

Experimental Determination of the Avogadro Constant

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Since the time Cannizzaro expounded a system of atomic weight determination in the Karlsruhe Congress in 1860 [10], and firmly established Avogadro hypothesis, there have been dozens of experimental methods for determining the Avogadro number. Many of these methods seek to determine a fundamental physical constant such as charge of an electron or the Boltzmann constant whose value for one mole of particles is precisely known. Ingenious methods that have been devised for the measurement of these fundamental constants are discussed in this article.

Introduction

Although Avogadro's hypothesis, that equal volumes of different gases under identical temperature and pressure conditions contain the same number of molecules, was postulated in 1811 [1], it took almost fifty years for it to be taken seriously. There were several reasons for the lack of attention to Avogadro's hypothesis [2]. Avogadro's geographical isolation from the chemistry community of that period, (most influential chemists of that era were in France and Germany) which limited his intellectual interaction with other chemists, was one of the factors. Furthermore, the fact that the focus in chemistry of the times was on organic chemistry was also, to an extent, responsible for this lack of attention. Besides these sociological factors, there were scientific issues as well. To name a few, lack of clarity in the use of the term 'molecule' was one, and the fact that Avogadro's hypothesis was in direct conflict with the ideas of Berzelius (that similar atoms repelled each other) and of Dalton (which equated particles with atoms thereby eliminating the possibility that a particle of oxygen could yield two particles of water, a conclusion that follows from employing Avogadro's hypothesis to



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interpret Gay-Lussac's law), was another. However, the foremost reason for the difficulty in accepting Avogadro's ideas was that the number of particles or molecules in a gas of given volume could not be directly measured. One of the grand challenges for scientists of that era was to devise a method for carrying out such measurements.

Only indirect methods can be devised to determine the number of particles in a given volume of gas, since a macroscopic volume of the gas under ordinary conditions of temperature and pressure would contain innumerable large number of molecules. This problem has the parallel with counting the number of tablets in a large bottle filled with identical tablets. In this case, we could use a weighing balance to obtain the total weight of all the tablets in the bottle as well as the weight of a single tablet. The ratio of the two weights then gives the number of tablets in the bottle. Just as this method requires knowledge of the weight of one tablet, the determination of the number of molecules in a given volume also requires knowledge of at least one property of a single molecule.

Loschmidt Number

First successful attempt at determining the number of molecules in a unit volume of a gas under standard conditions of temperature and pressure was made in 1865, by the Austrian physical chemist Josef Loschmidt, who was born in what is now the Czech Republic [3]. He estimated the volume of a single molecule using the kinetic theory of gases and density of liquid air. Loschmidt had to estimate, instead of measure, the density of liquid air, since air was not yet liquefied in 1865! He used the concept of specific volume, V_s (molecular weight divided by its density in the liquid state), which had been introduced by Hermann Kopp. From measured densities of liquids formed from compounds with the same constituent elements in different proportions, Kopp had established the approximately additive property of specific volumes. Assuming that air consists of 77% nitrogen and 23% oxygen, Loschmidt estimated the density

Loschmidt estimated the volume of a single molecule using the kinetic theory of gases and density of liquid air.



of liquid air from the densities of liquid NO_2 (1.5 g/cm^3) and liquid N_2O (1.3 g/cm^3) to be 1.22 g/cm^3 , which is about 30% higher than the measured value [4]. Loschmidt recognized that the liquid can expand on warming and also that the molecules in a liquid can diffuse past one another. Hence, to obtain the actual volume occupied by the molecules, from the data on specific volume, he introduced a factor that he called the liquid condensation factor (f) whose value he assumed to be greater than unity ($1.17 < f < 1.91$). Thus, he estimated the volume, V_m , occupied by N_A molecules as

$$V_m = V_s/f = N_A v = N_A (4/3 \pi r^3), \quad (1)$$

where, r is the radius of the molecule, assuming the molecules to be spherical in shape.

The kinetic theory of gases relates the coefficient of viscosity, η , to the mean free path, λ , by the relation,

$$\eta = \frac{1}{2} \rho \bar{u} \lambda, \quad (2)$$

where \bar{u} is the average speed of an air molecule and ρ is the air density [5]. The average molecular speeds for oxygen and nitrogen were known from the work of Clausius in 1857. Thus, viscosity coefficient measurement and density yielded the mean free path, λ . Loschmidt computed the total molecular cross section, $N_A \pi r^2$, again using the kinetic theory [1] from the relation,

$$N_A \pi r^2 = V / (\sqrt{2} \lambda) \quad (3)$$

Using equation (1) and the above equation, Loschmidt determined the number of molecules per unit volume under standard temperature and pressure conditions. The number of molecules per cubic centimeter of gas under conditions of standard temperature and pressure (STP) came to be known as the Loschmidt number. The best value estimated by Loschmidt for the Avogadro

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number was $\sim 4 \times 10^{23}$. Perrin obtained the best estimate for the atomic volume from the van der Waals' equation of state,

$$(P+a/V^2)(V-b)=RT \quad (4)$$

The parameter 'b' in the above can be determined experimentally and as van der Waals argued it is four times the atomic volume. Perrin, by measuring b for mercury vapour, obtained a value of 6.25×10^{23} for the Avogadro constant.

