutetium (element 71) onwards (hafnium was not known at this time).

New elements

After becoming a teacher in 1867, Mendeleev wrote the definitive textbook of his time: *Principles of Chemistry* (two volumes, 1868–1870). It was written as he was preparing a textbook for his course[7]. This is when he made his most important discovery.

As he attempted to classify the elements according to their chemical properties, he noticed patterns that led him to postulate his periodic table; he claimed to have envisioned the complete arrangement of the elements in a dream:

"I saw in a dream a table where all elements fell into place as required. Awakening, I immediately wrote it down on a piece of paper, only in one place did a correction later seem necessary."— *Mendeleev, as quoted by Inostrantzev*.

Unaware of the earlier work on periodic tables going on in the 1860s, he made the following table:

Cl 35.5	K 39	Ca 40
Br 80	Rb 85	Sr 88
I 127	Cs 133	Ba 137

By adding additional elements following this pattern, Dmitri developed his extended version of the periodic table.

On 6 March 1869, Mendeleev made a formal presentation to the Russian Chemical Society, titled *The Dependence between the Properties of the Atomic Weights of the Elements*, which described elements according to both atomic weight and valence. This presentation stated that

1. The elements, if arranged according to their atomic weight, exhibit an apparent periodicity of properties.
2. Elements which are similar regarding their chemical properties either have similar atomic weights (e.g., Pt, Ir, Os) or have their atomic weights increasing regularly (e.g., K, Rb, Cs).
3. The arrangement of the elements in groups of elements in the order of their atomic weights corresponds to their so-called valencies, as well as, to some extent, to their

distinctive chemical properties; as is apparent among other series in that of Li, Be, B, C, N, O, and F.

4. The elements which are the most widely diffused have small atomic weights.
5. The magnitude of the atomic weight determines the character of the element, just as the magnitude of the molecule determines the character of a compound body.
6. We must expect the discovery of many yet unknown elements–for example, two elements, analogous to aluminum and silicon, whose atomic weights would be between 65 and 75.
7. The atomic weight of an element may sometimes be amended by knowledge of those of its contiguous elements. Thus the atomic weight of tellurium must lie between 123 and 126, and cannot be 128. *(Tellurium's atomic mass is 127.6, and Mendeleev was incorrect in his assumption that atomic mass must increase with position within a period.*)
8. Certain characteristic properties of elements can be foretold from their atomic weights.

The Rutherford-Bohr model and van den Broek

In 1911, Ernest Rutherford gave a model of the atom in which a central core held most of the atom's mass and a positive charge, which in units of the electron's charge, was to be approximately equal to half of the atom's atomic weight, expressed in numbers of hydrogen atoms (atomic structure now known as comprising 1 electron, 1 proton and 0 neutrons). This central charge would thus be approximately half the atomic weight (though it was almost 25% different from the atomic number of gold (Z = 79, A = 197), the single element from which Rutherford made his guess)[6].

Nevertheless, in spite of Rutherford's estimation that gold had a central charge of about 100 (but was proton number Z = 79 on the periodic table), a month after Rutherford's paper appeared, Antonius van den Broek first formally suggested that the central charge and number of electrons in an atom was *exactly* equal to its place in the periodic table (also known as element number, atomic number, and symbolized Z). This proved eventually to be the case.

Moseley's 1913 experiment – first experiment to determine the Atomic Number

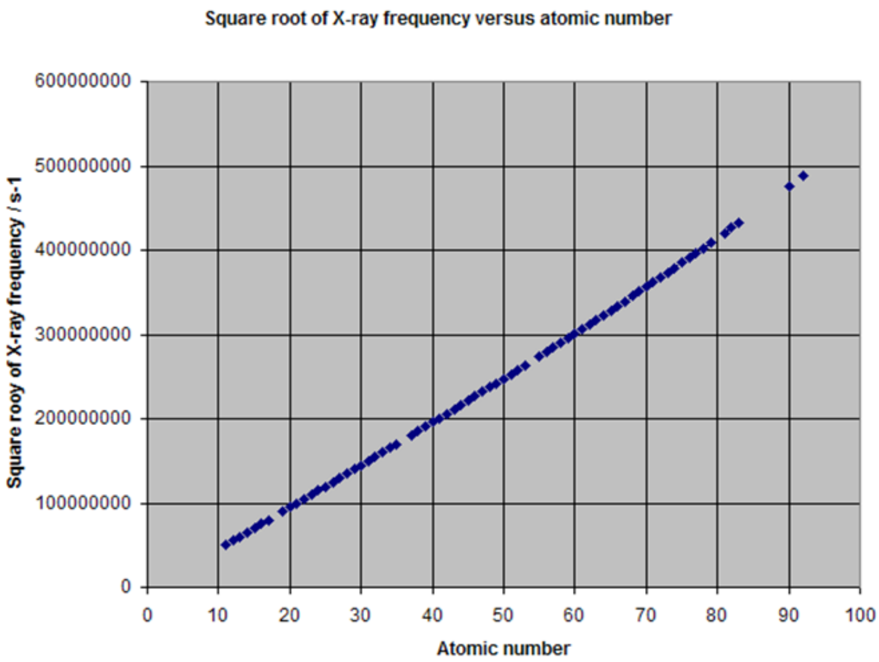
The experimental position improved dramatically after research by Henry Moseley in 1913. Moseley, after discussions with Bohr who was at the same lab (and who had used Van den Broek's hypothesis in his Bohr model of the atom), decided to test Van den Broek's and Bohr's hypothesis directly, by seeing if spectral lines emitted from excited atoms fitted the Bohr theory's postulation that the frequency of the spectral lines be proportional to the square of (proton or element number) Z.

