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The first and a recent experimental determination of Avogadro's number

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When a friend as Jesús is gone, your feelings of loss are overwhelming! Such that yourself can be lost, until you realize he is still influencing your own decision-taking processes. He is here as a model to follow! Sergio.

ABSTRACT

It has been almost two centuries since Avogrado presented his hypothesis, then, more than fifty years later Austrian Loschmidt developed a method for measuring the diameter of air molecules which was a big step for calculating a first approximation of the amount of molecules or atoms per unit volume. Computing Avogadro's with Loschmidt's diameter results give ten times the real value. It was until the beginning of the 19th century when Jean Perrin measured an accurate value of Avogadro's constant, which is the amount of elementary entities in one mole of substance. After him, many scientists have measured this constant using more accurate methods, one of them is the X ray diffraction method, which can reach accuracy of 99.99% using ^{28}Si.

Key words: Avogadro's constant, Avogadro's number, Loschmidt, Perrin, X-ray diffraction.

First experimental determination of Avogadro's number

It is not simple to decide who first determine Avogadro's number experimentally, in the following paragraphs we talk about some of the methods used for measuring this physical constant history. Afterwards, we compare it with a recent method that gives more accurate values for the constant. Avogadro's constant (formerly called Avogadro's number) is known as a physicochemical constant and is equivalent to the number of "elemental

entities", usually atoms or molecules contained in one mole of substance [1]. The value recommended since 2006 by the U.S. National Institute of Standards and Technology (NIST) is: N_A = 6.022 141 79(30) x 10^{23} mol^{-1} [2].

Avogadro's constant is named after the italian scientist Amedeo Avogadro (Figure 1), who in 1811 published "Essai d'une manière de determiner les masses relatives des molécules élémentaires des corps et les proportions selon lesquelles ells entrent dans ces combinaisons". In this paper Avogadro proposed that the volume of a gas at a given pressure and temperature is proportional to the number of molecules or atoms regardless to the nature of the gas [3].

Figure 1. Amedeo Avogadro

In 1865, the Austrian physicist Johann Loschmidt published "Zur Grösse der Luftmoleküle" which is translated into English as "On the Size of the Air Molecules". In this work, based on the Kinetic Gas Theory and previous results of Clausius, Maxwell and Meyer, Loschmidt derived an approximation of the size of the diameter of air molecules in normal conditions (0,970 nm, which is 2.7 times the real value). He also cites in his work "This result is only worthy for being an approximation, but it is not 10 times bigger or too small", then defined a condensation coefficient with the mean free path of a molecule at temperature of 273 K [4]. Knowing the diameter for molecules, and assuming that in the liquid state molecules touch each other, Loschmidt derived an approximation for the number of particles (atoms or molecules) of an ideal gas in a given volume (the number density) at standard temperature and pressure, N_L = 2,092 2 × 10^{25} m^{-3} [5]. The recommended value by NIST nowadays is N_L = 2.686 7774(47) x 10^{25} m^{-3} [2]. Now, let's not confuse the Loschmidt's constant with the Avogadro's constant, but if the Avogadro's constant would have been calculated using Loschmidt's method, by means of his result for the air molecular diameter, then N_A = 72 x $10^{23}mol^{-1}$ [6]. In 1873, James Clerk Maxwell also calculated Loschmidt's constant, obtaining N_L = 1,9 × 10^{25} m^{-3} [7]. Given that there are 2,24 × 10^{-2} m^3 in a mole of gas at normal temperature and pressure, this leads to an estimate of the number of molecules in a mole of 4.3 x 10^{23} mol^{-1}. In his Rutherford Memorial Lecture [8] Sir Charles Darwin wrote "The first estimate of Avogadro's number is due to Maxwell himself", expressing his astonishment that Maxwell "should have published a fact of such tremendous

manner that cannot have drawn much attention to it". Maxwell thought that he did not claim to communicate anything fundamentally new, but only to discuss a line of reasoning which Loschmidt had published eight years earlier in the *Proceedings of The Vienna Academy* [9]. Maxwell wrote [10] that he followed the track of Prof. Loschmidt, who had been the discoverer of a fact of tremendous importance; in his paper Loschmidt stated explicitly only the radius of the molecules, but as his argument included the assumption that in a liquid state the molecules physically touch each other, the number of atoms in 1 cubic centimeter can instantly be inferred from his result.

Brownian motion led to a more accurate determination at the beginning of the 20th century by Perrin [11] (1909, N_A = 6,7 x 10^{23} mol^{-1}), this is the first accurate result for the determination of the Avogadro's constant, after which more methods have been used: Millikan's oil drop experiment [12], Rutherford's counting of alpha particles emitted from radium and uranium [13], and Du Nouy's molecular monolayers on liquids [14]. In this text we are not going to focus on any of these methods but they are mentioned for historical reasons.

