Avogadro and His Constant

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Dedicated to Prof. *Edgar Heilbronner* on the occasion of his 80th birthday

An account is given of the historical development of *Avogadro*'s hypothesis, and of the principal methods of determining *Avogadro*'s constant which have been used over the past 200 years. These include the kinetic theory of gases, Brownian motion, measurement of the electron charge, black-body radiation, alpha particle emission, and X-ray measurements.

Avogadro's Constant. – *Avogadro*'s constant is the number of molecules in a mole, or the ratio of the molar mass to the molecular mass. Its great importance is that it provides a link between the properties of individual atoms or molecules and the properties of bulk matter. For example, it links the energies of individual atoms and molecules, which can be determined from spectroscopy, to the thermodynamic energies of bulk matter which are obtained from calorimetric experiments. Its most recent value is

$$N_A = 6.02214199(47) \times 10^{23} \text{ mol}^{-1}$$

This is, for example, the number of water molecules in 18.0152 g, roughly 18 ml, of water (a mole of water). To appreciate the magnitude of this number note that, if each water molecule were the size of a grain of sand (volume say 1 mm^3), then one mole of water would cover the UK with a layer a few kilometres thick. There are more water molecules in a cup of tea than there are stars in the universe (estimated to be 10^{22}).

Background History. – The idea that matter was composed of minute indivisible components (atoms), and was not capable of subdivision without limit, goes back to the Greek philosophers *Leucippus* and *Democritus*. In 1599 *Shakespeare* wrote in '*As You Like It*', '*It is as easy to count atoms as to resolve the proposition of a lover*'. The first person to write seriously about the number and size of atoms was *Johann Magnenus*. In a book, '*Democritus Reviviscens*', published in 1646, he describes an experiment in which he studied the diffusion of incense in a church; quite a nice idea if one knows how many molecules it takes to smell incense. However, in his book he concludes that it cannot be said that fire atoms are bigger or smaller than earth or water atoms¹). Atomism was also notably propagated by *Pierre Gassendi* who wrote several books

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¹) *Magnenus*'s book was the first comprehensive alternative to Aristotelian science. He also wrote a book on the medical usage and effects of tobacco.

early in the 17th century, and was supported later in the century by *Isaac Newton* and *Robert Boyle*. Boyle developed his '*mechanical philosophy*' around the concept that matter consisted of particles in motion.

The beginning of modern chemistry is commonly attributed to the publication in 1789 of '*The Elements of Chemistry*' by *Lavoisier* [1]. In this book he stressed the importance of quantitative measurements, and emphasised the principle of the conservation of matter in chemical reactions. He also revived the idea of chemical elements which were substances that could not be broken down to anything simpler by chemical means; he listed 23 such elements.

Lavoisier's, book led quickly to the development of several empirical laws in chemistry, one of the first being *Richter*'s law of equivalent proportions introduced in 1791 [2]2)*. Richter* discovered that if A and B combined with relative weights w_a and w_b, and A and C combined with relative weights w_a and w_c, then B and C would combine with relative weights w_b and w_c. *Proust* [3], in 1797, found that these relative weights were independent of how the compounds were made. Although this was disputed for many years by *Berthollet*, it was this evidence that finally led to the distinction between compounds and mixtures.

Atomism grew further in importance with the developments of chemistry early in the 19th century, particularly from *Dalton*'s conclusion that atoms of different chemical substances were not identical. *Dalton* assumed, like *Newton*, that atoms of the same substance repelled one another (to explain gas pressures), but he further assumed that atoms of different species did not repel one another. From this he arrived at his law of partial pressures; the total pressure of a gas is the sum of the pressures from the gases individually3)). This is a true result obtained from an incorrect argument.

Dalton held that atoms of different elements differed in size, weight, and number per unit volume, and he concluded that, when two elements combined to form compounds, they did so in different simple proportions of their numbers of atoms. He published his law of multiple proportions in 1804. An important step in his analysis was that, when only one combination of two elements is known, it was assumed to be a binary compound unless there was some evidence to the contrary, and from this *Dalton* drew up the first table of the relative weights of atoms (taking hydrogen as unity) in 1803.