Neils Bohr

Antonius Van Den Broek

To do this, Moseley measured the wavelengths of the innermost photon transitions (K and L lines) produced by the elements from aluminum ($Z = 13$) to gold ($Z = 79$) used as a series of movable anodic targets inside an x-ray tube.

The square root of the frequency of these photons (x-rays) increased from one target to the next in an arithmetic progression, as plotted in the graph[5].



This led to the conclusion (Moseley's law) that the atomic number does closely correspond (with an offset of one unit for K-lines, in Moseley's work[8]) to the calculated electric charge of the nucleus, i.e. the element number *Z*.

Among other things, Moseley demonstrated that the lanthanide series (from lanthanum to lutetium inclusive) must have 15 members - no fewer and no more - which was far from obvious from the chemistry at that time.

Missing elements

After Moseley's death in 1915, the atomic numbers[6] of all known elements from hydrogen to uranium ($Z = 92$) were examined by his method. There were seven elements (with $Z < 92$) which were not found and therefore identified as still undiscovered, corresponding to atomic numbers 43, 61, 72, 75, 85, 87 and 91.

From 1918 to 1947, all seven of these missing elements were discovered. By this time the first four transuranium elements had also been discovered, so that the periodic table was complete with no gaps as far as curium ($Z = 96$).

The proton and the idea of nuclear electrons

In 1915 the reason[6] for nuclear charge being quantized in units of (proton number or element number) Z, which were now recognized to be the same as the element number, was not understood. An old idea called Prout's hypothesis had postulated that the elements were all made of residues (or "protyles") of the lightest element hydrogen, which in the Bohr-Rutherford model had a single electron and a nuclear charge of one.

However, as early as 1907 Rutherford and Thomas Royds had shown that alpha particles, which had a charge of +2, were the nuclei of helium atoms (atomic structure of helium-4 now known as comprising 2 electrons, 2 protons and 2 neutrons and is most abundantly found in nature), which had a mass four times that of hydrogen, not two times. If Prout's hypothesis were true, something had to be neutralizing some of the charge of the hydrogen nuclei present in the nuclei of heavier atoms.

In 1917 Rutherford succeeded in generating hydrogen nuclei from a nuclear reaction between alpha particles and nitrogen gas, and believed he had proven Prout's law. He called the new heavy nuclear particles “protons” in 1920 (alternate names being proutons and protyles).

It had been immediately apparent from the work of Moseley that the nuclei of heavy atoms have more than twice as much mass as would be expected from their being made of hydrogen nuclei, and thus there was required a hypothesis for the neutralization of the extra protons presumed present in all heavy nuclei.

A helium nucleus was presumed to be composed of four protons plus two "nuclear electrons" (electrons bound inside the nucleus) to cancel two of the charges. At the other end of the periodic table, a nucleus of gold (atomic structure now known as comprising 79 electrons, 79 protons and 118 neutrons) with a mass 197 times that of hydrogen, was thought to contain 118 nuclear electrons in the nucleus to give it a residual charge of + 79, consistent with its atomic number.

The discovery of the neutron makes *Z* the proton number - (Birth of term “neutron”)

All consideration of nuclear electrons ended with James Chadwick's discovery of the neutron in 1932. An atom of gold now was seen as containing 118 neutrons rather than 118 nuclear electrons, and its positive charge now was realized to come entirely from a content of 79 protons.