Recent determination of Avogadro's number

A modern way to get the Avogadro´s number is the X-ray diffraction experiments using the silicon ^{28}Si, which determines the size of an edge for a cubic crystal system [15]. The unit cell volume is then deduced, and used to calculate a value for Avogadro's constant. First, one must get an adequate crystal, pure in composition and regular in structure, with no significant internal imperfections. In principle, an atomic structure could be determined from applying X-ray scattering to non-crystalline samples. However, crystals offer a much stronger signal due to their periodicity since they are composed of many unit cells repeated indefinitely in three independent directions. Hence, using a crystal concentrates the reflection from the unit cell. The crystal is then placed in an area where monochromatic X-rays (single wavelength) are emitted. They are produced by a radioactive beam. The crystal is mounted for measurements so that it may be held in the X-ray emission and rotated. The principle is to place the crystal in a tiny loop, which will be rotated in respect of three different angles of rotation. Since both the crystal and the beam are very small, the required accuracy is about 25 micrometers. When the mounted crystal is irradiated, it scatters the X-rays into a pattern of spots. The relative intensities of these spots provide the information to determine the arrangement of molecules within the crystal in atomic detail. The reflected or deviated X-rays produce spots recorded on a screen placed behind. The intensities of these reflections are recorded with photographic film. Because a crystal structure consists of an orderly arrangement of atoms, the reflections occur from what appears to be planes of atoms [16]. A rotation step-by-step through 180° must be done in order to collect several data all around the crystal. Indeed, one image of spots is insufficient to reconstruct the whole crystal. It represents only a small slice. A full data set may

consist of hundreds of separate images taken at different orientations of the crystal. Finally, these data are combined computationally to produce and refine a model of the arrangement of atoms within the crystal. One must determine which variation corresponds to which spot. The final refined model of the atomic arrangement is called a crystal structure [17].

Since the crystal structure is determined, one can get the value of the parameter, a, length of one side. As the unit cell is cubic, the volume is the cube of the length. Hence, the unit cell volume is now known. The Avogadro´s constant is determined using the ratio of the molar volume, V_m, to the unit cell volume, V_{cell}, for a single crystal of silicon [1]:

$$N_A = \frac{8Vm(Si)}{Vcell}$$

The factor of eight arises because there are eight silicon atoms in each unit cell. Silicon occurs with three stable isotopes: the major stable isotope of silicon, 28 14Si, has fourteen protons and fourteen neutrons. It appears to over 92% of the element in nature. The atomic weight A_r is based on the stoichiometric proportions of chemical reactions and compounds [18]. Given that M_u, the molar mass, is constant, and with the measured density ρ of the sample, one can find the molar volume V_m by:

$$V_m = \frac{A_r M_u}{\rho}$$

In 2005, Fujii et al. measured Avogadro's constant with a X ray diffraction experimental setup, obtaining N_A = 6.0221353(18) × 1023 mol-1 [19].

Conclusion

In summary, Avogadro's constant was not measured by Avogadro, but it was measured based on his hypothesis. Loschmidt was the first to measure a similar concept called Loschmidt number that includes the number of molecules or atoms per unit volume for given a pressure and temperature. The accuracy was not very good (10 times the accepted value), due to his assumptions i.e. that the molecules are spherical and that all touch each other in a liquid phase in the same way, that does not happen exactly that way, but was sufficient to get an idea on the statistical errors and to prove Avogadro's hypothesis. Maxwell also obtained a value for the Loschmidt's number that was more precise. The Avogadro's number is the number of elemental entities per mole. Perrin was the first to give a real accurate estimation of the Avogadro's constant (differing ~10% of the 2006 NIST recommended value), and also to use the concept of mole in the definition, He also proposed that the constant would be named after Amedeo Avogadro. Till today more methods have been used for measuring the constant with better precision, one of the newest methods use enriched silicon-28 due to its known properties. In the X-rays diffraction method, the result of the experiment is quite more accurate than the approximation using Loschmidt assumptions. It can give 99.99% accuracy. This is explained by the precision of the used instruments, which enable placing accurately the crystal to the beam and

enable measuring the inference from reflections. Also, the molar mass and the atomic weight of the 28Si are known with precision. The 28Si is stable and enables to repeat the experiment in order to validate it. On another hand, one can say that it is uncommon to get all the instrumentations to manage this experiment, especially to get the adequate crystal or the X-ray beam which requires specific recommendations. Moreover the experimenter must have good experience and knowledge to analyze the results from the spots. In addition, the reflection of the X-ray will not always give clear inference. Hence, the X-ray diffraction enables to get accurate atomic structure but is not easy to implement.

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