In France at the beginning of the 19th century, a young chemist called *Gay-Lussac* was working with *Berthollet* on the physical properties of gases. With *Humboldt* [6] he did a number of experiments to examine the composition of air and how this varied

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2) *Richter* was a pupil of the philosopher *Immanuel Kant*, and he followed his teacher in thinking that all physical sciences were branches of applied mathematics.

3) It is difficult to track down precise references to much of *Dalton*'s work because he presented it in many lectures, and published his work frequently, often in slightly different forms (see a bibliography [4]). What became known as the Law of Partial Pressures arose from a series of essays on gases, which were given verbally in 1801 and published in 1802 in '*Memoirs of the Literary and Philosophical Society*', Vol. V, Part *ii*, Manchester. His atomic theory appears in '*A New System of Chemical Philosophy*', which was published in several parts from 1808 to 1827. *Partington* [5] gives an excellent account of *Dalton*'s work, with particular attention to the different views which were being propounded in 1800 on the nature of mixed gases.

from place to place and with the height above sea level. The oxygen content of air was determined by a method developed by *Volta* of explosion with hydrogen, and in a number of experiments (1805) they found that 100 volumes of oxygen combined with 199.89 volumes of hydrogen; the deviation from 200 they attributed to a small amount of nitrogen in the hydrogen.

In 1808, *Gay-Lussac* published his law for the combining volumes of gases [7], namely that gases combine among themselves in very simple proportions of their volumes, and if the products are gases their volumes are also in simple proportions. He published a few new experiments and re-examined the results of others. His data were as follows:

100 muriatic acid (HCl) + 100 ammonia = solid
100 fluoboric gas (BF_3) + 100 ammonia = solid
100 fluoboric gas + 200 ammonia = solid (disproved in 1948)
100 carbonic acid (CO_2) + 200 ammonia = solid
200 sulphurous gas (SO_2) + 100 oxygen = sulphuric acid
100 carbonic oxide (CO) + 50 oxygen = 100 carbonic acid
100 nitrogen + 49.5 oxygen = 100 nitrous oxide (Davy)
100 nitrogen + 108.9 oxygen = 200 nitrous gas (NO) (Davy)
100 nitrogen + 100 oxygen = 200 nitrous gas
100 nitrogen + 204.7 oxygen = 200 'nitric acid' (NO_2) (Davy)
300 muriatic acid + 103.2 oxygen = oxymuriatic acid (Cl_2)
100 nitrogen + 300 hydrogen = 200 ammonia (Berthollet)

Gay-Lussac said that his results were very favourable to *Dalton*'s 'ingenious idea' about the composition of molecules, but, strangely, *Dalton* never accepted the '*round numbers*' of *Gay-Lussac*. In a letter to *Berzelius* in 1812 he said '*The French doctrine of equal measures of gases combining is what I do not admit, understanding it only in a mathematical sense. At the same time I acknowledge there is something wonderful in the frequency of the approximation*'. Even in 1827 he said '*Combinations of gases in simple volume ratios occur but they are only approximate and we must not suffer ourselves to be led to adopt these analogies till some reason can be discovered for them*'. Of course *Dalton* was correct according to our current knowledge that real gases do not exactly obey the ideal gas laws, but he was wrong for the knowledge of his time.

In 1809, *Gay-Lussac* and *Thenard* studied the combining volumes of chlorine and hydrogen [8]. They placed mixtures of equal volumes of these two gases, one in the dark and one in the light, for several days. In the vessel exposed to the light, the characteristic colour of the chlorine disappeared in less than 15 minutes, but there seemed to be no change to that in the dark. This lead them to say, '*Being no longer able after these experiments to doubt the influence of light in the combination of these two gases, and judging from the rapidity with which it has operated that if the light had been more vivid it would have operated much more quickly, we made new mixtures and exposed them to the sun. Scarcely had they been exposed when they inflamed with a large detonation and the jars were reduced to splinters and projected a great distance. Fortunately we had provided against such occurrence, and had taken precautions to* *secure ourselves against accident*'[4]). This famous chain reaction was important in leading to the chemical equation

$$H_2 + Cl_2 = 2\ HCl$$

and this disproved *Dalton*'s view that atoms of the same type could not join together.

In his 1809 paper, *Gay-Lussac* said '*I hope we are not far removed from the time when we shall be able to submit the bulk of chemical phenomena to calculation*', so he has a good claim to be called the father of theoretical chemistry.

