

Solution to the Avogadro constant challenge

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The winner of the Avogadro constant challenge (published in issue 397/1) is:

Martin J.T. Milton, National Physical Laboratory, Teddington, UK

The award entitles the winner to select a Springer book of his choice up to a value of €75.

Our Congratulations!

The Avogadro constant has long been defined as the number of molecules of a substance in a gram molecular weight [1]. In a modern parlance, it is a fundamental physical constant representing the number of entities comprising 1 mol. It is clear that any modification to the definition of macroscopic (kilogram) or microscopic mass scales (atomic mass) will affect the numerical value of the Avogadro constant. The definition of kilogram has remained unaltered since the very first *Conférence Générale des Poids et Mesures* in September of 1889, when it was declared that the international prototype of the kilogram “shall henceforth be considered to be the unit of mass,” not so with the definition of the atomic mass scale. In 1803/1805, John Dalton established the first atomic mass scale in which hydrogen was assigned $A_r(\text{H})=1$, whereas the current definition sets $A_r(^{12}\text{C})=12$. In addition, there were *numerous* other scales used during the intervening years (Table 1). Though Dalton's H=1 mass scale was used in chemistry for nearly a century, many of these alternative scales, following a suggestion by Wollaston, employed oxygen as the standard instead—an idea which resurfaced near the end of the nineteenth century as the O=16 scale. With the discovery of

Table 1 Relative atomic mass scales through the centuries

19th century: average mass scale	
H=1 (O=5.5)	Dalton, 1803–5
H=1 (O=16)	Davy, 1812
O=10	Wollaston, 1813
O=1	Thomson, 1813, 1825
O=100	Berzelius, 1814
O=4	Griffin, 1834
O=16	Clarke, 1893
C=12	Hinrichs, 1893
20th century: isotopic mass scale	
$^{16}\text{O}=16$	Aston, 1931
$^{12}\text{C}=12$	IUPAC, 1961

Notations O=16 or $^{12}\text{C}=12$ describe the relative atomic mass (atomic weight) scale. When $m(\text{E})$ is the average mass of atoms of element E, the atomic weight of E is given by $A_r(\text{E})=m(\text{E})/m_u$, where m_u is the atomic mass constant. In the O=16 scale $m_u=m(\text{O})/16$, whereas $m_u=m(^{12}\text{C})/12$ in the $^{12}\text{C}=12$ scale

isotopes, the oxygen scale was refined to the ^{16}O isotope, albeit only among physicists.

The most recent change in the atomic mass scale occurred during the height of the cold war when the oxygen scale, $A_r(^{16}\text{O})=16$, was abandoned in favor of the current $A_r(^{12}\text{C})=12$ by the International Union of Pure and Applied Physics (Ottawa 1960) and by the International Union of Pure and Applied Chemistry (Montreal 1961) [2].

The relative atomic mass of the ^{16}O isotope in the ^{12}C -scale is 15.9949—a difference of 0.03% from the “old” value of 16.0000. This shift, in turn, alters the value of the Avogadro constant from 6.024×10^{23} to $6.022 \times 10^{23} \text{ mol}^{-1}$. This “change” in the numerical value of the Avogadro constant can be easily spotted by inspection of twentieth century chemistry textbooks [3].

It may be of interest here to mention an earlier story regarding the value of the Avogadro constant when determination of N_A involved measurements of lattice spacing in crystals [4]. In 1919, at a time when wavelengths could not be measured directly, Manne Siegbahn (1924

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Nobel Prize in Physics) proposed the 'local' non-SI unit of length for measuring the wavelength of x-rays. A student of Siegbahn, Erik Bäcklin, in his 1928 dissertation showed that wavelengths measured at incidence angles near grazing were 0.2% higher than the equivalent wavelengths measured by traditional crystal diffraction methods. This single discrepancy initially challenged the work of no less than five Nobel laureates-Richards, Bragg, Millikan, Siegbahn, and Compton. By the mid 1930s, however, a mistake was found in Millikan's classic elementary charge measurement due to an error in the value for the viscosity of air. Once this was

corrected the accepted value of the Avogadro constant dropped by 0.6% [5].

References

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