Early Atomism

S Ramasesha

If all scientific knowledge were lost in a cataclysm, what single statement would preserve the most information for the next generation of creatures? I believe it is the atomic hypothesis that "All things are made of atoms – little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another." In that one sentence, you will see, there is an enormous amount of information about the world, if just a little imagination and thinking are applied.

– R P Feynman

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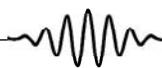
1. Divisibility of Matter

One of the earliest questions pondered over by natural philosophers concerned the limit of divisibility of matter. This question was common to many cultures and early recorded answers to this question are to be found in the Hindu and the Greek cultures, though it is not quite clear if the thoughts originally introduced by the Hindu School actually made their way to the Greek culture. The concept that matter cannot be divided infinitely was introduced in the Hindu culture by Kanada around sixth century BC who founded the *Vaisesika* school of philosophy to propagate his views [1]. He concluded that the limit of divisibility of matter was finite and called this *anu*. He also concluded that atoms of different materials were different in form. Furthermore, he postulated that atoms could combine to give new substances. Similar conclusions were arrived at by Leucippus and Democritus in the Greek school in the late fifth century, BC. They were of the opinion that world was made up of

atoms and voids [2]. Atoms, which are eternal, made up matter, and void, which is empty space, was required for motion of matter. This school also held opinions similar to Kanada; the form of atom was different in different matter. They went on to suggest that the shape of atoms in matter depended on its property, like for instance, the shape of atoms in sharp matter was angular, small, thin and much twisted, while atomic shape of sweet matter was round and quite large. Shapes and properties of atoms of a substance were thought to be derived from the color, taste, hardness and such other properties of the matter [3].

Empedocles, around the fifth century BC, introduced the four classical elements – earth, air, water and fire and suggested that all matter in the world was made up of these four elements. Combination of these elements in different proportions resulted in different materials. While this line of thinking is also to be found in other cultures of that period, the latter Greek philosophers who were strongly influenced by the Pythagorean School further assumed that the atoms were geometric solids, the faces of which were made up of isosceles triangles. They associated the regular shapes, tetrahedron, octahedron, icosahedrons and cube with the atoms of the four elements, fire, air, water and earth respectively. This school argued that since these shapes were all made up of triangles, atoms of a given element could be decomposed into triangles and reassembled into atoms of different elements [4]. The Hindu School digressed from theory of matter to issues concerning the spirit and inner self and thus material theories did not advance further. The Greek theories also did not make any further progress; Aristotle asserted that the fundamental 'elements' were not made up of discrete atoms but were continuous and considered the existence of void to be violation of the physical principles. This essentially led to the rejection of the hypothesis of atoms. Indeed,

this conflict between atomistic viewpoint of matter and continuous view of nature continued well into the early twentieth century! However, it is worth recalling at this point, one of the theories concerning fire which was propounded during the Middle Ages. It was proposed that all matter which can burn consists of a substance called phlogiston. When phlogiston leaves matter, it causes the matter to catch fire. The different inflammability of matter was attributed to different amounts of phlogiston in the matter.

2. Dawn of Experiments

These theories of matter and fire continued to dominate thinking until quantitative experiments were conducted, most notably by the French scientist Lavoisier. He introduced the practice of carefully weighing substances before and after a process such as burning. His careful experiments showed that the weight of a substance increased upon burning. This experimental result was contrary to phlogiston theory which would require a substance to lose weight upon burning due to loss of phlogiston. Thus, for the first time a postulate stemming from theory was subjected to experimental scrutiny and the consequence was that the phlogiston theory was discarded and quantitative experimental analyses of many chemical processes were undertaken. Based on these experiments the first operational definition of an element, namely, *an element is the limit of chemical analysis*, was arrived at.

This definition allowed for reclassifying a substance as a non-element, if new experiments showed that the substance could be chemically divided into simpler substances. Thus for instance, lime which was considered an element was reclassified as a non-element when it decomposed at temperatures which before that time could not be achieved in the laboratory. Chemical analysis thus produced a list of elements numbering about thirty

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during the early part of the eighteenth century. Most importantly these experiments gave rise to the laws of chemical combination [5].