Amedeo Avogadro was born in Turin in 1776 to *Count Filippo Avogadro* and his wife *Anna Vercellone*. He first followed the family by training as a lawyer; he became a bachelor of jurisprudence when he was only 16, and had a doctorate in ecclesiastical law at the age of 20. When he was 24 he began studies of mathematics and physics, and in 1809 he became professor of natural philosophy in the Royal College of Vercelli. In 1820, he was appointed to the first Italian chair of mathematical physics at the University of Turin.

Avogadro was greatly influenced by *Gay-Lussac*'s law of combining volumes. In 1811, he published a paper in French on a manner of determining the relative masses of the elementary particles of bodies and the proportions to which they enter into their compounds [10]. '*Essai d'une maniere de determiner les masses relatives des molecules elementaires des corps et les proportions selon lesquelles elles entrent dans ces combinations*'. In this paper, he coined the word *molecule* (diminuitive of the Latin *mole*, a mass), for the smallest particle that normally exists in a free state[5]).

Avogadro's hypothesis, expounded in his 1811 paper, is that equal volumes of all gases at the same temperature and pressure contain the same number of molecules. He applied this principle to the determination of the relative masses of gas molecules; the ratios of the masses of the molecules are the same as the ratios of the densities of the different gases at the same temperature and pressure. He further proposed that the relative number of atoms in a molecule can be derived from the ratio of the volumes of the gases that form its compound.

Avogadro, in his paper, discusses *Dalton*'s atomic theory[6]) and calculates, for example, from gas densities that the molecular weight of nitrogen is 13.238 relative to hydrogen as 1. He was the first to propose that the gaseous elements, hydrogen, oxygen, and nitrogen, were diatomic molecules. He deduced that the molecule of water contains half a molecule of oxygen and one molecule (or two half molecules) of hydrogen. *Dalton* had assumed that water is formed from a molecule each of oxygen and hydrogen. *Avogadro* also concluded that ammonia had the formula NH_3, and, in later papers, he used his hypothesis to deduce quite complicated formulae, for example, C_2H_6O for alcohol [12]. However, as far as we know, *Avogadro* never speculated on the number of molecules in a given gas volume, or on the size of molecules.

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[4]) *Gay-Lussac*'s obituary notice for the *Royal Society* [9] reports that, in 1808, he was gravely ill from an explosion which had nearly blinded him.

[5]) Partington in '*A History of Chemistry*', Vol. 4 [11], quotes earlier sources for the word.

[6]) According to *Partington* [5], *Dalton* was close to adopting *Avogadro*'s hypothesis in 1801, but he later called this a confused idea and abandoned it.

Avogadro's hypothesis was proposed again by *Ampere* in 1814, in a letter to *Berthollet*. This work received much greater publicity, and *Ampere* was often given the credit for the idea; there are many references in the literature to *Ampere*'s law. However, *Cannizaro*, at an international conference in 1860, reclaimed the priority for his countryman *Avogadro*, and it has been his ever since.

First Measurements from the Kinetic Theory of Gases. – The first estimate of *Avogadro*'s constant is attributed to *Loschmidt*, although his work '*Zur Grösse der Luftmolecüle*', published in 1865, is concerned with the size of molecules rather than their number [13]. However, in the same year a summary of *Loschmidt*'s paper appears which, although full of errors, gives a value for the number of molecules in 1 cm^3 at STP, which is called *Loschmidt*'s number, as 8.66×10^{17}. The correct number which, according to *Hawthorne* [14], can be deduced from *Loschmidt*'s data, is 1.83×10^{18}; the *Avogadro* equivalent⁷) of this is

$$N_A = 4.10 \times 10^{22}\ \mathrm{mol}^{-1}.$$

The first estimates of *Loschmidt*'s number are all based on the measurements of two quantities. One is the total volume of the molecules, and the other is a quantity based on molecular cross sections, that is, the area within which two molecules can be said to collide. Assuming that molecules can be represented as hard spheres with diameters d, their total volume is $N_A \pi d^3/6$, and their total cross section is $N_A \pi d^2/4$, if these two quantities are known, their ratio allows one to deduce both d and N_A.