The term Avogadro constant was first used by Perrin who identified the number of molecules in a gram molecular weight of a substance. The present day definition of the Avogadro constant is the number of carbon atoms in exactly 12 grams of pure ^{12}C . To appreciate the magnitude of Avogadro number, imagine that we have a powerful counting machine which can count about one crore (ten million) particles each second. Then it will take the machine approximately two billion (two hundred crore) years to count an Avogadro number of particles! Compare this with the age of the earth, which is about 4.5 billion years.

Brownian Motion

Perrin's determination of the Avogadro's constant was based on measuring the distribution of colloidal particles of identical sizes (monodisperse) in a vertical column under isothermal conditions under the influence of gravity [6]. The ratio n_2/n_1 of the number density of particles of mass m , at two different heights h_2 and h_1 , at a temperature, T , is given by the Boltzmann distribution,

$$n_2/n_1 = \exp(- (V_2 - V_1)/kT), \quad (5)$$

where $V_i = mgh_i$ is the potential energy at height h_i , with g being the acceleration due to gravity. When the colloidal particles of density ρ_m are suspended in a liquid of density ρ_l , g is replaced by $g(\rho_m - \rho_l)/\rho_m$ to account for buoyancy. If we know the mass and density of the Brownian particle and density of the liquid, then by measuring the number of Brownian particles at two different



heights, it is possible to obtain a value for the Boltzmann constant k ; the Avogadro number is the ratio of the gas constant R to the Boltzmann constant. Perrin prepared tiny spheres of gamboge, a resin, all of uniform size and density, by elaborate fractional centrifuging. He dispersed about 17000 particles of the resin in a water column of height 0.1mm. Using a microscope with a resolution of a quarter micron, he measured the vertical distribution of colloidal particles. The small height of the column was advantageous in reducing convection currents. Mass of the Brownian particle was obtained by directly weighing a known number of particles. The particle size was obtained from Stokes–Einstein law,

$$D = kT / (6\pi\eta a), \quad (6)$$

by measuring the diffusion coefficient, D , and using the known viscosity coefficient, η , of the medium, in terms of k . The resulting equation is then solved for k .

In the present day, with the help of computers to analyze experimental data, it is possible to directly obtain k from studies on Brownian motion. The random motion of monodisperse polystyrene beads of known size in water at a fixed temperature can be tracked using a video camera at intervals of say, $\Delta t = 0.1$ second. The mean square displacement, per time step, averaged over all the beads, σ^2 , can be obtained from a frame-by-frame analysis of the video over a sufficiently long period of time. The diffusion coefficient D is given by $\sigma^2 / (2\Delta t)$. Once again using Stokes–Einstein relation (equation 6) we can obtain the Boltzmann constant and hence the Avogadro number.

Counting α Particles

Rutherford in 1903 demonstrated that α particles are positively charged and subsequently they were shown to be He^{++} ions. Rutherford and Geiger succeeded in counting the number of α particles emitted per second from a gram of radium and found this to be 3.4×10^{10} particles per second. Each emitted α particle very quickly becomes a Helium atom by picking up electrons

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from surrounding gas molecules. By measuring the volume of helium gas produced by radium in a known interval of time, and from a knowledge of the rate of production of α particles, it should be possible to obtain the number of particles in a unit volume of helium gas under STP conditions [7]. However, this is complicated by the fact that radon (Rn^{222}), the radioactive decay product of the most abundant (> 99%) isotope of radium, Ra^{226} , is also a α emitter. Besides, radon, the subsequent decay products, namely Po^{218} and Po^{214} are also α emitters. However, the half-lives of Rn^{222} , Po^{218} and Po^{214} (3.83 days, 3.1 mins, and 0.00016 sec, respectively) are very much shorter than the half-life of Ra^{226} (1620 years). Therefore, it is possible to obtain the rate of production of helium gas from the initial decay of Ra^{226} by measuring the volume of helium gas produced by radium in a period much longer than the half-life of radon. Boltwood and Rutherford in 1911 measured the amount of helium produced by a sample containing only radium as the radioactive element, by trapping the α particles emitted by radium and its decay products. Their studies provided the volume of helium at STP produced by a known amount of radium at the end of two well-specified periods; 83 days and 132 days. Since the time periods after which the quantity of helium gas produced was much longer than the half-life of radon and other α emitters, the total amount of Helium produced, Q , in time, T , could be related to the rate of production of helium from one gram of radium alone, x , by the kinetic equation for successive reactions as, $Q = 4(1 - \frac{3}{4} \lambda_{1/2} T)Tx$, where $\lambda_{1/2}$ is the half-life of radon. Boltwood and Rutherford determined average x (from the two time periods) to be 0.107 mm^3 per day at STP which is equivalent to 5.55×10^{-14} mole per second. From this and the rate of emission of α particles from a gram of pure radium determined earlier, the Avogadro number turns out to be 6.1×10^{23} .

