'I don't know how far away the moon lies, but here is how I rediscovered Avogadro's constant'

$N_A = 6.02214199 \times 10^{23}\ mol^{-1}$

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Kelvin Science Prize

March 2017

Avogadro's number is a dimensionless quantity, first defined by Jean Baptiste Perrin as the number of atoms in one gram-molecule of atomic hydrogen. This means for example, that if you took a 1 gram mass of the element hydrogen and measured the number of hydrogen atoms within the element, the number of atoms would be Avogadro's number- approximately $6.022*10^{23}$. Perrin's definition was later revised to be the number of atoms in 12 grams of the isotope carbon-12, which is effectively the same definition; both relate amounts of a substance to the molecular weight of the same substance.

To understand the magnitude of Avogadro's constant, imagine that if each water molecule was the size of a grain of sand (with a volume of $1mm^3$), then one mole of water would cover the UK with a layer a few kilometres thick. It is believed that there are more water molecules in a glass of orange juice than there are stars in the universe.

A method of finding the number of atoms in an element, and hence an ability to calculate the relative atomic masses of the elements, is fundamental to almost every chemical experiment. Avogadro's number is used as the scaling factor between macroscopic and microscopic observations of nature, which gives chemists the ability to fully comprehend the behaviour of atoms. The discovery in 1909 of an accurate number was a monumental breakthrough in science, the result of many very ingenious and thorough experiments by several talented physicians and chemists.[1]

For this essay prize I will be recreating some of these experiments with the goal of being able to calculate the number, which is now seen universally as one of the most important constants in science, in a similar way to the methods used by the scientists 100s of years ago.

I will be providing an account of the historical development of Avogadro's hypothesis, and of the foremost methods of determining Avogadro's constant which have been used over the past 400 years. These include the kinetic theory of gases, Brownian motion, measurement of the electron charge, and X-ray measurements.

The original scientist to suggest that matter constituted of minute components (atoms) was the Greek philosopher Democritus. He came to the conclusion that the universe consisted of two elements: 'the atoms and the void in which they existed and moved', and his hypothesis stated that atoms cannot be destroyed, differ in size or stop moving.

However, the first person to write about the number and size of atoms, with experimental proof, was Johann Magnenus, a German monk, whose research provided the first comprehensive alternative to Aristotelian science. In the book Democritus Reviviscens, published in 1646, he describes an experiment in which he studied the diffusion of incense in a church, which is seen as the very first attempt to calculate Avogadro's number. He obtained a number that we would consider an acceptable estimation, yet not accurate enough for his achievement to be widely known. We can cite him here literally:

'fuissent in hoc thuris grano, pisi magnitudinem non superante, atomi elementales ad minimum 777 600 000 000 000 000, ex quibus patet quantae sit parvitatis atomus una, concjicique potest, quantus sit atomorum numerus in toto universo'

[1] A.Avogadro, J de Phys., 1811,73,58

The English translation of this is: 'In this piece of incense, which itself was not larger than a pea, there were at least 7.7763 x 10*17 elementary atoms. From this one can see how small an atom is and one can guess how large the number of atoms might be in the whole Universe'.[2]

It is difficult to track down precise references to much of Magneus's work because he only wrote one short book on the topic of atoms, which just so happens to be in Latin, and makes no reference to the measurements he took to calculate his results. As far as I can understand, in his experiment he burned a grain of incense at one side of an empty church, whilst he stood at the opposite end. Using the theory of his time, that atoms were invisible units, he assumed there was a single unit, or a single molecule to us, of incense in his nose when he could faintly smell it. He took this to mean that the molecules of incense had diffused around the entire church before reaching him, as he was as far away from the incense as possible. He then compared the volume of the cavity of his nose with the volume of the church-dividing one by the other- which resulted in the value which he published.

After many attempts to perform this experiment I have come to the conclusion that Magneus must have been performing his experiment in a cathedral, as no space I can find provides the dimensions needed to yield such a monumental number. He must have just been within smelling distance of the incense; I cannot get far enough away, whilst indoors, to a point where the smell of incense is faint enough to justifiably assume that only a single atom of incense has entered my nose.