Cross sections are linked to experimental observables through the kinetic theory of gases. The development of this subject has a fascinating history. Our current interpretation of gas structure has its origins in a chapter in the book '*Hydrodynamik*' by *Bernoulli*, published in 1738, but this work was overlooked for more than a hundred years. Also, in 1845 *J. J. Waterston*, a school teacher in Bombay, submitted a paper to the *Royal Society* with the title '*On the physics of media composed of free and perfectly elastic molecules in a state of motion*', in which many of the currently accepted concepts of kinetic theory were set out. Unfortunately this paper was rejected by the society as '*nothing but nonsense, unfit even for reading before the society*'. However, the manuscript was rediscovered in the archives by *Lord Rayleigh* who deduced that it was essentially correct, and the paper was published in the *Philosophical Transactions* in 1892 [15]. *Rayleigh* wrote a preamble to the paper describing its treatment, in which he says that the referee of *Waterston*'s paper was one of the best qualified authorities of the day, and that the failure to publish the paper probably held back the subject by 10 to 15 years. In the meantime there had been major developments of the theory, particularly by *Clausius*, *Maxwell*, and *Boltzmann*.

The ideal gas law, $PV = RT$ (for one mole of gas), can only be deduced by assuming that the molecules exert no forces on one another, and that their size is negligible compared with the average distance between molecules. It is clear from these assumptions that one cannot deduce *Avogadro*'s constant directly from the gas constant

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⁷) In German literature one often finds *Avogadro*'s constant referred to as *Loschmidt*'s number per gram molecule.

R. Although this constant is related to *Boltzmann*'s constant k by $R = k\,N_A$, one needs a separate measure of k to deduce N_A by this route, a possibility that only came much later through studies of individual molecules[8]).

Loschmidt obtained his cross section from an expression due to *Maxwell* and *Clausius* for the mean free path of a gas molecule[9]); this is the mean distance a molecule travels before it is in collision with another molecule. The mean free path was deduced from measurements of gas viscosity, using *Maxwell*'s kinetic theory in which the molecules are treated as hard spheres. *Loschmidt* deduced his molecular volumes from some work of *H. Kopp* [16] on atomic volumes (and the extent to which they can be considered as additive in making up a molecular volume), making adjustments for molecular packing and the effect of temperature.

Apart from the uncertain knowledge of most relevant quantities at that time, *Loschmidt*'s work was the first to show that *Avogadro*'s constant (or *Loschmidt*'s number) was very large, and that molecular volumes were very small. Later, in 1870, *Lord Kelvin* [20], used *Loschmidt*'s approach and three other ingenious methods to deduce that molecular diameters were of the order of 0.5 Å, although in summary he concluded that the possible range was 0.05 Å to 1 Å. This underestimate of diameters leads to an overestimate of *Loschmidt*'s number. In 1873, *Maxwell* [21] used his kinetic theory of the diffusion coefficient of a gas, another quantity related to the cross section, to obtain 1.9×10^{19} for *Loschmidt*'s number; this is quite close to the currently accepted value of 2.70×10^{19}.

A much simpler method for getting the actual volume of molecules is to use the *PVT* behaviour of real gases and to represent their behaviour by *van der Waals*' equation

$$(P + a/V^2)(V - b) = RT \tag{1}$$

This was published in *van der Waals*' Ph.D. thesis '*Continuite des etats liquides et gazeux*', in 1873, and he explained the significance of the parameters a and b.

The parameter b was interpreted by *van der Waals* as the excluded volume due to the finite size of the molecules. For close packed spheres this would be 1.35 times the actual volume of the spheres, and for random close packing the appropriate factor is about 1.57. However, for these values the system is not gas-like, and *van der Waals* argued that the excluded volume should be four times the volume of the spheres[10]). Later, *Perrin* [22] used this result, and, by measuring b for mercury vapour and

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[8]) Although the famous equation of *Boltzmann* $S = k \ln W$ is carved on his tombstone, the equation never appears in his written work, although he clearly understood the relationship between entropy and probability. *Planck* was the first to write the equation and define k as *Boltzmann*'s constant in 1906 in his book '*Vorlesungen über die Theorie der Wärmestrahlung*'.

[9]) *Maxwell* published his work in 1860 [17] and obtained, in addition, a result for the collision number which conflicted with the result of *Clausius* published a little before [18]. Later [19], *Clausius* attempts to explain why *Maxwell* is wrong.

