

On the need for analytical chemists (incl isotope mass spectrometrists) to re-think the mole

By Paul De Bièvre, August 2013

The discussion of a possible re-definition of the mole (as well as of the kilogram) is going on since several years in ... fairly small circles of persons commonly -but erroneously- called “metrologists” by people in the field. *Anybody* who makes measurements is a ‘metrologist’ (see entry 2.2 in [1]). Making the distinction between chemists (and physicists) performing measurements and “metrologists”, has caused havoc and confusion over decades.

We should stop making that distinction. All people doing measurements are metrologists and they should use a common language.

In the 2012 International Vocabulary of Metrology, VIM [1], we find the definition of ‘measurement unit’ (entry 1.9 in [1]) as well as that of that special unit called ‘SI unit’ (entry 1.16 in [1]). SI units are claimed to have to be available “to anybody any time” [2] which is an impressively useful concept coming straight out of the French Revolution: A L Lavoisier (1743-1793), one of the fathers of chemical insight in matter, stated in 1793 about the first SI units kilogram and metre: “man has never issued something grander than this” [3].

The acceptance of common units for analytical-chemical measurements should be “universal” to avoid unfair trade whenever analytical-chemical measurement results are involved (which is increasingly the case). The debate on a re-definition is also a debate on the concept of the quantity ‘amount-of-substance’ (and its unit mole, symbol mol), as chemical measurement is described by the Comité Consultatif pour la Quantité de Matière, Consultative Committee on Amount of Substance, CCQM. Hence, that debate should be intensely followed by the entire chemical measurement community, especially in IUPAC [4], and in bodies such as the IUPAC Commission on Isotope Abundances and Atomic Weights (CIAAW) and the IUPAC Analytical Chemistry Division Committee, as well as in EURACHEM, in CITAC, and in the Division of Analytical Chemistry of the European Association of Chemical and Molecular Sciences, EuCheMS. This need was stated in the 2010 and 2011 sessions of the CCQM [5-6].

That debate does not take place, let alone is it intense.

That constitutes a conceptual problem.

Modern chemical measurement instrumentation was developed to become impressively sensitive, enabling to measure concentrations of *very small numbers* of atoms and molecules per mass or per volume, rather than being based on the idea of working with “aggregates” of concentrations of *extremely large numbers* of atoms and molecules (of the order of 10^{23}) called a “mole”, per mass or per volume, or on the use of balances and weighing, a measurement procedure which implies chemically pure substances. To measure minor, trace and ultra-trace substance concentration, we use other -more direct- measurement procedures than weighing. Modern analytical instrumentation was developed, based on the exploitation of the particulate nature of matter from which we now know that it consists of particles (atoms and molecules). Tens of

thousands of such instruments (most of them called “spectrometers”) were built over the last decades.

It now seems that, very slowly, the chemical community is starting to pay an increasing interest in the matters related to the re-definition of the mole. It was the justification in 2011 for ACQUAL [7] to monitor these discussions and report on a number of remarks and criticisms of the proposals for such a re-definition (and -on the sideline- of the kilogram). Also stressed is now the importance of the acceptance -or lack thereof- of a re-defined mole in the analytical chemists’ community.

The basically different properties of matter called ‘mass’ and ‘numerosity’ [8-9] (better: ‘countability’ or ‘granularity’?), point to the need of dissociating these two quantities as well as their units, used to measure these properties. Since these two are independent ‘concepts’ in our description of nature -as prescribed by the International System of Units, SI [10]- one wonders whether both should not have their own -also independent- unit. It should be remembered that the original idea for an implied concept ‘mole’ in the new science called “chemistry” (which includes the notion of “analysis”), predated any official definition of a “mole” in the course of time (from 1743-1793: A L Lavoisier, to 1754-1826: to J L Proust, to 1766-1844: J Dalton, to 1776-1856: A Avogadro, to 1779-1848: J Berzelius, to 1826-1910 S Cannizzaro). An official unit mole was coined as SI unit only in 1971 [10]. *This definition only defined a kind of “thermodynamic mole”, not a number-of-entities.* For a long time, chemists used it in their thinking in stoichiometric work. It resulted in the elaboration of hypotheses about molecular structures, later proven to be impressively correct and easy to understand as they were a matter of ratios of integer numbers of atoms [11] and the at that time new entity called molecule. The thermodynamic unit was useful in physical chemistry as an ‘aggregate’ of an extremely large number (of the order of 10^{23}) per mol, rather than as ‘number-of-entities’ expressed in the unit one (symbol 1).