In 1827 Robert Brown, a notable botanist, was studying the sexual relations of plants and looking in detail at the function of pollen. He began with a plant in which he found the pollen grains were filled with oblong granules about 5 microns long. He noticed that these granules were constantly vibrating and in motion, and came to the conclusion that this motion was not caused by currents in the fluid or evaporation. He found the same results for inanimate objects such as fossilized wood, enabling him to rule out the hypothesis that the effect was life-related. In 1905 Albert Einstein provided precise detail in a paper of how the motion that Brown had observed was a result of the pollen being moved by individual water molecules. His explanation of what is now called Brownian motion served as convincing evidence that atoms and molecules are the constituents of matter.

When Perrin learned of Einstein's 1905 predictions regarding diffusion and Brownian motion, he devised an experimental test of those relationships. His approach was simple. Using a microscope in a camera lucida setup, he could observe and record the Brownian motion of a suspended gamboge particle at a constant temperature, in a liquid with a set viscosity. The camera lucida allowed him to observe, at the same time, both the particle and its projection on a sheet of paper. Thus, Perrin and his assistant could mark the particle's position on a piece of graph paper at timed intervals. In his own words, "[We took] turns at the microscope, each dotting the granules every 30 seconds at the call of the other."

Perrins first values for Avogadro's constant was $N_A = 7.05 \times 10^{23}$, and subsequent experiments of Brownian motion by other scientists confirmed numbers in this region with an accuracy of about 1×10^{23}.

[2] J.R.Partington, A history of chemistry, vol. 3, ch.17, Macmillan, 1962

Unfortunately I was unable to secure the equipment needed to perform such experiments, so I missed out on recreating the very first experiment to accurately calculate Avogadro's constant.

One-hundred years later Amedeo Avogadro, a lawyer by trade, was making a name for himself in science. This was an era in which chemists such as John Dalton and Joseph Louis Gay-Lussac were slowly coming to terms with the properties of molecules and atoms, as well as the behavior of these particles.

Gay-Lussac's law of combining volumes particularly interested Avogadro. His law stated that when two volumes of gases react with each other, and reacted/mixed to create a third gas, the ratio between the volume of the reactants and the volume of the product is always made of simple whole numbers.

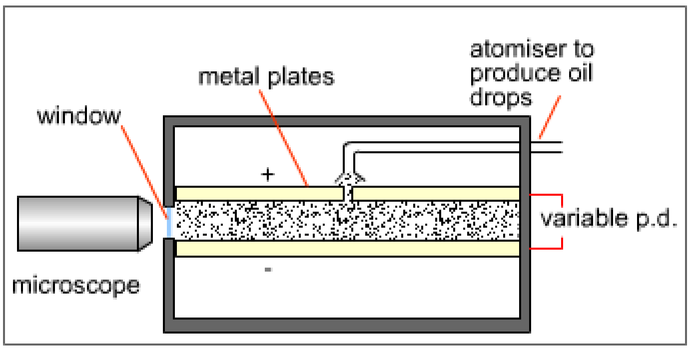
From this Avogadro made his famous hypothesis, that equal volumes of different gases at the same temperature and pressure contain the same number of particles.

However he never made a successful attempt to calculate the number of particles in a certain volume of gas. The first attempt was made by an Austrian teacher named Loschmidt in 1865, who used kinetic molecular theory to estimate the mean diameter of the molecules in air, which he achieved with surprising accuracy given that nitrogen would not be liquefied for another 12 years.

The first accurate estimate by today's standards came courtesy of physicist Robert Millikan, who measured the charge of an electron by applying a vertical electric field so that a drop becomes stationary. When this occurs, the upward force from the electric field is equal and opposite to the weight of the drop. Millikan was able to show that the total charge on a drop was always a multiple of a fundamental unit of charge, thus he worked out the charge on a single electron.