[10]) *Kauzmann* [23] gives a good account of the analysis by *van der Waals* and an alternative analysis by *Boltzmann*. The most convincing argument that the factor 4 is the appropriate one comes by relating b to the second virial coefficient for gases, and using the statistical mechanical expression for this for a hard sphere interaction potential.

combining this with cross sections from viscosity measurements, he calculated *Loschmidt*'s number to be 2.8×10^{19}, which is fortuitously a very good value.

Brownian Motion. – The phenomenon of Brownian motion was first described by *Robert Brown* in 1828 as the '*tremulous motion*' of pollen grains observed as suspensions in liquids. *Wiener* [24], was the first to give the correct explanation that it is due to internal motions characteristic of the liquid state, and, in 1888, *Gouy* [25] concluded that the suspended particles '*do not play an essential part in the movement, but only make manifest the internal agitation of the liquid*', thus furnishing us '*with a direct and visible proof of the real exactness of our hypothesis concerning the nature of heat*'.

The kinetic theory of Brownian motion was developed by *Einstein* [26] in a series of papers from 1905 to 1911, and by *Smoluchowski* [27], using a different approach but reaching the same conclusions, in 1906. Several different aspects of this theory have been used to determine *Avogadro*'s constant, the first being by *Perrin* [28] in 1908. He considered the distribution of Brownian particles in a vertical column in a normal gravitational field, and he used a similar mathematical approach to that which leads to the distribution of gas molecules in a vertical column of the atmosphere. A simple way of attacking the problem is to use the *Boltzmann* distribution formula for the number density of molecules in an isothermal gas at temperature T

$$(n_2/n_1) = \exp(-(v_2 - v_1)/kT) \tag{2}$$

For a column of gas in a uniform gravitational field, the potential energy is,

$$v = mgh \tag{3}$$

where g is the acceleration due to gravity, h is the height in the column, and m is the molecular mass. As the number density is proportional to the local pressure, we can derive from *Eqn. 2* the barometric formula for the pressure at height h relative to the ground pressure

$$P(h) = P(0)\exp(-mgh/kT) \tag{4}$$

To obtain *Perrin*'s formula for the vertical distribution of Brownian particles, one has only to make a correction to *Eqn. 3* for the buoyancy of the particles in the liquid (*Archimedes* principle), by using the expression

$$v = mgh(\varrho_m - \varrho_l)/\varrho_m \tag{5}$$

where ϱ_m, and ϱ_l are the densities of the particles and the liquid respectively. Substituting *Eqn. 5* into *Eqn. 2* then gives

$$(n_2/n_1) = \exp((mg/kT)(h_2 - h_1)(\varrho_m - \varrho_l)/\varrho_m \tag{6}$$

Both *Einstein* and *Smoluchowski* showed that this formula is a necessary consequence of the principle of equipartition of energy; both the Brownian particles and the molecules of the liquid have the same kinetic energy, $3kT/2$ per particle.

If we know the mass of the Brownian particles (m), the densities of the particles, and the liquid in which they are suspended, then measuring the numbers of particles at two different heights allows one to determine *Boltzmann*'s constant, k, and *Avogadro*'s constant through $k = N_A/R$ (R being known with high precision).

Perrin, in his first experiments in this field, prepared a monodisperse colloid of a gum called gamboge by elaborate fractional centrifugation, and he counted the distribution in layers of about 17000 particles in a water column using a microscopic technique. The experiment was carried out with a column whose height was only 0.1 mm, using a microscope that focused with a depth resolution of a quarter of a micron. One advantage of this set-up was that convection currents were absent. The particle masses were determined by direct weighing of a specified number, and their radii (hence their volumes and densities) by using the *Stokes-Einstein* law for diffusion[11]). *Perrin*'s first value for *Avogadro*'s constant (he was actually the first person to calculate this quantity rather than *Loschmidt*'s number), was $N_A = 7.05 \times 10^{23}$ mol^{-1}, and subsequent experiments based on various aspects of Brownian motion confirmed numbers in this region with an accuracy of about 1×10^{23} [29][12]).