These laws stated that (i) matter cannot be created or destroyed; (ii) elements combine in simple proportions by weight to form compounds; and (iii) if two elements, say A and B form more than one compound then the weights of B (for a fixed weight of A) in each of the compounds are in simple proportions. For example, it was observed that water is formed by the combination of eight grams of oxygen and one gram of hydrogen; similarly ammonia by the combination of fourteen grams of nitrogen with three grams of hydrogen. The third law is illustrated by considering the compounds ammonia and water both of which contain hydrogen. The ratio of nitrogen in ammonia to oxygen in water for one gram of hydrogen in each is 14:24. Those compounds that did not follow the second law of simple proportions were generally termed nonstoichiometric compounds. The understanding of these compounds, based on multiple valencies exhibited by some elements, such as the transition elements, had to wait till the early twentieth century.

3. Dalton's Atomic Theory

The laws of chemical combination led Dalton[1] to propose the classical atomic theory. He postulated that (i) an element is made up of identical atoms, and the atoms of an element are unique; (ii) individual atoms have a mass; (iii) atoms cannot be destroyed or created; and (iv) atoms combine to give molecules which are the basic units of a chemical compound. Dalton's theory, combined with the operational definition of elements and compounds, provided a definite experimental challenge, that of determining the atomic weight of the atom of an element. Since it was perceived that atoms were invisible, weighing a single atom of an element was

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considered experimentally impossible.

Dalton and others set out to establish a relative scale of the atomic weights. Since hydrogen was the lightest element known, it was used as a standard with its atomic weight taken to be unity. Furthermore, it was assumed by Dalton that the most abundant compound of two elements A and B consisted of diatomic molecules AB. Thus, it was assumed that water which is the most abundant compound of oxygen and hydrogen consisted of the molecule OH, in the current symbols for elements. Similarly, it was assumed that ammonia, the most abundant compound of nitrogen and hydrogen had the molecular formula NH and nitric oxide, the most abundant compound of nitrogen and oxygen, the formula NO. Since hydrogen and oxygen combined in the mass ratios 1:8, the relative atomic mass of oxygen was fixed to be 8. Similarly, the relative atomic mass of nitrogen was fixed to be 7 from the mass ratios of nitrogen and oxygen in NO. However, the experimental mass ratio in which hydrogen and nitrogen combined to give ammonia were 1:14/3, yielding a relative atomic weight of 14/3 for nitrogen, in conflict with the mass ratio fixed at 7 based on the assumed molecular formula for nitric oxide.

This inconsistency in determining the atomic weight of nitrogen could be traced to the molecular formula assumed for ammonia. However, moving away from this assumption threw up too many possibilities for this approach to be practical in determining relative atomic weights. This result was also in conflict with Prout's hypothesis that all atomic weights are exact multiples of that of hydrogen.

4. Avogadro's Hypothesis

During this period, a very important, yet seemingly simple, experimental development concerning the study of gases took place. This was the ability to collect gases

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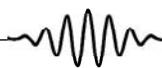
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evolved in a chemical process by the downward displacement of water. This method was modified by using mercury in place of water to collect water-soluble gases produced during a chemical process [4]. Together with the gas laws which had already been established, it was possible to have quantitative measure of gases involved in chemical processes. Based on the study of various chemical reactions involving gases, Gay-Lussac postulated his celebrated law of combining volumes: In a chemical reaction the gases of the constituent elements or compounds combined in simple proportion of their volumes measured under the same conditions. This was recognized to be the volume equivalent of the laws of chemical combinations.

Based on Dalton's atomic theory and Gay-Lussac's law, Avogadro[2] made his brilliant hypothesis: Equal volumes of gases under identical conditions of pressure and temperature contain the same number of particles. The hypothesis at first sight is counter-intuitive since the sizes of molecules of different compounds are not identical. Applying Avogadro's hypothesis to the observation by Gay-Lussac that two volumes of hydrogen and one volume of oxygen yield two volumes of water vapor, led to the conclusion that a molecule of water consists of half an atom of oxygen and one atom of hydrogen, which was in direct conflict with Dalton's atomic theory of the indivisibility of atoms. To counter this difficulty, Avogadro suggested that a particle of oxygen contains two oxygen atoms in combination. This suggestion was in direct conflict with the opinion of the time, influenced by people like Dalton and Berzelius, that two atoms of the same element repel each other.

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Although Avogadro's hypothesis was postulated in 1811, it took almost fifty years for it to be taken seriously. There were several reasons for the lack of attention to Avogadro's hypothesis. One of the factors was Avogadro's geographical isolation from the chemistry com-

munity of that period (most influential chemists of that era were in France and Germany), which limited his intellectual interaction with other chemists. Furthermore, the fact that the focus in chemistry at that time had shifted to organic chemistry was also, to an extent, responsible for this lack of attention. Besides these sociological factors, there were scientific issues as well. Lack of clarity in the use of the term 'molecule' was one. Besides, Avogadro's hypothesis was in direct conflict with the ideas of Berzelius that similar atoms repelled each other as well as 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 interpret Gay-Lussac's law. 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.