The oldest form of measurement was counting a ‘number of things’, called in generic terms: counting a ‘number of entities’ where entity is the more generic term applicable to whatever things are meant: apples, cattle, soldiers, events, currency units, etc. That is particularly true in analytical-chemical measurement where various forms of measuring ‘number-of-entities’ is ubiquitous up to and including in very basic usages:

- counting ‘number of protons’ (atomic number) is the very basis for categorization of the elements (in the Periodic Table of the Elements), which -in their combinations- give rise to an enormous variety of forms of matter
- counting ‘number of electrons’ in the atom, which constitute the very tool for interaction of matter thus leading to an enormous number of molecules each with a different property (the science of chemistry) [12],
- counting the ‘number of active sites’ on a complex protein molecule in modern insight in medicine (of basic importance in the battle between defending proteins from the immune system with invading proteins of viruses and bacteria)

- counting a ‘number of fission atoms’, products of radioactive decay, in river sediment and constituting proof of possibly unauthorized nuclear activities upstream which are to be reported to the Security Council of the United Nations Organization,
- etc

Yet, ‘number-of-entities’ does not have a place in the SI system. In the VIM [1], this deficiency has been remedied in entry 1.4, Note 3 in which it is stated that ‘number-of-entities’ can be regarded as a base quantity in any system of units (the SI is only one of the possible systems of units). Note that counting a ‘number of entities’ always requires the identification of the entities counted.

‘Numerosity’ [8-9] (better: ‘countability’ or ‘granularity’?) seems to be conspicuously absent in the SI whereas it is a basic property of matter and basically different from mass (apples, soldiers, atoms, molecules, active sites on proteins, generically termed “entities”), all being “counted” but all requiring the *identification of an entity* as well as a *base unit one*. Is this not given to us by nature? Is counting (for very large numbers this means “measuring”) [12] not a basic measurement technique requiring a base unit for measurement of entities (again: the idea of ‘entity’ being given to us by nature)? Formally speaking, this base unit is provided by the 2012 VIM [1], entry 1.10 Note 3: for number of entities, the number one, symbol 1, can be regarded as a base unit in any system of units.

There are a number of questions circulating which deserve an answer at the occasion of the re-definition of the mole. We make an attempt to identify them; their formulation is intended to confront the reader with his/her capability (or lack thereof) to answer them.

Question 1:

should ‘number-of-entities’ not be a base quantity in the SI as already hinted at in entry 1.4 Note 3 in [1]?

The mole is termed a base (measurement) unit of the SI in entry 1.16, Note 1, in [1]. Each of the seven base units is attached to a presupposed base quantity (entry 1.10, Note 1, in [1]). These base quantities are assumed to be independent of each other in the SI. Each base unit corresponds to only one base quantity (entry 1.14 in [1]). Should the mole not be independent in view of the totally different nature of the quantity ‘number-of-entities’? Since its inception in the SI, the mole is not independently defined, it is dependent on the kilogram. Doesn’t this dependence on the kilogram ignore the basic difference between two basic properties of matter: ‘mass’ and ‘numerosity’ (better: ‘countability’ or ‘granularity’?) upon which these two base quantities are to be based? Measurement results using the property of mass are expressed in the unit kilogram. Measurement results using the property of numerosity (countability/granularity?) are most easily expressed in ‘number-of-entities’. There seems now to be a growing consensus that this link with mass, although having been there for 40 years, should be cut, as is indeed done in the present state of the re-definition of the mole.

Question 2:

Shouldn't any re-definition of the SI unit mole not comply with the new VIM [1] patronized by eight international organizations through a formal internal review and internal voting procedure?

