# Think It Over

This section of *Resonance* presents thought-provoking questions, and discusses answers a few months later. Readers are invited to send new questions, solutions to old ones and comments, to 'Think It Over', *Resonance*, Indian Academy of Sciences, Bangalore 560 080. Items illustrating ideas and concepts will generally be chosen.

## Avogadro Number

Answer to a question posed in Volume 1, No. 10, 1996 issue of *Resonance*.

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Avogadro number represents the number of elementary entities, which may be atoms, molecules, ions, electrons, or specified groups of such particles, in one mole of the substance. How was this value determined experimentally? Here is a summary, including some historical details which may interest readers.[1]

Amedeo Avogadro was born in Turin, Italy, in 1776. He began his career as a lawyer, but after taking some private instruction switched to the natural sciences. He eventually became professor of mathematical physics. His interests centred around chemistry. In 1809, Gay–Lussac reported that all gases expand by an equal amount when subjected to an equal rise in temperature. From this finding Avogadro deduced in 1811 that 'equal volumes of all gases at a given temperature and pressure contain the same number of atoms/molecules'. It was a remarkable insight. For example, Avogadro could derive the formula of water from the relative volumes of oxygen and hydrogen released during electrolysis of water. Unfortunately, the proposals remained obscure for over 50 years. Two years after Avogadro's death, Cannizzaro (famous for the reaction which bears his name) drew attention to the significance of Avogadro's Law. The 1811 paper was read again in 1860 at a conference in Germany to an appreciative audience. Many of the experimental findings of the intervening period fell into place.

Although Avogadro recognised that the number of molecules per unit volume of gas at a fixed temperature and pressure was

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[1] It took some time before the first response arrived. But the wait was worth it. Instead of a single answer, a collection of answers was sent by Tilottama Shrinivasa, a 12th standard student from Kendriya Vidyalaya, Indian Institute of Science, Bangalore, who used the internet effectively to find a lot of information.

constant, he could not estimate the number. Of particular interest is the number of molecules in one molar volume (22.414 litres) of a gas at standard temperature and pressure (STP, 0°C and 1 atmosphere pressure).[2] This corresponds to Avogadro number (denoted $N$, $N_A$, or $N_0$), a term introduced only in the twentieth century! In 1867 J Loschmidt, an Austrian high school teacher, attempted to quantify a related value, *viz.*, the number of molecules per cubic centimetre of an ideal gas at STP. The kinetic theory of gases was used to relate viscosity coefficient to the mean free path $l$, from which the number of molecules per unit volume was obtained. The estimate of molecular volume needed for this calculation was derived from the volume of the liquid formed by condensing the gas. He obtained a value for the Loschmidt number $L$, which was off only by a factor of 30.[3] In 1873, Maxwell used more accurate estimates and derived $N_A$ to be $4.3 \times 10^{23}$. Kelvin used scattering of light to determine molecular volume and obtained a value of $5 \times 10^{23}$ for $N_A$.

Avogadro number is related to two other important fundamental constants. The value $R/N_A$, where $R$ is the gas constant, is known as Boltzmann constant, $k_B$, while the charge of $N_A$ electrons is known as Faraday constant, $F$. Since $R$ and $F$ are accurately known from gas phase and electrolysis experiments, respectively, $N_A$ can be obtained from reliable measurements of $k_B$ or the charge of an electron, $e$.

Max Planck achieved a grand slam of sorts with his theory of black body radiation. In 1900 he derived the famous formula for the energy radiated by a black body at any frequency $\nu$ by postulating that the system was composed of oscillators whose energies were quantised in integral multiples of $h\nu$. Since the number of oscillators with a given energy needed to be computed, the Boltzmann constant entered the theory in a natural manner. By fitting his expression to the experimental data, Planck obtained the values of $h$ and $k_B$. From the latter, he worked out $N_A$ to be $6.18 \times 10^{23}$. Using the known value of $F$, he also calculated $e$ to be $4.69 \times 10^{-10}$ esu. Thus, one good theory could extract four fundamental constants from experimental data.

