PAUL'S COLUMN ON MIC

The Avogadro number is an integer multiple of the number "1"

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In early civilizations, the question "how much is there?" could be related to a number of cattle, soldiers, days, or denarii (a denarius is a Roman silver coin current 187 B.C.-274 A.D.). It gave rise to the development of a numbering system 1, 2, 3, ... enabling to quantitatively express a number of things (generically called entities). Counting them by means of numbers is a very old way of obtaining an answer to the question "how much is there?" It also gave rise to special names for defined numbers such as a dozen (for 12) or a gross (for 144, i.e. 12 dozens). However, counting of things is only related to discrete entities since a fraction-of-entity is not meaningful nor even possible (that would destroy the very concept of discrete entity). The unit for measuring such numbers is quite simple: it is (the natural number) 1. Contrary to the requirement that results of measurements are expressed as a number times a stated unit [1], the unit is not written after the number in the case of counting because adding "times 1" after a number, is somewhat superfluous.

[Numbers are termed "natural" when fractions are not possible and "real" when fractions are possible such as in 17.52 m]

Numbers used in counting are independent of the nature of the entities. The quantity involved is "number of entities" which "can be regarded as a base quantity in any system of units" according to entry 1.4 NOTE 3 in [2]. Their measurement unit is one, symbol 1 "which can be

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P. De Bièvre (⊠) BE-2460 Kasterlee, Belgium e-mail: paul.de.bievre@skynet.be regarded as a base unit in any system of units" according to entry 1.10 NOTE 3 in [2]. According to another usage, the term used to designate a quantity ("number of entities") must not be used in naming the unit.

Twenty-first century analytical sciences make it possible that (very) small numbers of atoms and molecules can be counted in, e.g. a measurement of a few hundreds of atoms or molecules by isotope dilution mass spectrometry. Single electron tunnelling has been achieved and opens the possibility of counting single electrons. The number of particles in a specified volume of laboratory air in "clean" laboratories" for (ultra-) trace analysis, serves to express the quality of the laboratory air is, e.g. "class 100" when the air contains 100 or less than 100 particles of less than 0.5 µm per cubic foot (a US standard in the field). The simplest and most convenient unit to express such measurement results is (the natural number) 1. As the number of entities measured in analytical work becomes larger, counting of discrete entities comes with a significant measurement uncertainty (a rate of 10⁵ s⁻¹ can be achieved by modern ion counters with an acceptably small counting uncertainty such as $\sqrt{(10^5)/10^5} = 0.0031$).

For measuring or working with extremely large numbers such as of the order of 10^{23} , a unit consisting of an extremely large number (of the order of 6×10^{23}) was coined for use in the equations of statistical thermodynamics (nineteenth/twentieth century) where packages of extremely large numbers of atoms or molecules in gases are involved. It was coined the "mole". A value for this unit, formulated as a natural number, i.e. a multiple of 1 (and therefore an integer number, but that was not—yet—relevant) was not realistic as the idea of "single atom or molecule counting" was unimaginable in those days. Therefore, the large number in a unit "mole" was not defined as a fixed number of entities (multiple of 1)



contained in one "mole", but defined as "as many entities as there are ¹²C atoms in 12 g of ¹²C", still the definition of the mole today. This reference is usable for all kinds of entities. It is also metrologically appropriate to serve as "reference" in the meaning of entry 2.41 NOTE 1 in [2] for establishing metrological traceability, the conditio sine qua non for achieving "comparability of measurement results" (entry 2.46 in [2]) for the same kind of quantity. No need to know the "absolute" number of entities, taking a "package" is enough. An example of where large numbers of entities (e.g. OH⁻ ions in a solution) become measurable when they are compared to another equally large number of other entities (e.g. H⁺ ions)—defined as unit—is titration. When "equivalence" between number of OH⁻ and H⁺ ions is attained (as indicated by a colour change of the solution), the comparison of the very large unknown number to the very large known number leads to the unknown becoming a known thus being a "measurement". The number of entities involved is of the order of 10¹⁸ in a mL of solution containing a concentration of solute of about 2 µmol/mL. The operation "measurement" requires the concept of an appropriate unit "mole" as described above.

The possibility was created to think and work with a unit consisting of packages of entities of the same size. The unit was even termed a "base unit". It served well the intended use.

The question now arises: "of which quantity is the 1971 mol the unit?"

The answer to the question was coined for the 1971 definition of the base unit "mole": it is the base quantity "amount of substance". The problem was—and still is—that this base quantity was not a current concept in the minds and was not described before the coining of its unit. Thus, parlance developed in the laboratory practice to call it the "quantity of which the mole is the unit", which is not a logical application of the same rule as applied for all other quantities. A base quantity is either well known or conceived and described first, then a measurement unit is allocated to it [1]. For instance, we first conceived or simply understood "mass", then defined a unit for it: the

kilogram. We first conceived or simply understood "time", then defined a unit for it: the second. We first conceived or simply understood "electric current", then defined a unit for it: the Ampère.

Implementing the thinking in modern analytical science in terms of discrete atoms and molecules, the unit mole, defined as indicated above, can be replaced by a unit for large numbers which is defined as a multiple of the unit 1. Such a newly defined mole can equally serve as common reference for metrological traceability (entry 2.41 NOTE 1 in [2]) of measurement results, fulfilling the criterion imposed by the definition of metrological traceability and, hence, making these results mutually comparable, the goal of all measurement. The number of entities can be a number such as 10^{23} , the order of magnitude needed. But for reasons of continuity, it should be chosen as closely as possible to $6.022\ 14X\times10^{23}$. That is the Avogadro number.

It follows that the Avogadro number is a multiple of 1, thus providing a simple common reference, i.e. the definition of a simple common measurement unit (entry 2.41 NOTE 1 in [2]) for the analyst to make all results expressed in that unit, comparable to each other.

Even more important is the fact that this concept of a unit for analytical measurements is easily teachable from high school to undergraduate and graduate teaching levels.

As usual, any comment, question, or amendment is welcome, preferably as a contribution to the Discussion Forum of this Journal.

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