Measuring the Electron Charge. – The principle underlying *Perrin*'s experiments was based on the assumption that colloidal particles followed the same statistical laws as molecules and therefore their energy distribution was controlled by *Boltzmann*'s constant k; one did not have to handle a mole of particles, which would be governed by the gas constant R. The progress towards more accurate values of *Avogadro*'s constant was largely based on the study of individual atoms or molecules, and, in the first place, by studying individual electrons.

The electron was identified by several workers at about the same time as the negatively charged particles emitted from the cathode in a discharge tube. In 1897 *Weichert* [30] called the particles '*elektrons*', and in the same year *J. J. Thomson* [31], obtained their mass-to-charge ratio based on experiments in which electron beams were deflected in electric and magnetic fields. Also in 1897, *Townsend* [32] found that hydrogen and oxygen liberated by the electrolysis of dilute acid or alkali solutions picked up charges when bubbled through water and formed a cloud of charged droplets. By assuming that all droplets had the same charge (the charge of one electron), he obtained a value for this of 5×10^{-10} esu. Similar studies were made by *Thomson* [33] in 1898, and *Wilson* [34] in 1903, finally leading to a charge of 3.1×10^{-10} esu. It was this technique which *Millikan* developed further to obtain an accurate charge for the electron, but his experiments took nearly 10 years with many improvements along the way.

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[11]) Note that the diffusion of large particles in a liquid is, according to this law, related to the product $N_A d$, and not $N_A d^2$, as it is for a gas. *Perrin* actually used three different methods to determine the volume of the particles, and the agreement between these was better than 1% for the most homogeneous suspensions.

[12]) *Einstein* in his early work was also interested in *Avogadro*'s constant, and his Ph.D. thesis, accepted by the University of Zurich in 1905, was largely concerned with its evaluation from the diffusion of hard spheres in a continuous medium.

Millikan's first experiments were also on water droplets, but the problem with these is that they evaporate rather quickly and so can only be viewed for short times. A student of *Millikan*'s called *Harvey Fletcher* turned to oil droplets and forming these between charged plates he noted that some fell and others moved upwards, depending on the charge they acquired. Later, *Millikan* worked with single droplets of oil in air (he also used mercury and glycerine), which were charged by exposure to X-rays. The drop was held between the plates of a condenser and would move down under gravity or could be moved up under an applied electric field; the times for both rise and fall between cross wires on a telescope were measured. The ratio of the rate of fall under gravity and rise under a field of strength E is as follows

$$(v_{\text{down}}/v_{\text{up}}) = mg/(Ee - mg) \tag{7}$$

In this formula e is the charge of the electron for singly charged drops. In the experiments the rate of upward motion varied due to the multiple charging of drops (integer values up to 150 were found), but this was allowed for. The first results were published by *Millikan* and *Fletcher* in 1910 and 1911 [35][36]. *Millikan*'s final results, published in 1917, gave the result [37]

$$e = 4.770 \pm 0.005 \times 10^{-10}\ \text{esu}\ (1.591 \times 10^{-19}\ \text{C})$$

The current accepted value is 1.6022×10^{-19} C.

The charge carried by a mole of singly charged ions in an electrochemical cell, which is known as *Faraday's* constant, F, was known at that time to be $9.6489 \times 10^4\ \text{Cmol}^{-1}$, and as $F = e\ N_A$, this gave *Avogadro*'s constant as $N_A = 6.064 \pm 0.006 \times 10^{23}\ \text{mol}^{-1}$.

Black-Body Radiation. – In 1900, *Planck* showed that the distribution of black body radiation as a function of the radiation frequency could only be explained by assuming that oscillators in the body of frequency ν could only take up or release energy in integer packets of $h\nu$. This was the first evidence for the quantisation of the energy levels of atoms and molecules, and removed the conflict of classical radiation theory which lead to the so-called ultra violet catastrophe of black body emission. *Planck*'s radiation density law for frequency can be written

$$U(\nu) = 8\pi h\nu^3/c^3(\exp(h\nu/kT) - 1) \tag{8}$$

and *Planck* pointed out that a comparison with the experimental curve allowed the determination of h and k, and, from the ratio of k and the gas constant R, *Avogadro*'s constant could be determined. His estimate was $N_A = 6.175 \times 10^{23}\ \text{mol}^{-1}$, consistent with other estimates at the time [38].