The present -1971- definition [10] makes the mole difficult to teach for all involved in teaching chemistry in general, and is difficult to use in chemical measurement in particular. What is more, it does not explicitly refer to 'number-of-entities' as a base quantity, thus not providing much needed clarity and simplification to the practicing analytical chemist in modern chemical measurement. Is that the reason why s(he) interprets the present mole as a number of entities in his daily work?

Do we talk about amount of length, or amount of temperature? or amount of time? Why should then a definition of the mole talk about amount of substance?

Question 3:

Before re-defining the mole, shouldn't we first lift the fog surrounding the concept 'amount-of-substance', the base quantity for the base unit mole? The dissatisfaction about the term (or concept?) 'amount-of-substance', goes up to the CCU who have asked IUPAC for a better term at the IUPAC General Assembly in Glasgow (2009). IUPAC did not succeed in providing one, nor did a discussion about this request take place within its structures. The unclarity about amount-of-substance is best demonstrated by the often encountered definition that it is "the quantity of which the mole is the unit". An amazingly circular reasoning.

Shouldn't ISO TC 12, our formally responsible body for quantities, not be formally consulted on that?

The present quantity 'amount-of-substance' with unit mole, may be useful in thermodynamics, but basically only there. When measuring number-of-entities, wouldn't it be much simpler and more straightforward to have a simple base quantity 'number-of-entities' with a simple unit: one? What is needed in thermodynamics can be built on this natural unit by defining an integer number (hence a multiple of one) of the desired size (of the order of 10^{23}), then allocating a name to this number.

Question 4:

Should a definition of the mole not be simple and transparent to teach to the general public, and certainly to the chemists at large? And therefore avoid to be connected to the multi-purpose use of the very general term "amount" in the English language?

In modern measuring systems (entry 3.2 in [1]) in chemistry, particularly in any type of spectrometer, a 'number of entities' such as photons, atoms, molecules are converted into charged particles which, subsequently, are all measured as electric currents, another base quantity in the SI [10]; the original neutral entities (atoms, molecules) "intended to be measured" (entry 2.3 in [1]), are converted to a proportional number of charged particles, then become "subject to measurement" [13]. All of these instrumental techniques have numerosity (countability/granularity?) at the core of their conceptual thinking. No mass measurements are involved: mass is here used to *identify* the entities, not to measure their number).

Is the base quantity ‘number-of-entities’ with associated unit ‘mole’ not de facto used already in all spectrometer types where ion currents i.e. electric currents, are used as proportional to ‘number-of-entities’?

Definitions such as “the mass of the kilogram is such that the value of the Planck constant is ...”, or: “the value of the mole is such that the value of the Planck constant is ...” (the present formulation of the re-definitions of SI units), are very difficult to teach at many educational levels despite their possible intrinsic scientific value in theoretical physics (the interrelationship of fundamental constants is very interesting, but its “uncovery” is a *consequence of measurements of the fundamental constants*, we can not say that it is their cause). Fortunately, after massive criticisms, these definitions have been dropped by the CCU in the ongoing discussions. The present formulations are:

“The kilogram, kg, is the unit of mass; its magnitude is set by fixing the numerical value of the Planck constant to be equal to exactly $6.626\ 06X \times 10^{-34}$ when it is expressed in the unit $s^{-1} m^2 kg$, which is equal to J s.

And the new proposal for re-defining the mole is

The mole, mol, is the unit of amount of substance of a specified elementary entity, which may be an atom, molecule, ion, electron, any other particle or a specified group of such particles; its magnitude is set by fixing the numerical value of the Avogadro constant to be equal to exactly $6.022\ 14X \times 10^{23}$ when it is expressed in the unit mol^{-1} .

Question 5

Chemists use the property mass and its unit kilogram. Is it not of importance that the re-definition of a mass measurement unit be teachable on the undergraduate/high school level? And that each re-definition should be seen as proportional to a physical, comprehensible mass (such as the mass of the ^{12}C atom, or the mass of the electron) opening the possibility of re-defining the kilogram as the mass of a defined number of entities as the IUPAC Commission on Isotope Abundances and Atomic Weights of the Elements [14] propose?

