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No Rationale for a Redefinition of the Mole

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Abstract: In the wake of the redefinition of the kilogram, the last unit of the International System of Units (SI) that is still based on a man-made artefact, discussions were launched on the necessity of redefining other units, amongst other the unit mole. Since 1971 the mole is defined as the amount of substance of a system that contains as many elementary entities as there are atoms in 0.012 kilogram of carbon 12. The symbol of the unit is 'mol'. When the mole is used, the elementary entities must be specified and may be atoms, molecules, ions, electrons, other particles, or specified groups of such particles. The definition is based on the pre-existing choice to set the relative atomic mass of carbon 12 equal to 12 exactly. In the proposed new definition the mole is the amount of substance containing exactly $6.022\,141\,79 \times 10^{23}$ atoms or molecules, ions, electrons, other particles, or specified groups of such particles, *i.e.* the Avogardo constant would have a fixed value without an uncertainty. This contribution critically examines the submitted arguments to justify the proposed redefinition of the unit mole by 2011 for their persuasive power to change a scientific and cultural good such as a unit of measurement. As shown, there are no convincing scientific arguments for a redefinition of the mole that stand a closer examination. The current definition is well understood, established in science and technology for almost 50 years and is still up to date.

Keywords: Avogadro's constant · Base unit · International System of Units · Mole · Redefinition

1. Introduction

The continuous improvement of the units of measurement is a task that evolves in parallel with the evolution of science and technology. The early man-made units have been replaced in the course of time one by one by more stable units that are preferentially based on constants given by nature. The last unit of the International System of Units (SI) that is still based on a man-made artefact is the unit of the mass, the kilogram. There is no dispute that this 19th century artefact of the SI should be removed. The work on that is ongoing. In the wake of the redefinition of the kilogram discussions on the necessity of a redefinition of other units have been launched, amongst others a possible new definition of the mole.[1–12] The proposed new definition is based on a fixed value for the Avogadro's constant.

Mills and coworkers have brought forward a series of arguments to justify a redefinition of the mole, *e.g.*[2,5,11,12]

- quantum metrology;
- lack of comprehensibility of the current definition;
- the desire to establish base units on true invariants of nature, *i.e.* on fundamental constants;
- dependence of the mole on the kilogram.

In ref. [11] we read: "*This follows from our desire to define each of the base units in relation to one of the fundamental constants of physics, or the properties of a simple atom, because we believe these to be the most stable and reliable constants of nature available. Specifically, new definitions are being considered for the kilogram, ampere, Kelvin, and mole. This is the subject known as quantum metrology, and the proposals are discussed in detail elsewhere.*" and eventually "*It is something of a paradox that such concepts as the quantity 'amount of substance' and its unit 'mole', so widely used by practical chemists, are also the subjects of widespread misunderstanding*."

In ref. [12] the authors quote: "*As discussed below, it is now being proposed that the link between the quantity amount of substance and the underlying concept of a number of entities should be strengthened by the introduction of a definition for the unit of amount of substance framed directly in terms of a fixed number of entities. This would break the direct link that exists at present between the unit of amount of substance and the unit of mass.*"

Units of measurements are scientific and cultural goods that must not be changed without convincing arguments. In the following chapters we subject the arguments cited above to closer examination.

2. Is There any Misunderstanding in the Concepts?

The argument 'quantum metrology' is not applicable to the mole and needs no further discussion. What about the comprehensibility of the terms 'amount of substance' and mole? The current definition of the unit mole is given in the Table.[13] The quantity 'amount of substance' and its unit mole are concepts that have a long tradition. Scientists like Dalton, Avogadro and others established these concepts in the nineteenth century. It is therefore surprising that in publications and presentations promoting a redefinition of the mole it is repeatedly claimed that there should be a misunderstanding in the concepts.[5,11]

The evoked 'problem' in the comprehensibility of the quantity 'amount of substance' is in fact a very simple problem: When the amount of apples has to be specified, two pieces of information have to be given:

1. What is the substance under consideration? → apples; *e.g.* Golden delicious.
2. How many apples are there? → number (of apples).

That's all. The same concept is valid in chemistry:

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Table. Current definitions of the units mole and second.