After 1932, therefore, an element's atomic number *Z* was also realized to be identical to the proton number of its nuclei.

The symbol of Z

The conventional symbol *Z* possibly[6] comes from the German word *Atomzahl* (atomic number). However, prior to 1915, the word *Zahl* (simply *number*) was used for an element's assigned number in the periodic table.

Chemical properties

Each element has a specific set of chemical properties as a consequence of the number of electrons present in the neutral atom, which is *Z* (the atomic number). The configuration of these electrons follows from the principles of quantum mechanics.

The number of electrons in each element's electron shells, particularly the outermost valence shell, is the primary factor in determining its chemical bonding behavior.

Hence, it is the atomic number alone that determines the chemical properties of an element; and it is for this reason that an element can be defined as consisting of *any* mixture of atoms with a given atomic number.

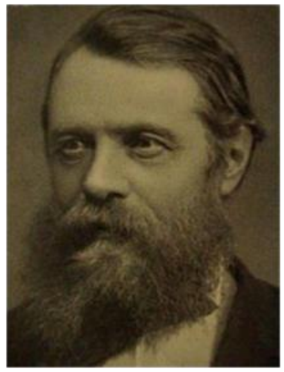
How was Avogadro's number determined?

Chemist George M. Bodner of Purdue University explains[9].

Contrary to the beliefs of generations of chemistry students, Avogadro’s number--the number of particles in a unit known as a mole--was not discovered by Amadeo Avogadro (1776-1856).

Avogadro was a lawyer who became interested in mathematics and physics, and in 1820 he became the first professor of physics in Italy. Avogadro is most famous for his hypothesis that equal volumes of different gases at the same temperature and pressure contain the same number of particles.

The first person to estimate the *actual number of particles* in a given amount of a substance was Josef Loschmidt (1821 - 1895), an Austrian high school teacher who later became a professor at the University of Vienna. In 1865 Loschmidt used *kinetic molecular theory* to estimate the number of particles in one cubic centimeter of gas at standard conditions.



Josef Loschmidt

Making the macro/micro connections in gases

The history of making a connection between the microscopic attributes of the atoms and molecules that makes up gases, their velocities and forces, to the observed macroscopic behavior of gases, especially pressure and volume they occupy makes very interesting reading.

In 1857, Rudolf Clausius[10] introduced the concept of mean free path of a particle. In 1859, after reading a paper on the diffusion of molecules by Rudolf Clausius, Scottish physicist James Clerk Maxwell formulated the Maxwell distribution of molecular velocities, which gave the proportion of molecules having a certain velocity in a specific range. This was the *first-ever statistical law* in physics. Maxwell also gave the first mechanical argument that molecular collisions entail an equalization of temperatures and hence a tendency towards equilibrium.

In 1873 Maxwell wrote, "we are told that an 'atom' is a material point, invested and surrounded by 'potential forces' and that when 'flying molecules' strike against a solid body in constant succession it causes what is called pressure of air and other gases."

In a lecture in 1873, eight years after Loschmidt in 1865 derived the result, Maxwell said,

“Loschmidt has deduced from the dynamical theory the following remarkable proportion:—As the volume of a gas is to the combined volume of all the molecules contained in it, so is the mean path of a molecule to one-eighth of the diameter of a molecule”[11].

All the molecules were assumed to be spherical in Loschmidt’s derivation. We briefly describe it.

To derive this "remarkable proportion", Loschmidt started from Maxwell's own definition of the mean free path:

$$l = \frac{3}{4n_o \pi d^2}$$

where n_o has the same sense as the Loschmidt constant, that is the number of molecules per unit volume, and d is the effective diameter of the molecules (assumed to be spherical). This rearranges to

$$\frac{1}{n_o} = \frac{16}{3}\frac{\pi l d^2}{4}$$

where $1/n_o$ is the volume occupied by each molecule in the gas phase and $\pi l d^2/4$ is the volume of the cylinder made by the molecule in its trajectory between two collisions. However, the true volume of each molecule is given by $\pi d^3/6$, and so $n_o \pi d^3/6$ is the volume occupied by all the molecules not counting the empty space between them.

To obtain a feel for the mean free path of air molecules, we give a few estimated values: at ambient pressure, it is roughly 68 nanometer (68×10^{-9}m) and increases in high vacuum to roughly a range of 10 cm to 1 kilometer ! A hydrogen molecule at room temperature has a mean velocity of about 9000 km/hr which is quite large[12] and a molecule of dry air about 1600 km/hr.