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5. Determination of Atomic Weights

Notwithstanding the above skepticism, Cannizzaro followed up on the suggestion of Avogadro and set out to obtain the relative atomic masses of elements. He obtained the relative mass of an element in many of its compounds and assumed the highest common factor of the relative mass as the atomic weight of the element. For example, the relative mass of chlorine in many of its compounds is 35.5 or 71.0 or 106.5, with the atomic mass of hydrogen taken to be one. Cannizzaro assigned the atomic mass of chlorine to be 35.5 which is the highest common factor. But, based on the laws of chemical combination, it is also possible that the actual atomic mass of chlorine is half of 35.5, but the fact that there did not exist compounds of chlorine in which the relative mass of chlorine was 17.75 or 53.25 meant that it was highly unlikely that the atomic mass of chlorine

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was 17.75 and not 35.5. Using this approach, Cannizzaro was able to obtain a set of atomic masses of various elements which was consistent and which was in agreement with Avogadro's hypothesis. The determination of relative atomic weights was a milestone in chemistry as it was possible to obtain molecular formulae of compounds from simple chemical analysis and the table of atomic weights. The relative atomic weights were calibrated with respect to oxygen atom whose atomic weight was taken to be 16 as this led to atomic weights of most elements being closer to whole numbers. Cannizzro presented his work at the 1860 Karlsruhe conference at which a consensus was arrived at on atomic weights, number and nature of the accepted elements and a cogent system of nomenclature. However, there was yet no experimental method for counting the number of molecules in a given volume of gas which would allow direct verification of Avogadro's hypothesis.

6. Periodic Properties of Elements

By the early 19th century, about fifty elements had been discovered and their properties investigated. Based on these studies, similarities in properties among groups of elements were observed. In 1829, Johann Dobereiner proposed his law of triads according to which elements can be grouped into triads and the properties of elements in a triad are similar. He also observed that the atomic weight of the middle member of the group was nearly the mean of the atomic weights of the end members. This law gained acceptance when the newly discovered element bromine had an atomic weight which was nearly the mean of the end members, chlorine and iodine. There were other interesting observations on groups of elements such as increase in the atomic weights in a given group in multiples of a fixed number, observed by Dumas.

More noteworthy contributions regarding the arrangement of elements based on atomic weights were the Chancourtois' telluric helix and the Newlands' law of octaves. The telluric helix was conceived on a cylinder with sixteen sections on the base (derived from the atomic weight 16 of oxygen) and a helix or line which descended from the top at an angle of 45 degrees, with the height of the helix from the top being proportional to the atomic weight. The elements were marked on the helix, according to their atomic weights. When the cylinder was laid out flat on a plane surface, the elements lying on the same vertical line on the helix were found to have similar properties. However, gaps in the helix were interpreted, not as new elements, but as different varieties of known elements.

Newlands, in 1865, after some earlier attempts, arranged 62 elements in order of increasing atomic weights from the work of Cannizzaro. He observed that the elements when classified into seven groups by collecting elements 1, 8, 15, etc., in the list into one group; 2, 9, 16, etc., in the list into a second group and so on, had very similar properties in a given group. It is worth mentioning that at the time of Newlands work, the inert gas elements were not known. However, there were some discrepancies and his work was very sharply criticized; but he was recognized later in life following the work of Mendeleev[3] and Meyer on the classification of elements in the form of a Table. The works of Meyer and Mendeleev were very similar and were almost done in parallel. While Mendeleev published his work in 1869, the work of Meyer was apparently given to a colleague in 1868 for evaluation, though it was published only in 1870. But, what is remarkable about the work of Mendeleev is that it showed similarities in properties in an entire network of vertical, horizontal and diagonal relationships. Mendeleev also found that seventeen elements had to be placed in new positions from those

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[3] See *Resonance*, Vol.5, May 2000.

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strictly indicated by atomic weights and some of these persisted even after correcting the atomic weights by careful redetermination. Mendeleev also predicted the existence of ten new elements of which seven were eventually discovered while three others do not exist. Understanding the origin of periodicity in the properties of elements had to wait until the discovery of the substructure of atoms.