Term	Definition
mole	1. The mole is the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon 12; its symbol is 'mol'. 2. When the mole is used, the elementary entities must be specified and may be atoms, molecules, ions, electrons, other particles, or specified groups of such particles. It follows that the molar mass of carbon 12 is exactly 12 grams per mole, $M(^{12}C)$ = 12 g/mol.
second	The second is the duration of 9 192 631 770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of the caesium 133 atom. It follows that the hyperfine splitting in the ground state of the caesium 133 atom is exactly 9 192 631 770 hertz, ν(hfs ^{133}Cs) = 9 192 631 770 Hz.

1. What is the substance under consideration? → chemical substance; *e.g.* methane.
2. How many atoms or molecules are there? → number (of atoms or molecules).

In principle the only relevant difference between apples and atoms or molecules with respect to the quantity 'amount of' is their size; but that hardly hampers the comprehensibility: When we speak of apples, it may be adequate to state their numbers in units of one. If there's a grocer trading with a lot of eggs, it may be adequate for him to trade them in units of dozen. And since atoms or molecules are very small, it is adequate to express their numbers in a much larger counting unit, namely in N_A, the Avogadro number. As most substances in chemistry are molecules, it is reasonable to call this counting unit a mole. These simple facts are well explained in many introductory chemistry textbooks.[14,15]

That the Avogadro number cannot be 'counted' in a normal way, but can be realised by weighing poses no problem in comprehension (see Figure). It is a common procedure in trade and industry to count large numbers of identical, small items using balances. For instance, coins are routinely counted by precision balances, and people understand the difference between 'number of coins' and mass well. That among scientists and technicians '*the name mole has been – and still is – the cause of some confusion*' we consider as an assertion that is in contradiction to the rich textbook literature.[11]

Summarising:

1. The concepts of the quantity 'amount of substance' and its unit mole are easily comprehensible and perfectly explained in many introductory textbooks.
2. For the sake of comprehensibility a redefinition of the mole falls out of discussion too.

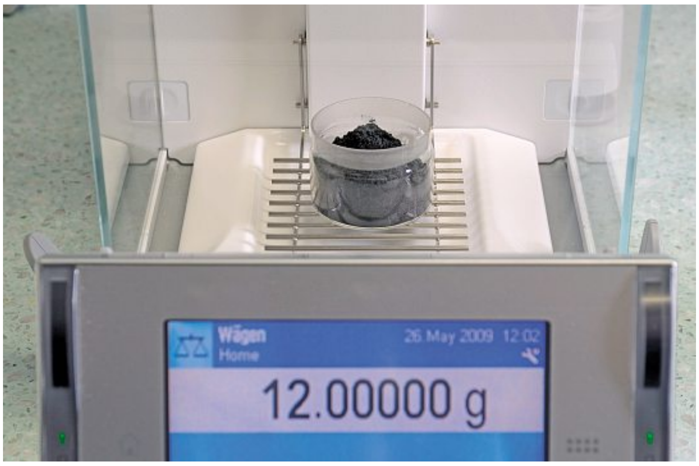

Fig. Primary realisation of the unit mole with gravimetry. 1 mol is the amount of substance of a system which contains as many elementary entities as there are atoms in 12 grams carbon 12. The depicted experimental realisation does not consider, among other factors, relative biases from the natural carbon isotopic composition ($\approx 10^{-3}$), the purity of graphite ($\approx 10^{-4}$), the air buoyancy correction ($\approx 10^{-4}$) and the chemical bonding energy of carbon in graphite ($\approx 10^{-8}$).

3. Is Avogadro's Constant a 'True Invariant of Nature,' *i.e.* a Fundamental Constant?

Avogadro's constant is an arbitrary number that has nothing to do with a 'true invariant of nature' or a fundamental constant. A fundamental constant in physics is understood as a constant that is given by nature and which is free of any human constructs, *e.g.* Planck's constant, the speed of light, the electronic charge or the rest mass of a fundamental particle. These constants are given by nature and can be measured. The Avogadro constant N_A is nowhere provided by nature, we have to prepare this number by using a balance. The mole definition tells us how we have to proceed.

For a comprehensive explanation of Avogadro's constant the reader is referred to the cited introductory textbooks.[14,15]

The status of the Avogadro constant is comparable with the number of periods used for the definition of the second, *s*. The current definition of unit 'second' is given in the Table.[13] This number tells us how many exactly fixed periods of the caesium radiation we have to sum up to get a second. In mass measurement of substances the Avogadro constant tells us how many atoms or molecules are contained in a mass with a value near the exactly fixed mass of the prototype of the kilogram.