Question 6:

Ratios of the same measured quantity values on the atomic and macroscopic levels are identical. When we measure them on the macroscopic level (which we can), we learn about them on the atomic level (where we want to know them); this is the case, e.g., in studies of “stoichiometry” which is of fundamental importance to chemical measurement. For example, in the reaction $Si + 2F_2 = SiF_4$, the number-ratios $1/2$, $1/1$, and $2/1$ are important, rather than the mass of Si, F_2 or SiF_4 or their ratios. (Integer) numbers and their ratios are very basic in the thinking of chemists, especially in stoichiometric thinking and studies up to and including the ratios of numbers of (very) large molecules in immunology (see above).

Question 7:

Has the Avogadro number been changed/promoted to the state of being a fundamental constant whereas the concept conceived by Avogadro himself is in fact built around the concept ‘number-of-entities’ whereby the chemical identity of the entities was not important, just their number? That led to the need of a connecting (i.e. numerical) factor between the atomic and the macroscopic level. Any suitably large scaling factor could do, but it is just convenient to agree on 6.022×10^{23} exactly (x, y, z, being measured right now), “exactly” implying that all following decimals are zero. Wasn’t this underlying Perrin’s thinking when he made the first determination of the Avogadro *number* [15]?

Question 8:

Is the present dimension of the unit mole (being mol^{-1}) not an anomaly in a quantity equation for a number-of-things $Q = \{Q\} \cdot [Q]$, where $\{Q\}$ is a numerical value and $[Q]$ is a unit i.e. one thing? Then, with all three symbols standing for numbers, it is difficult to understand a unit $[Q]$ as another unit than one, i.e. mol^{-1} as is now the case. One would expect a positive integer number for the unit $[Q]$.

In other words, for measuring a number-of-entities, would quantity calculus not benefit if it would include the possibility of $Q = \{Q\} \cdot [Q]$ where every symbol stands for a number with dimension one?

Did not working with numbers (of entities) since a very long time make mathematics and their unchallengeable “stability” available as tools for describing measurement results in a very simple way?

Question 9:

Must not a (re)definition of a measurement unit for amount-of-substance refer to an ultra-stable reference which is unlikely to change for decades e.g. for measurement results of CO_2 number fractions in air, or for isotope abundances in elements? That can never be achieved by a measurement because a measurement result always carries a measurement uncertainty. But it can be achieved by a definition which does not carry a measurement uncertainty since it is not a measurement. Isn’t, therefore, not the simplest way to follow, and, most transparent, to define a (large) number (measurement uncertainty zero because not being measured but defined) as a unit?

General remark:

We cannot assume that we have now found the “ultimate” values of the fundamental constants. But we can assume that something like that exists. Hence, in the product of a numerical value and a unit (in the quantity equations above), we can consider to fix the unit by definition; better formulated: to fix a numerical value of the concerned quantity as unit. In the present proposal for re-definitions of the SI units, numerical values of the fundamental constants are fixed (the so-called “fixed constant” definitions) and the units made into variables. What is then the basis for picking a particular value for the numerical value concerned (see the quantity calculus under Question 8)? In particular in the light of the latest CODATA-evaluated values for the so-called fundamental constants, which have (again - as usual) changed relative to the previous CODATA-evaluated values?

Has the term “fundamental constants” been misused in all previously evaluated CODATA values because, apparently, the title should have been “numerical values for the fundamental constants” according to the presently used logic in naming?

Is the diagnosis given above, also valid for the Avogadro constant? If, indeed, it would only be a man-made concept for a number-ratio connecting the macroscopic and atomic level in the chemists' studies of molecules and their properties. It should not be dependent on changing CODATA-evaluated values every 6 to 10 years. Because that would then yield “variable” units as a matter of principle. Shouldn't it be the other way around? Shouldn't invariant units continue to be defined as abstract concepts in our model of nature (as is now the case) thus safeguarding the possibility in principle of observing (extremely small) changes of our fundamental constants in the future? If it is true that the Avogadro number is really what matters for chemists, and if it is simply defined as a number, then we would not make chemists' unit dependent on such possible variations. This leads to question 10.