[2] I thank N K Maitra of Sri Aurobindo Institute of Applied Scientific Research, Pondicherry who drew attention to the fact that I had incorrectly stated normal temperature to be 25°C in the October 1996 issue.

[3] In German speaking countries, Loschmidt number refers to Avogadro number!

Molecular diffusion of colloidal particles provides a convenient means for determining Avogadro number. Einstein used his theory of Brownian motion to show that the diffusion coefficient is inversely related to the viscosity of the medium and the radius of the colloidal particles with the proportionality constant being $RT/6\pi N_A$. In 1906 he worked out a value of $4 \times 10^{23}$ from some experimental data on sugar solutions. He corrected the estimate to $6.56 \times 10^{23}$ in 1911. It is evident that the accuracy of the value depends strongly on the reliability of the estimate of the particle size. J Perrin carried out a series of classic experiments in 1908 using resins with uniform particle size. He used an ultramicroscope for accurate measurement of average displacements and the sedimentation technique to determine the particle radius. The resultant value of $N_A$ was $6.85 \times 10^{23}$. The credit of coining the term Avogadro number goes to Perrin.[4]

Rutherford and Geiger literally counted the number of $\alpha$ particles emitted from radium and uranium and estimated $N_A$ to be $6.2 \times 10^{23}$.

The well known Millikan oil drop experiment provided the first accurate measure of the charge of the electron and in turn, through the Faraday constant, a reliable value for $N_A$. In 1917, Millikan assigned a value of $6.06 \times 10^{23}$, which was used by American textbooks for decades.

A simple experiment by which Avogadro number can be determined was suggested by Lecomte de Nuoy. The amount of sodium oleate molecules required to form a thin monolayer film on the surface of water is determined. By estimating the size of a single molecule, the value of $N_A$ can be obtained. The value obtained in 1924 by this simple procedure[5] was $6.004 \times 10^{23}$.

An accurate method for determining $N_A$ is through X-ray diffraction in single crystals. Via Bragg's law, the procedure yields the dimensions of the unit cell to high precision, from which the unit cell volume $V$ can be obtained. The density of the crystal is given by $MZ/VN_A$, where $M$ is the molecular weight

[4] J Perrin received the Nobel Prize in Physics (1926) for his discovery of sedimentation equilibrium.

[5] Details of a simple version of this experiment can be obtained from J Chandrasekhar.

and $Z$ is the number of molecules per unit cell. The value of $M$ is obtained from mass spectrometry, while $Z$ is readily found through X-ray diffraction. Hence, a reliable value for crystal density would yield $N_A$. Many such experiments were reported during 1930–70. Using a combination of X-ray diffraction and optical interferometry, R Deslattes and coworkers studied very pure silicon crystals in 1974. The interferometry measurement was repeated by P Becker and coworkers in 1981. The value of $N_A$ by combining these studies is $6.02213 \times 10^{23}$.

After a detailed analysis of all the available data, the National Institute of Standards & Technology, USA recommends a value of $6.0221367 \times 10^{23}$, with an uncertainty of $0.0000036 \times 10^{23}$.

Many attempts have been made to highlight the enormity of this number through analogies. I welcome suggestions from readers.

By the way, larger numbers are encountered in chemistry. For example, if we decide to label the molecules in 18 ml of water, there would be $N_A$ factorial ways it can be done. In statistical mechanics, the logarithm of this quantity has to be computed. Remember the simple approximation for calculating this value?

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**A Poser**

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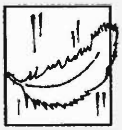
When we bombard $^{235}U_{92}$ with a neutron it undergoes fission, while $^{238}U_{92}$ on bombarding with neutron initiates $\beta$-decay and changes into $^{239}Pu_{94}$. According to neutron/proton ratio $^{238}U_{92}$ should be less stable than $^{235}U_{92}$. Then why does not $^{238}U_{92}$ undergo fission?



**Microexperiment**

Take a rubber tube and slide a metal ring onto it such that the ring stays put when you hold the tube vertically. Now stretch the rubber tube... What happens to the ring, and why?

*Quantum Kaleidoscope*
Sept–Oct. 1995.