At the time when Millikan made his discovery, the charge on a single mole of electrons was already known, so Millikan simply had to divide the charge of a mole of electrons, called a Faraday, by his newly discovered charge on an electron to calculate a value for Avogadro's number.

Despite his experiment being a breakthrough in science, Millikan's experiment is fairly easy to replicate. The apparatus consists of a pair of parallel, flat, circular metal plates. The atomiser produces a fine mist of oil drops (much like an aerosol spray can) and small holes in the top plate allows the drops to enter the region between the plates. Friction during the spraying process charges the drops of oil. An electric field can be produced between the plates by connection to a variable voltage supply.



The viscosity of air, $\eta = 1.8 \times 10^{-5}$ N s m^{-2}

The density of the oil, $\rho = 800$ kg m^{-3}

Sadly the equipment I borrrowed from the physics department is fairly out of date, and as a result yeilded horrible results for the experiment. Therefore I chose to recreate the Millikan's experiment using a simulation, which not only provided better results but significantly reduced the percentage uncertainty of the experiment due to the accuracy of it's measurements.

To begin with I set the voltage between the plates to zero and measured the terminal velocity of an oil drop.

The drop took 9 seconds to fall 1mm, so its velocity is equal to $0.001 \div 9 = 1.1 \times 10^{-4}\ ms^{-1}$

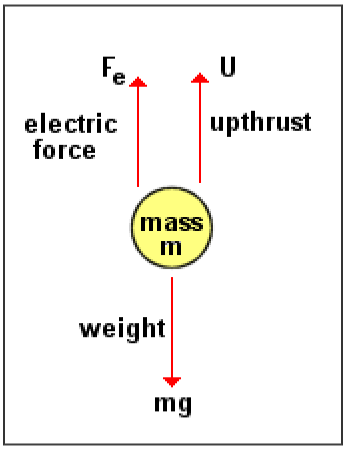
The forces acting on the drop at its terminal velocity are the weight, the upthrust (U) and the drag (F_d). Since the drop moves at a constant velocity, the resultant force is zero.

$$U + F_d = mg$$

The upthrust U = weight of air displaced by the oil drop and the drag force is given by Stokes's law:

$$\pi r^3 \sigma g + 6 \pi \eta v = \frac{3}{4} \pi r^3 \rho g^3$$

σ and ρ are the densities of air and oil respectively, r is the radius of the drop, v the terminal velocity, g the acceleration due to gravity η then viscosity of air.
The radius of the drop is too small ($\sim 10^{-3}$ mm) to measure directly, but the terminal velocity can be found by timing the drop as it falls a measured distance and hence r can be calculated.[4] My calculated value for the radius of the oil drop was 1×10^{-5} m.



Next I adjusted the voltage and found a value that held the drop stationary.

$$F_e + U = mg$$

$$.\ \pi r^3 \sigma g + EQ = \frac{4}{3}\pi r^3 \rho g$$

Where E is the electric field strength and Q the charge on the drop.

The voltage I used to halt the drop was 2.431 kV.

Subtracting Stoke's law from $\pi r^3 \sigma g + EQ = \frac{4}{3}\pi r^3 \rho g$ leaves me with

[3] https://www.britannica.com/biography/Robert-Millikan

[4] R.A.Millikan, The Electron, Univ.of Chicago

$Q =$

$$\frac{6\pi\eta r v}{E}$$

from which I can calculate the charge on a single electron. As the density of air is about 1000 times that of oil, it will not significantly affect the results of this calculation, and as a result can be discarded. The electric field strength can be found from $E = V/d$, where V is the voltage applied to the plates and d is their separation (1×10^{-2}).

$$Q = \frac{6 \times \pi \times (1.8 \times 10^{-5}) \times (1 \times 10^{-5}) \times (1.1 \times 10^{-4})}{(2.431 \times 10^{3} \div 1 \times 10^{-2})}$$

$Q = 1.688783743 \times 10^{-18}$ Coulombs

When Millikan performed this experiment for the first time, he repeated the process for several hundred different oil droplets; recording the charge on each one.[5] He realised that every single oil droplet had a charge which was a multiple of the constant $1.6021766208 \times 10^{-19}$, thereby he correctly deduced that $\approx 1.6 \times 10^{-19}$ was the charge on a single electron.