7. The Concept of Valence

Another important concept that evolved from early atomism was that of valence. The laws of chemical combination had shown that the capacity for an atom to bind with others is finite and integral. This observation should have given rise to the concept of valence by the early part of the 19th century. However, the experiments of Davy as well as those of Berzelius led to the dualistic theory of atoms which held back the development of the concept of valence. In the dualistic theory it was assumed that electrical and chemical affinities were essentially the same. Atoms could be classified as electropositive or electronegative based on the electrode at which they were liberated in an electrolysis experiment. Thus, oxygen was considered the most electronegative element while metals were generally electropositive. Chemical combination was assumed to result from the mutual neutralization of the electropositive and electronegative elements. However, the compound thus formed was not necessarily neutral and could exhibit polarity, leading to further chemical combinations. It was also postulated that atoms themselves exhibited polarity, being positive towards some atoms and negative towards some others. While the dualistic theory was of some success in the understanding of inorganic compounds, the dawn of organic chemistry in 1830 and 1840 led to the demise of the dualistic theory.

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The modern theory of valence owes its origin to Edward

Frankland. Through his work on organometallic chemistry, he showed that a metal combined with one or more organic groups. Frankland considered organometallic compounds as those formed from inorganic counterparts by the replacement of an equivalent amount of organic radical. This was followed by the work of Williamson who suggested that certain specific atoms were required to hold other atoms together in a molecule. He showed that oxygen could hold two hydrogen atoms in water or two ethyl groups in ether. This idea was made explicit by Kekule[4] (1858), who through his analysis of organic compounds showed that a carbon atom is tetravalent in all its compounds. He further concluded that a carbon atom could bind to four atoms of a monovalent element or two atoms of a divalent element. He also pointed out that the apparent valence of two carbon atoms is six and not eight as each carbon atom uses one valence in bonding to the other.

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[4] See *Resonance*, Vol.6, May 2001.

8. Isomerism and 3-Dimensional Valence

Around this time, the molecular weights of organic compounds had been obtained by methods such as the vapor density method. The empirical formula was obtained from chemical analysis. Laurent and Gerhardt used the molecular weights and the corresponding empirical formula to obtain molecular formula of a large number of organic compounds. However, it was noted that there existed compounds with the same molecular formula but different chemical and physical properties. These were termed isomers by Berzelius. Kekule's theory of valence was developed further by Couper who represented molecules by structural formulae. It was recognized that isomers differed from each other in structure, in terms of the connectivity between atoms and hence possessed different properties. By about the mid 19th century, another form of isomerism was observed by Pasteur[5] in his study of the crystals of tartrate. He noted that there were two types of crystals which were mirror images

[5] See *Resonance*, Vol.12, January 2007.

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and rotated the plane of polarization of light incident on them in aqueous solution in opposite directions. In 1874, vant Hoff and Le Bel independently postulated that the four valencies of carbon are directed along the corners of a regular tetrahedron. This gave rise to the possibility that two molecules can be structurally identical but still possess different properties due to different arrangement of atoms in space. It is indeed a tribute to the far-reaching insights of the 19th century chemists that the concepts of molecular structure and valency have not undergone any major change subsequent to the discovery of atomic structure and developments of quantum mechanics.

9. 'Physicists' Views on Atomism

While much of the discussion above centers on the development of the atomic viewpoint by 'chemists', it is interesting to note that there was also a divide amongst the physicists until early 20th century. Influential physicists of that time such as Mach, Ostwald and Planck (the latter two in their earlier days) did not believe in atomism. Mach held matter to be continuous and was strongly opposed to the idea of atoms. On the other hand Boltzmann[6] used the atomistic models for developing the kinetic theory of gases and a statistical mechanical understanding of the thermodynamic behavior of matter. Indeed, in later years, the use of Boltzmann distribution by Planck[7] to explain black-body radiation led him to believe in atomism. Einstein's[8] explanation of Brownian motion as a fluctuation phenomenon further strengthened the atomistic view held by Boltzmann and his followers.

[6] See *Resonance*, Vol.6, September 2001.

[7] See *Resonance*, Vol.13, February 2008.

[8] See *Resonance*, Vol.5, March 2000.

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10. Determining Avogadro's Constant

One of the basic hypotheses on which the whole of atomic theory rested was the Avogadro's hypothesis. Experimental proof of this required counting the number of

particles in a given volume of gas. However, 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 an innumerably large number of molecules. This problem has a 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. Experimental determination of the number of particles in a given volume of gas would directly verify Avogadro's hypothesis and this presented a grand challenge to scientists which continued well into the 20th century.