4. Is There any Advantage with a Fixed Avogadro Constant?

For chemical reactions the numbers of reacting atoms or molecules have to be provided in stoichiometrically correct ratios. The mass ratios of single atoms and molecules are well known, whereas their absolute mass is less well known because of the approximately twenty six orders of magnitude between their mass and the unit of mass, the kilogram. For the analytical chemist, this is no problem. To get the correct particle number ratios he has to weigh the reactants simply according to their relative mass ratios. To that end the relative mass scale of atoms and molecules has to be fixed in some way. Initially, this was done by setting the relative atomic mass of hydrogen arbitrarily to 1, later the mass of oxygen 16 was chosen to be exactly 16, and nowadays the mass scale is determined by setting the atomic mass of carbon 12 to exactly 12.[16–18] For the sake of chemistry the choice to which entity the atomic mass scale is fixed is unimportant since it is sufficient for chemical reactions to know the mass ratios of the substances.

As mentioned in the introduction, a new definition is proposed based on a fixed value of the Avogadro constant.[2,5,10–12] If we could simply count the atoms and molecules one by one it would make sense to give Avogadro's constant N_A a fixed value and to work then with packaging units of N_A, similar to the grocer that may pack his eggs conveniently in packaging units of dozens. But since we cannot count the excessive large numbers of atoms and molecules in a mole we have to prepare packaging units of approximately N_A using the balance (see Figure). An Avogadro constant decoupled from the kilogram has neither a practical nor a scientific meaning. It is a simple number that we cannot count directly because of its excessive size. Decoupling Avogadro's constant from the kilogram is about the same as decoupling the number of periods in the definition of the second from the exactly fixed period of the caesium radiation: The number of periods would lose any meaning. In particular, giving N_A a fixed value does not remove in any way the uncertainty which is associated with the measurement of the mass of nucleons, atoms or molecules in a mass unit that is twenty six orders of magnitude larger.

It is evident that the unit mole is linearly dependent on the unit of mass, the kilogram. This does not hamper anybody, as the chemist is interested only in particle number ratios, not in absolute numbers. Amongst the base units of the SI there are many other dependencies (meter on the second, ampere on the kilogram, second and meter, and so on), and nobody cares about these because they have no scientific relevance. These dependencies arise from the fact that the definitions of the base units have changed over the last century and lost their initial status as independent reference measures.[19]

It is worth to note that if we were to introduce a fixed value for Planck's constant h in order to replace the kilogram prototype, the today's independent mass unit would become dependent on the second and the meter. This fact has never been used as an argument against the introduction of Planck's constant into the SI. Thus, the dependence of the unit mole on the kilogram is not a valid argument for a redefinition of the unit mole.

Summarising:

1. Avogadro's constant is a highly arbitrary constant that has nothing to do with a 'true invariant of nature' or a fundamental constant.
2. Giving Avogadro's number a fixed value would remove any practical and scientific significance from the constant. It would lose its natural significance as a link between the unit of mass and the mass of the atoms or molecules.
3. The uncertainty of measurement of the tiny mass of nucleons and atoms in terms of the kilogram cannot be removed by giving the Avogadro constant a fixed value.
4. The dependence of the mole on the kilogram is no argument against the mole definition.

5. Fixed Constants and Units

In order to make all quantities measurable that are used in science and technology, some measurable constants must be fixed by convention. Units are then a multiple or fraction of these fixed constants or of a combination of them. All other units and values can be derived. At least since Planck's paper in 1899 it became clear that five constants which allow the determination of values for length, mass, time, temperature and an electromagnetic quantity are sufficient (Planck did not adopt any electromagnetic units).[20] The underlying constants fixed in the SI are given in ref. [19].

No new 'invariant of nature' is needed to indicate the amount of a substance. This is the reason why the mole has never been addressed in all the many systems of units that have been studied in the past.[21,22]

Moreover, the 'constants' associated in the official SI brochure with the base units mole and candela are neither measurable artefacts nor measurable constants given by nature in contrast to constants fixed with the other base units.[13] Therefore, the 'constants' associated with the mole and the candela are not available for gauging a measuring instrument and shall not be listed with the constants fixed with the other five base units.

6. Conclusion

The definitions of base units are reproduced in innumerable official, scientific, educational and other texts. Therefore, a redefinition is justifiable only if there are important reasons to do so. As it was shown above, there are no convincing scientific arguments for a redefinition of the mole that stand closer examination. The current definition is well understood, established in science and technology for almost 50 years and is still up to date.

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