My calculated value, divided by the charge on a single electron, shows that the oil droplet I chose to perform measurements on consisted of 11 electrons.

$1.688783743 \times 10^{-18} \div 1.6 \times 10^{-19} = 11$ electrons (2 decimal places)

Armed with the newfound knowledge of the charge on an electron, Millikan was able to determine a value for the number of electrons in a mole, thus discovering the most accurate value yet for Avogadro's constant.

He took the previously calculated charge of a mole of electrons, called a Faraday (96485.33289), and divided it by his value for the charge on an electron.[6]

$96485.33289 \div 1.6021766208 \times 10^{-19} = 6.022140857 \times 10^{23}$

The value he calculated, in 1909, is outstandingly accurate - to this day we use the same number to 4 decimal places as the recognised value for Avogadro's constant. My results were not too dissimilar to that of Millikan's; all of his results were 1-12 times larger than 1.6×10^{-19}. Though I have only written up the calculations for one oil drop, I repeated the experiment several times, each time getting values in the correct range. This meant that I could deduce that than 1.6×10^{-19} was the common constant in all of my values, and was thereby able to calculate a value for Avogadro's number, just like Millikan did. Millikan won a Nobel Prize in 1923 'for his work on the elementary charge of electricity…', a recognition of his contribution to the advancement of science.

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[5] https://www.britannica.com/biography/Robert-Millikan

[6] Retrieved 17 Mar. 2017 from https://www.boundless.com/chemistry/textbooks/boundless-chemistry-textbook/mass-relationships-and-chemical-equations-3/molar-mass-41/avogadro-s-number-and-the-mole-220-3701/

Avogadro's constant can also be calculated reasonable accurately by simple experiments such as depositing a single drop of oily liquid onto water- the theory being that it will spread out to form a layer of oil which can be considered to be a single molecule thick. This idea can be used to find an estimate for the number of molecules in a mole.

I performed the following method three times, and took an average of the readings. It is surprisingly simple to perform this experiment. I simply create a clean water surface in a large dish, before covering the surface in a fine powder such as talc or lycopodium powder. Using a teat pipette, drop one drop of the solution of stearic acid in petroleum ether onto the surface of the water. I measured the diameter of the surface film created, then halved it to find the radius:

Radius of surface film = (5.3, 4.9, 2.4) ÷ 3 = 4.2 cm

Number of drops making $1cm^3$ of solution = 70 (=a)

This solution contains 0.1g stearic acid in $1000cm^3$ ($0.1gdm^{-3}$) so 1 drop must contain

(1 x 0.1g)÷(a x 1000) of stearic acid, which is equal to 2.875×10^{-6}g.

As Volume = Mass ÷ Density , with the density of stearic acid being $0.941\ gcm^{-3}$

The volume of 1 drop must be $(2.875 \times 10^{-6})\div(0.941)$ which is equal to 3.04×10^{-6}.

I assumed the layer on the water to be 1 molecule thick, so the volume has completely spread out. The volume of the drop must therefore be area x thickness = πr^2 x T (thickness). This means I can calculate the thickness of the layer T:

$T = (3.04 \times 10^{-6}) \div (\pi \times 4.2^2) = 5.4856 \times 10^{-8}$ cm

If I assume the layer to be 1 molecule thick and a molecule to be a cube, the volume of a molecule must therefore be T^3.

$T^3 = 1.65072751 \times 10^{-22}\ cm^3$

1 mole of stearic acid has a mass of 284g and its density is $0.941\ gcm^{-3}$.

This means that 1 mole of stearic acid has volume 284 ÷ 0.941=301 cm^3.