We have seen that *Avogadro*'s constant can be obtained by combining measurements of the electron charge e and the *Faraday* constant F, and by combining measurements of *Boltzmann*'s constant k and the gas constant R. The values of e and k are also connected with the other fundamental physical constants h, and the mass of the electron m, to observable quantities such as the *Rydberg* constant for H or He^+ atoms (giving e/m), and the '*black body*' radiation curve (giving h/k). *Loeb* [39], in his book '*The Kinetic Theory of Gases*', lists eleven relationships which, through experimental measurements, link the fundamental physical constants, so that assumptions about the values of e and N have implications for the values of others. *Bond* [40] was the first to optimise the values of *Avogadro*'s constant and the other fundamental constants to a set of experimental results (36 in all over a wide spread of physics), and obtained the value $N_A = 6.054 \pm 0.03 \times 10^{23}$ mol^{-1}. *Birge* [41], whilst accepting this principle, criticised the choice of data, and has proposed more reliable values for N_A and the other fundamental constants.

Counting *α* Particles. – In 1903, *Rutherford* [42] showed that the α rays emitted from radium consisted of positively charged particles (later shown to be He^{++}), and he and *Geiger* developed a method for counting them by observing the scintillation points on a screen coated with small crystals of zinc sulfide. *Rutherford* at first believed that only a small fraction of the α particles produced scintillation, but, by 1908, he and *Geiger* had compared the number counted with the amount of electrical charge produced by α particles in a gas at low pressures (a *Geiger* counter), and they concluded that the scintillation technique recorded 100% of α particle collisions. *Rutherford* and *Geiger* counted the α particles emitted from a standardised radium source after they had passed down a long tube, and, after multiplying by the appropriate solid angle, they deduced that a gram of radium emitted 3.4×10^{10} α particles per second [43]. They stated, '*It is the first time that it has been found possible to detect a single atom in nature*'. Counting individual atoms clearly provides a method for determining *Avogadro*'s constant. One needs to know the number of α particles produced and the volume of He gas that they give rise to.

In 1911, *Boltwood* and *Rutherford* [44] reported that they took a mixed salt of barium and radium chlorides (about 7% of the latter), care having been taken to ensure that there were no other radioactive elements present than the radium. The sample was placed in a platinum capsule with a perforated cover, and the whole was sealed in an evacuated glass tube. The amount of radium present was determined by measuring the γ radiation and comparing it with that from a standard sample. The seal was broken after 83 days, and the amount of helium present was determined by measuring pressure and volume (water from the heated salts had previously been removed by passing the gas over KOH and P_2O_5). This experiment gave 6.58 mm^3 of gas at 0 °C and 760 mm pressure. Spectroscopic examination established the gas to be essentially pure helium. A second determination over a period of 132 days using a slightly different technique gave 10.38 mm^3 of He.

Radium is a very long-half-life α particle emitter. Its first product is radon which is also an α emitter, with a half life of $\lambda = 3.83$ days, and this undergoes further decay, leading to two other α emitters with short half lives; effectively the α particles in total come from the radium as an amount proportional to the time, and from the radon and its decay products as an amount that builds up with time. For a time T much longer than the radon half life, the total amount of helium produced Q can be shown to be given by

$$Q = 4(1 - 3/4\lambda T)Tx \tag{8}$$

where x is the rate of production from the radium itself. From the two measurements made by *Boltwood* and *Rutherford*, x was found to be 2.09×10^{-2} mm^3/day and

2.03×10^{-2} mm^3/day, which are satisfactorily consistent results. The average of these results gave a production of He per gram of radium of 0.107 mm^3 per day, which is equivalent at NTP to 5.55×10^{-14} mole per second. Although *Boltwood* and *Rutherford* did not state the value of *Avogadro*'s constant, which can be deduced from their experiments and the rate of production of α particles, it is clear that

$$N_A = 3.4 \times 10^{10}/5.55 \times 10^{-14} = 6.1 \times 10^{23}\ \text{mol}^{-1}$$

which was by far the most accurate value available in 1911.

There were several later developments of these radioactivity measurements, the most accurate being the measurement of the equilibrium concentration of radon produced from radium. *Wertenstein* [45] in 1928 used this to obtain a value $N_A = 6.16 \times 10^{23}$ mol^{-1}, which is about the limit of accuracy for this approach because of the difficulty of measuring small gas volumes with high accuracy.