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10.1 Loschmidt's Number

The 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

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

and 23% oxygen, Loschmidt estimated the density 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

$$V_m = V_s/f = N_A v = N_A \left(\frac{4}{3} \pi r^3 \right), \qquad (1)$$

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,

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

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, from the relation,

$$N_A \pi r^2 = V / \left(\sqrt{2} \lambda \right). \qquad (3)$$

Using equations (1) and (3), 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

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be known as the Loschmidt number. The best value estimated by Loschmidt for the Avogadro number was $\sim 4 \times 10^{23}$. Perrin obtained a better estimate for the atomic volume from van der Waals' equation of state,

$$(P + a/V^2)(V - b) = RT. \tag{4}$$

The parameter b in the above can be determined experimentally and as van der Waals[9] argued, it is four times the atomic volume. Perrin, by measuring b for mercury vapour and employing Loschmidt's approach, 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.

10.2 Perrin's Experiments

Perrin also devised a method for determining the Avogadro constant 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, and at a temperature T is given by the Boltzmann distribution

$$n_2/n_1 = \exp(-(V_2 - V_1)/kT), \tag{5}$$

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 $g(\rho_m \times \rho_l)/\rho_m$ 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

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size and density, by elaborate fractional centrifuging. He dispersed about 17,000 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. To determine the density of the particles, the mass of the Brownian particle was obtained by directly weighing a known number of particles. The radius of the particle and hence its volume (assuming perfectly spherical beads) was obtained from Stokes–Einstein law,

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

by measuring the diffusion coefficient D and using the known viscosity coefficient η of the medium, in terms of k. Then from (5), the value of k is obtained and subsequently, from the gas constant, the Avogadro number is determined.

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, s^2, per time step, averaged over all the beads, 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 (6) we can obtain the Boltzmann constant and hence the Avogadro number.

10.3 Avogadro's Constant from α-Decay

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 sec-

ond 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 from surrounding gas molecules. By measuring the volume of helium gas produced by radium in a known interval of time, and from 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 an 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 collected, 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 x of helium from one gram of radium alone by the kinetic equation for successive reactions as, $Q = 4(1 - \frac{3}{4}\lambda_{1/2}T)T\,x$ 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.

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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}.

10.4 Avogadro's Constant from Planck's Law

In 1900, Planck obtained the radiation density law for the distribution of intensity as a function of frequency at a fixed temperature by postulating that an oscillator can take up or release energy in discrete amounts (called quanta). 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 get 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.

10.5 Avogadro's Constant from Electronic Charge

Following the discovery of the electron towards the end of the 19th century, there were several attempts to measure the quantity of charge of 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, one could obtain 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
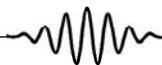
data, Townsend obtained the number of droplets in the cloud. The total charge in the cloud was measured using a quadrant electrometer. Assuming that each droplet grew around a single ion, Townsend was able to obtain the electron charge. However, this experiment was very error-prone due to evaporation of the water droplets. Millikan, by using oil drops, was able to measure accurately the charge of 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; it was determined from the charge that is required to deposit one gram atomic weight of a monopositive 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.

10.6 Avogadro's Constant from X-ray Crystallography

The determination of the contents and dimensions of the unit cell of a crystal from X-ray diffraction techniques has been well established since the 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 non-trivial [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, it was possible to obtain an accuracy of $\pm$ 1 part per million in the measurement of X-ray wavelength. With this development, the accuracy was now

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limited by the presence of crystal imperfections, undetermined isotopic abundances in the sample and difficulties in the measurement of density. To overcome the first two, 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 $(6.0221415 \pm 0.0000010 \times 10^{23}) \text{mol}^{-1}$, from these measurements is currently the best established value [9].

11. Conclusions

The progress in establishing the existence of atoms and using this to understand the structure of matter took the whole of the 19th century and can truly be called the century of the atom. Of course, the final proof of atomism rested on the determination of atomic weights and the Avogadro constant. These quantities have now been established with incredible precision by ingenious methods. The most accurate method to date for the determination of the Avogadro constant has been the one in which X-ray diffraction technique 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. The Avogadro number determined from this method is accurate to better than one part per million. What is most impressive is that the values of the Avogadro constant measured from completely unrelated techniques agree very well with each other validating the hypothesis postulated nearly two centuries ago! With this the existence of atoms was firmly established.

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