As I now have the volume of a molecule and the volume of 1 mole, I can calculate the number of molecules in a mole:

$301 \div 1.65072751 \times 10^{-22} = 1.823441105 \times 10^{24}$

This is reasonably accurate for such a simple experiment. My result, though 3 times larger than the accepted value for Avogadro's constant, allowed me to attempt a new approach to rediscovering the constant that is not heavily documented due its significance in history. It was enjoyable to perform a less well known experiment and still achieve reasonable results, though it is of course understandable why this result is not favoured as a means to calculate Avogadro's number, given its inaccuracy compared to the other experiments I have written about.

Although X-Rays have been used since 1912 to determine the lattice spacing in a crystal, it was not until 1930 that the technique was used to determine Avogadro's constant.[7] The problem before that date was that X-ray wavelengths were not known with accuracy. The problem was that X-ray lines are broad, and it was not until 1965 that a better scale of wavelengths was proposed by Bearden, who established an absolute scale to an accuracy of ±1ppm.

Avogadro's constant is equal to the ratio of the molar mass to the molecular mass, and the latter is equal to the density of the crystal multiplied by the volume occupied by one molecule.[8] The molecular volume can determined from the lattice spacing, together with a geometrical factor which converts this to the volume of the unit cell, and a divisor which is the number of molecules per unit cell.

In the early X-ray evaluations of Avogadro's constant the uncertainty in the wavelength was the factor which limited accuracy, but later the uncertainties in density and even the molar masses had to be addressed. The densities were determined by weighing with the sample immersed in water of a carefully measured density. [9]

The values deduced by X-ray studies for Avogadro's constant during the first half of the 20th century showed that its accuracy had a floor of about 70ppm; this was small enough to show that the electron charge deduced by Millikan was probably in error by about 0.2%. The breakthrough to better than 1ppm came after 1965 by the use of combined optical and X-ray interferometry.

Essentially it allows one to use more nearly monochromatic X-rays, which is far better as their absolute wavelengths can be more precisely determined. The measurements use highly polished spheres of silicon with a mass of one kilogram.[10] Spheres are used to simplify the measurement of the size (and hence the density) and to minimize the effect of the oxide coating that inevitably forms on the surface.[11]

The 1998 CODATA recommended value as maintained by NIST (National Institute of Standards and Technology), is

NA= $6.02214199 \times 10^{23}$ mol^{-1}

Regrettably I was also unable to attempt these experiments as well, but it was to be suspected, as only a handful of labs around the world have the equipment and trained scientists to perform the measurements.

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[7] 'On the Theory of the Energy Distribution Law of the Normal Spectrum', 1900, in 'Planck's Original Papers in Quantum Physics' Translated by D. ter Haar, and S.G.Brush, Taylor and Francis, 1972.

[8] https://chem.libretexts.org/Core/Physical_and_Theoretical_Chemistry/Atomic_Theory/The_Mole_and_Avogadro%27s_Constant

[9] http://proceedings.spiedigitallibrary.org/proceeding.aspx?articleid=1687375

[10] https://statscdn.com/?s=d1xsnKE%2Fwr31TxH6UfSn%2F4Z%2Fq85lYbEGGCaLvIWlvNRMFMfM63v%2Ffq6nos6AvrkrYhXlC6uHextUD5rgOQ8rLA%3D%3D

[11] J.C.Maxwell, Phil.Mag.,1860.19,19.

Through-out writing this essay I have been constantly astounded that scientists at the start of the 20th century had the resourcefulness to devise experiments, often based on the findings of other scientists, which led to the discovery of a constant which today we may take for granted. Their contribution to the progress of science is undeniable; without Avogadro's constant science would still be without the knowledge of the dimensions of atoms, as well as one of chemistry's most important units- the mole. The mole is used as the scaling factor between macroscopic and microscopic observations of nature, providing scientists the ability to understand the relationship between the observable behaviour of elements and compounds, and their atomic structure. The chemical changes observed in any reaction involve the rearrangement of billions of atoms. As it is impractical to try to count or visualize all these atoms, scientists needed a way to refer to the entire quantity. Hence the importance of Avogadro's number, and its significance in the field of science.

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