Question 10: can the mole not be defined as $6,022\ 14 \times 10^{23}$ entities exactly (i.e. an integer number)?

In the margin of this question, some basic questions pertaining to the re-definition of the kilogram are:

1. Is the present definition not circular (at least in part)?
2. Can it not be defined as $1/12^{\text{th}}$ of the mass of a ^{12}C atom at rest and in the nuclear ground state i.e. one dalton (symbol: Da), multiplied by $6.022\ 14 \times 10^{23}$ exactly?

Acknowledgement: The author acknowledges with pleasure the exact sources of references [2-3] from Dr R Davis, until 2010-10-31 official guardian of “the” kilogram at BIPM in Paris-Sèvres

*The present definition of the kilogram (symbol: kg) (1989/1901/1999) is [12]:

The kilogram is the unit of mass; it is equal to the mass of the international prototype of the kilogram.

NOTE

The change of title from the 1st edn of the VIM in 1983 [16] and of the 2nd edn of the VIM in 1993 VIM [13] to the 3rd edn of the VIM in 2008/2012 [1] reflects a fundamental change of paradigm in our thinking about measurement. In the title of the VIM, 3rd edn, the definition of concepts has been given precedence over the definition of “terms” still explicit in the 1st and 2nd edns.

That is clarifying for the shift of accent from terms to concepts in the 2008/2012 VIM [1].

References

[1] BIPM, IEC, IFCC, ILAC, IUPAC, IUPAP, ISO, OIML (2008-2012), International vocabulary of metrology – Basic and general concepts and associated terms (VIM), 3rd edn, JCGM 200:2012 (JCGM 200-2008 with minor corrections)

<http://www.bipm.org/vim>

[2] quoted by J de Boer in his introduction to “Le Bureau international des Poids et Mesures 1875-1975, p 28, Ch 1, Fig 1, Médaille du Système Métrique frappée en 1840 d’après un projet de 1789: “A tous les temps. A tous les peuples”

[3] A L Lavoisier (1794), quoted by J de Boer in his introduction to “Le Bureau international des Poids et Mesures 1875-1975, p 13, Durand, Paris, ISBN 92-822-2031-1 as: “Jamais rien de plus grand et de plus simple, de plus cohérent dans toutes ses parties, n’est sorti de la main des hommes”, quoted in NBS Special Publication 420, p 6

[4] Consultative Committee on Amount of Substance, 16th session, April 2010, p 9,

http://www.bipm.org/en/committees/cc/ccqm/publications_cc.html

[5] CCQM 2010 Report 15th session, <http://www.bipm.org>

[6] CCQM 2011 Report 16th session, <http://www.bipm.org>

[7] The re-definition of the mole must be of high quality (2011), *Accred Qual Assur* 16:117-174

[8] R F Rocha, *J Chem Educ* 67 (1990) 139-140[

[9] De Bièvre P (2007), *Numerosity versus mass*, *Accred Qual Assur* 12 (2007) 221-222

[10] *Le Système international d’unités – The International System of Units SI*, edn 8, pp 115, 157, BIPM 2006, Paris-Sèvres, ISBN 92-822-2213-6 <http://www.bipm.org/vim>

[11] De Bièvre, P 2011, Integer numbers and their ratios are key concepts in describing the interactions of atoms and molecules, *Accred Qual Assur* 16:117-120

[12] De Bièvre, P (2006) Counting is measuring, *Accred Qual Assur* 11:

[13] BIPM, IEC, IFCC, IUPAC, IUPAP, ISO, OIML, International Vocabulary of Basic and General Terms in Metrology (VIM), 2nd edn, ISO 1993, entry 2.6

[14] Letter from the IUPAC–CIAAW (Commission on Isotope Abundances and Atomic Weights to the Secretary of CIPM and President of CCQM, 2011-09-23

[15] Perrin JB (1926) Discontinuous structure of matter, Nobel lecture 1926,

http://nobelprize.org/nobel_prizes/physics/laureates/1926/perrin-lecture.html

[16] BIPM, IEC, ISO, OIML, International Vocabulary of basic and general terms in metrology (VIM), 1st edn, ISO 1983, entry 2.09