X-Ray Determination. – 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. The problem before that date was that X-ray wavelengths were not known with accuracy. This problem was partly solved by *Backlin* in 1928 [46]; by measuring the diffraction angles at grazing incidence from a plane grating with known period, he determined the wavelength for the unresolved Al $K\alpha_{1,2}$ doublet. However, X-ray lines are broad, and it was not until 1965 that a better scale of wavelengths was proposed by *Bearden* [47], based on the W $K\alpha_1$ line; this established an absolute scale to an accuracy of ± 1 ppm.

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. The molecular volume is 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. After 1950, the molar masses began to be derived from the known nuclidic masses and determined isotopic abundance.

Almost all early X-ray work was based on calcite crystals and stemmed from *Bearden*'s [48] determination of the unit cell volume in 1931. However, it was later clear that calcite could show considerable density variation, and other crystal types were used, particularly Ge and Si. But always the question of chemical purity came in when seeking an accuracy of better than 10 ppm.

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 70 ppm; 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 1 ppm came after 1965 by the use of combined optical and X-ray interferometry [49]. The technical set-up is quite complicated, but essentially it allows one to use more nearly monochromatic X-rays, and their absolute wavelengths can be more precisely determined. But solving the X-ray problem brought the accuracy of the molar masses and of the density to the fore, and for both of these highly purified silicon crystals are now being used, with isotopic abundance compared to a NBS standard reference material. Density is still measured by hydrostatic means, but the fluid is a fluorocarbon and comparison made to the densities of precisely engineered steel spheres whose diameters had been determined by optical interferometry [50].

Despite all care in their preparation, a study of three silicon crystals showed variations of density and molar mass of the order of 5 ppm, but these two quantities were strongly correlated, so that the ratio of the two was accurate to better than 1 ppm. The X-ray determined value for *Avogadro*'s constant quoted by *Deslattes* in 1980 [50] was

$$N_{\mathrm{A}} = 6.0220978(63) \times 10^{23}\ \mathrm{mol}^{-1}$$

Further analysis has improved the accuracy further. The 1998 CODATA recommended value, as maintained by NIST (National Institute of Standards and Technology), is

$$N_{\mathrm{A}} = 6.02214199(47) \times 10^{23}\ \mathrm{mol}^{-1}$$

An *ad hoc* working group on the *Avogadro* constant was set up in 1994 under the umbrella of BIPM (Bureau International de Poids et Mesures, Paris), as a link for all groups working in the field.

Tidying up. – With a subject whose development covers about 200 years, it has not been possible to go back to all the original work. I acknowledge a great deal of help from *J. R. Partington*'s '*A History of Chemistry, Vol 4*' [10], and *M. J. Perrin*'s '*Brownian Movement and Molecular Reality*' [29]. The book '*Physicochemical Calculations*', by *E. A. Guggenheim* and *J. E. Prue* [51], has a chapter showing 10 different calculations which lead to *Avogadro*'s constant. Most of these are based on experiments which I have discussed, but with a few others of less importance. *R. M. Hawthorne* [14] gives a good analysis of the early work with an important examination of *Loschmidt*'s measurements and calculations. An early review of the field was made by *Kelvin* in 1904, in a book based on his Baltimore lectures [52]. He described seven lines of attack, three of which were to some degree due to *Rayleigh*. Amongst these were estimates of molecular dimensions based on observing very thin films; both their surface tension and the minimum thickness of surface films on water. Later, *Virgo* [53] summarised the results up to 1933, and lists 80 different measurements leading to *Avogadro*'s constant. The X-ray studies have been thoroughly reviewed by *Deslattes* [48]. More recently there have been developed a number of Internet pages devoted to *Avogadro* and his works.

Lastly, with increasing accuracy of *Avogadro*'s constant, we are approaching the point at which we will no longer need separate standards for microscopic masses (based on the mass of the carbon-12 isotope) and macroscopic masses (the standard kilogram held in Sevres, France). The measurement of absolute atomic masses is being pursued through the development of very accurate mass spectrometers.

I have had comments on early versions of this text from a number of people, and I particularly acknowledge the advice of *Ian Mills*, *Nenad Trinajstic*, and *Martin Quack*.

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Received February 19, 2001