Black-Body Radiation

In 1900 Planck, by postulating that an oscillator can take up or release energy in discrete amounts (called quanta), obtained the radiation density law for the distribution of intensity as a func-



tion of frequency at a fixed temperature. Planck's law explained the then long standing puzzle of black-body radiation. Besides this remarkable achievement, amazingly, Planck could extract values for both the Planck's constant and the Boltzmann constant by fitting his expression to the existing data on black-body radiation. Since the gas constant, R , was experimentally known, he could obtain the Avogadro number. Equally remarkable was the fact that he could also obtain the charge of an electron from the value of a Faraday of charge measured from electrochemical experiments and the Avogadro number. The values of Planck's constant and the Boltzmann constant obtained by Planck are only off by less than 5% from their most modern values.

Electrochemical Method

Following the discovery of the electron towards the end of the 19th century, there were several attempts to measure the quantity of charge on an electron. Townsend in 1897 found that hydrogen and oxygen liberated by electrolysis of dilute acid or alkali solutions picked up charges (the fraction of molecules picking up the charge was one in one million) and when bubbled through water formed a charged cloud. Passing it through drying tubes and measuring their weight gain measured the total mass of the cloud. The average mass of the droplets was determined from the terminal velocity with which they fall in a viscous medium. From this data, Townsend obtained the number of droplets in the cloud. The total charge in the cloud was measured using a quadrant electrometer. Assuming that each droplet grew around a single ion, Townsend was able to obtain the electron charge. However, this experiment was very error prone due to evaporation of the water droplets. Millikan by using oil drops was able to measure accurately the charge on an electron. The charge of an electron given by the National Institute of Standards and Technology (NIST), is $- (1.60217653 \pm 0.00000014) \times 10^{-19}$ C. The charge carried by a mole of electrons, the Faraday, was known from electrochemical studies, being determined from the charge that is required to deposit one gram

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atomic weight of a monovalent metal ion (such as sodium from a solution of sodium chloride) at the cathode. The ratio of Faraday to the charge carried by an electron gave the Avogadro constant.

X-Ray Diffraction Method

The determination of the contents and dimensions of the unit cell of a crystal from X-ray diffraction techniques has been well established since early 20th century. From this data, it is possible to know the volume occupied by a single molecule in the crystalline state. The volume occupied by one gram molecular weight of the substance can be measured using a pycnometer. The ratio of the volume occupied by one mole of the substance in the crystalline state to volume occupied by one molecule in the crystal is the Avogadro number. While the underlying principle is simple, obtaining an accurate estimate of the Avogadro number by this method is nontrivial [8]. Firstly, the wavelength of the X-ray needs to be determined accurately and the X-ray source should be sharply peaked. Only in 1965, with the use of Tungsten $K\alpha_1$ line, was it possible to obtain an accuracy of ± 1 part per million in the measurement of X-ray wavelength. With this development, the accuracy was now limited by the presence of crystal imperfections, undetermined isotopic abundances in the sample and difficulties in measurement of density. To overcome the first two, highly perfect silicon single crystals of very high purity with Si isotopic abundance comparable to a standard reference material was used. The volume of the crystal was measured by hydrostatic means, using a fluorocarbon and this was standardized against the volume of precisely engineered steel spheres whose diameter was determined from optical interferometry. The Avogadro number given in the NIST website is $(6.0221415 \pm 0.0000010 \times 10^{23}) \text{ mol}^{-1}$, from these measurements is currently the best established value [9].

Summary

Beginning with the experimental efforts of Loschmidt in 1865,



the determination of Avogadro number has a fascinating history with many of the greatest names that laid the foundations of physics and chemistry being associated with it. Diverse experimental techniques that depend upon different properties of a single particle have been devised and in the process the atomic theory of matter has been firmly established. The most accurate method to date has been the one in which X-ray diffraction method is used to measure the microscopic density of a Silicon unit cell in an isotopically well characterized and highly perfect single crystal. The macroscopic density of the crystal is also precisely measured using highly sophisticated methods. Avogadro number determined from this method is accurate to better than one part per million. What is most impressive is that the value of the Avogadro constant measured from completely unrelated techniques agree very well with each other confirming the hypothesis postulated nearly two centuries ago!

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Suggested Reading

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