Loschmidt equated this volume with the volume of the liquified gas. Dividing both sides of the equation by $n_0 \pi d^3/6$ has the effect of introducing a factor of $V_{\text{liquid}}/V_{\text{gas}}$, which Loschmidt called the "condensation coefficient" and which is experimentally measurable. The equation reduces to:

$$d = 8\frac{V_{liquid}}{V_{gas}} l$$

relating the diameter of a gas molecule to measurable phenomena.

The number density, the constant which now bears Loschmidt's name, can be found by simply substituting the diameter of the molecule into the definition of the mean free path and rearranging:

$$n_o = \left(\frac{V_{liquid}}{V_{gas}}\right)^2 \frac{3}{256\pi l^3}$$

However, Loschmidt decided to estimate the mean diameter of the molecules in air, a very difficult task at the time, because the condensation coefficient was unknown and had to be estimated. The mean free path was also uncertain. Nevertheless, Loschmidt arrived at a diameter within one nanometer of the correct order of magnitude. He estimated the diameter of an air molecule to be 0.000000969 mm or in round numbers one millionth of a millimeter for the diameter of an air molecule[13].

Loschmidt's estimated data for air gives a value of $n_o = 1.81\times10^{24}$ m^{-3}. Eight years later, Maxwell was citing a figure of "about 19 million million million" per cm^3, or 1.9×10^{25} m^{-3}.

Loschmidt's derivations laid the foundation for deriving the number of atoms or molecules that are contained in the amount of substance given by *one mole*, a requirement of physicists and chemists.

Relating the number of atoms to one mole of a substance

Avogadro's number was initially defined by Jean Baptiste Perrin as the number of atoms in one gram-molecule of atomic hydrogen, meaning one gram of hydrogen. For instance, to a first approximation, 1 gram of hydrogen element (H), having the atomic number 1, has 6.022×10^{23} hydrogen atoms. The atomic mass is the total number of protons and neutrons in an atomic nucleus.

The number density n_o of particles in an ideal gas, the Loschmidt constant is related to the Avogadro constant, N_A, or Avogadro number by[14]

$$n_o = \frac{p_o N_A}{R T_o}$$

where p_0 is the pressure, R is the gas constant and T_o is the absolute temperature.

Amadeo Avogadro

The Avogadro constant was later *redefined* as the number of atoms in 12 grams of the isotope carbon-12, and still later generalized to relate amounts of a substance to their molecular weight. Similarly, 12 grams of Carbon, with the mass number 12 (atomic number 6), has the same number of carbon atoms, 6.022×10^{23}, the Avogadro's number. Older standards refer to Oxygen (isotope O-16) but this was a difficult substance to obtain in pure form and difficult to weigh also. Therefore, carbon – 12 (isotope 12) became the preferred choice being easier to obtain and weigh. And, its mass number is a whole number, 12.

Definition The unit *mole* is defined as the amount of a chemical substance that contains as many representative particles, e.g., atoms, molecules, ions, electrons, or photons, as there are atoms in 12 grams of carbon-12 (^{12}C), the isotope of carbon with standard atomic weight 12 by definition.

This number is expressed by the Avogadro constant or Avogadro's number, which has a value of approximately 6.022140857×10^{23} mol^{-1}.

The reader should note carefully that 12 grams (the molar mass of Carbon-12) of a sample of Carbon-12 contains as many (Avogadro's number) *atoms* as would one gram of Hydrogen (the molar mass of Hydrogen). There are as many (Avogadro's number) *large and heavier* atoms of Carbon – 12 in 12 grams of Carbon-12 as there are in 1 gram of the *tinier and lighter* Hydrogen.

This is how the periodic table links the Avogadro's number of atoms with their atomic mass.

More accurate determinations of Avogadro's number require the measurement of a single quantity on both the atomic and macroscopic scales using the same unit of measurement. This became possible for the first time when American physicist Robert Millikan measured the charge on an electron. The charge on a mole of electrons had been known for some time and is the constant called the Faraday[15]. The best estimate of the value of a Faraday, according to the National Institute of Standards and Technology (NIST), is 96,485.3383 coulombs per mole of electrons. Millikan's experiment is described at the end of this article.

The best estimate of the charge on an electron based on modern experiments is $1.60217653 \times 10^{-19}$ coulombs per electron. If you divide the charge on a mole of electrons by the charge on a single electron you obtain a value of Avogadro's number of $6.02214154 \times 10^{23}$ particles per mole.

Another approach to determining Avogadro's number starts with careful measurements of the density of an ultrapure sample of a material on the macroscopic scale. The density of this material on the atomic scale is then measured by using x-ray diffraction techniques to determine the number of atoms per unit cell in the crystal and the distance between the equivalent points that define the unit cell (see *Physical Review Letters*, 1974, 33, 464).

What's the Difference between Mass Number and Atomic Weight ?

Atomic mass (m_a) is the mass of an atom. A single atom has a set number of protons and neutrons, so the mass is unequivocal (won't change) and is the sum of the number of protons and neutrons in the atom. Electrons contribute so little mass that they aren't counted[16].

Atomic weight is a weighted average of the mass of all the atoms of an element, based on the *abundance* of isotopes. The atomic weight *can change* because it depends on our understanding of how much of each isotope of an element exists. Both atomic mass and atomic weight rely on the atomic mass unit (amu), which is 1/12th the mass of an atom of carbon-12 in its ground state.

Can atomic mass and atomic weight ever be the same ?

If you find an element that exists as only one isotope, then the atomic mass and the atomic weight will be the same. Atomic mass and atomic weight may equal each other whenever you are working with a single isotope of an element, too.

Why is the atomic mass of an element a decimal number ?

Isotopes are atoms of an element with the same number of protons but a different number of neutrons.

The atomic mass of an element is the number of protons plus the number of neutrons.

However if different versions of the atom have different numbers of neutrons then the atomic masses will be different for each.

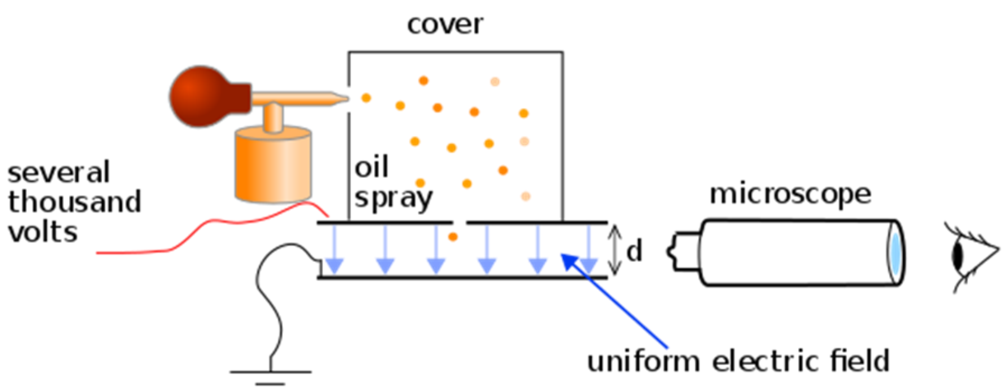
So the atomic mass on a periodic table can be a decimal because it is the *weighted* average mass of the isotopes (in comparison to 1/12 of carbon-12).

Also, watch this video for a nice explanation https://www.youtube.com/watch?v=_jmKgdi3jjQ

Millikan's Oil Drop Experiment to determine the charge of an electron

The experiment[17] (performed by Millikan and whose results were published in 1913) entailed observing tiny electrically charged droplets of oil located between two parallel metal surfaces, forming the plates of a capacitor.

The plates were horizontally orientated with one plate above the other. A mist of atomized oil drops was introduced through a small hole in the top plate. First, with zero applied electric field, the velocity of a falling droplet was measured.



At terminal velocity (see the topic "Working Definition of Current" in Section 1.18, Chapter 1 in the book for a description of terminal velocity), the drag force equals the gravitational force. As both forces depend on the radius in different ways, the radius of the droplet, and therefore the mass and gravitational force, could be determined (using the known density of the oil). Then, a voltage, inducing an electric field, was applied between the plates and adjusted until the drops were suspended in mechanical equilibrium, indicating that the electrical force and the gravitational force were in balance. Using the known electric field, Millikan and Fletcher could determine the charge on the oil droplet.

By repeating the experiment for many droplets, they confirmed that the charges were all *small integer multiples* of a certain base value (a droplet may hold more than a single electron), which was found to be $1.5924(17)\times10^{-19}$ C, about 0.6% difference from the currently accepted value of $1.602176487(40)\times10^{-19}$ C.

They proposed that this was the positive version of the negative charge of a single electron.

In the paper[18] "On the elementary electrical charge and the Avogadro Constant" published in 1913, Millikan has described the experiment in detail and presents the calculations which led to the determination of the charge on an electron to be (see last page of the paper) 4.774×10^{-10} electrostatic unit (esu in cgs-esu system) which converts to 1.592415×10^{-19} Coulombs (SI).

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