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FUNDAMENTAL PROBLEMS IN METROLOGY

IS THERE AN OBJECTIVE NEED FOR AN URGENT REDEFINITION OF THE KILOGRAM AND MOLE?

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Reasons for postponing the adoption of the new definitions of the SI kilogram and mole based on Resolution 1 of the 24th CGPM are discussed.
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At present, it is generally believed that the SI system of measurement needs modernization [1], particularly in relation to the definitions of the kilogram and mole. There is some disagreement about how and over what times the SI should be modernized. New definitions were proposed for four basic quantities – kilogram, mole, ampere, and kelvin – at the 24th General Conference on Weights and Measures (CGPM). However, because of some discrepancies in the results for the values of the Planck and Avogadro constants obtained by two different methods (Watt-balance [2] and crystalline silicon spheres [3]) the adoption of the new definitions was postponed until at least 2014, when the 25th CGPM will be held.

The International Bureau of Weights and Measures (BIPM) and the Consultative committee on the amount of matter and metrology in chemistry, in particular, have confirmed their encouragement for the study and discussion of possible variants of a review of the SI system, as noted in Resolution 1 [1]. We shall show that some important questions remain unsolved and even ignored and support the view that it is better to be conservative in adopting new definitions of the SI units of mass and amount of matter. In this regard, we examine three substantial reasons for the delay in adopting the new definitions of the kilogram and mole: first, since the publication of the new definitions, there have been substantial advances in experimental physics and technology and in data analysis, which could be used for redefining the SI units. Second, the scientific critique of the new SI by a number of writers and experts from international metrological organizations has not been answered by the architects of the new SI units and the BIPM. Third, correcting the deficiencies of the new SI units, if they are to be adopted in 2014, will require the expenditure of much time and money, so it is better to make the necessary corrections before the new SI units are adopted.

New Aadvances in Experimental Physics and Technology and in Data Analysis. Since the proposed redefinitions of the SI basic units were introduced in 2005 and 2006 [4, 5], there have been a number of key advances in physics and experimental data analysis which will have a direct effect on the basic principles of the proposed new SI units.

First, additional proof was provided that the fine structure constant and, therefore, the Planck constant, may vary with time and in space [6]. The authors of that study were awarded the Eureka Science Award in 2012. Changes of this sort in the constants may cause problems in fundamental metrology [7] and the existing proposals for the definition of the kilogram in terms of a fixed value for the Planck constant should be studied further in light of this new circumstance.

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Second, theoretical advances in statistics have led to new mathematical methods for combining data from different experiments [8]. In particular, CODATA uses a linear method and assumes normal distributions for the data in matching the values of the fundamental physical constants. A more general and unique "merging" technique was proposed [8] with which the calculations are easily done and which leads to a minimum loss of Shannon information when data from fundamentally different experiments are combined. The proposed new statistical method may help minimize the existing discrepancies in the experimental determinations of the Planck and Avogadro constants using Watt-balances and silicon spheres and, thereby, influence the choice of variants for redefining the four basic SI units.

Third, which may have the most direct bearing on the existing and new or modified SI units, there have been new discoveries in experimental physics and technology. In particular, the enhanced accuracy of the results from the International Avogadro Project for determining the Avogadro constant by the silicon sphere method [3] makes it the most precise method for determining the Avogadro and Planck constants. Thus, the definition of the kilogram by fixing the Avogadro constant and the mass of the carbon-12 atom is the most natural. This definition can be realized using spheres of crystalline silicon, as well as, for example, prisms consisting of sheets of graphene [9].

Another fact that casts doubt on the choice of defining the kilogram in terms of the Planck constant is an experiment in which researchers at the University of California and the Lawrence Berkeley National Laboratory used pulsed spectroscopy on recoil atoms to stabilize an oscillator and thereby provided a direct link between time and mass. As opposed to the auxiliary measurements and additional theoretical assumptions used in the Watt-balance method, the recoil method is based on simple physical principles and is reported to be 10 times more accurate than the methods for the existing SI units [10]. Recently, an optical clock based on spectroscopy of the Al^+ ion with quantum logic was constructed at NIST, which may be 100 times more accurate than cesium clocks [11]. Each of these discoveries requires a profound analysis by the BIPM before a final decision is reached on the redefinition of the kilogram and, perhaps, a new redefinition of the second [12].

Unanswered Questions Regarding the Shortcomings of the New SI Units. Claims of serious inadequacies in the proposed new SI units have appeared recently [13–19]. In a discussion of the planned transition to new definitions of the SI units, it was concluded [16] that "all the necessary conditions for this transition are not yet satisfied." The most important criticisms include the following: the proposed redefinition of the kilogram requires the introduction of a new quantum standard for current [13]; and the order of 10^{41} for some of the constants entering in the proposed new definition for the kilogram is physically unrealistic [14] as are the inconsistency and (or) circularity of the arguments in the proposed new definitions [15, 17, 20] (for example, in the definition of the second a temperature in kelvins is used for cesium atoms, while the definition of the kelvin depends on a value of the Boltzmann constant expressed in units involving the second [1, 21].)

On the Use of the New Definition of the Kilogram in the Educational Process. The President of the Consultative Committee for Units and other architects of the new SI units have declared that "since it is important that the basis of our measurement system be taught in schools and universities, it is preferable, as far as modern science permits, that the definitions of the base units be comprehensible to students in all disciplines" [5, p. 228]. However, over the seven years since the new SI units were proposed, no definition of the proposed kilogram on the basis of the Planck constant has been produced which would be suitable for publication in a textbook.

The following versions of a new definition of the kilogram based on the Planck constant exist [5]:

- *the kilogram is the mass of an object which is equivalent to an energy equal to the energy of a certain number of photons whose summed frequencies are* $(299792458^2/66260693)\cdot 10^{41}$ *Hz*;
- *the kilogram is the mass of an object whose De Broglie-Compton frequency is exactly equal to* $(299792458^2/6.6260693)\cdot 10^{-34}$ *Hz*; and
- *the kilogram is the unit of mass of an object such that the Planck constant is exactly equal to* $6.6260693\cdot 10^{-34}$ *J·sec*.

These definitions are not only hard to understand for "students in all disciplines." A detailed explanation of these definitions is also a complicated problem even for physics majors in universities, especially if they have not yet mastered quantum mechanics.

A Hidden New Fundamental Constant. As in the case of the redefined kilogram, the questions related to the redefinition of the mole are also confusing. A "new molar mass constant" M_u [1] in the proposed new SI is associated with a magnitude of 1 $g\cdot mol^{-1}$ in a way such that the difference between them "contains the same information carried by a coefficient

(1 + κ)” [22, p. L19], where κ was introduced in Ref. 5. In fact, κ could be designated as a new constant, so that the new SI depends on introducing a new or supplementary constant $M_u = (1 + \kappa)$ g·mol^{-1}.

It has also been noted [20] that unexplained and confusing *ad hoc* imprecise correction factors, such as (1 + κ), or the proposed “modified molar mass constant” still remain in the new SI. The question of changing the status of the molar mass constant has been discussed [13]. The developers of the new SI proposal simply conceal the constant κ inside the modified molar mass constant, by setting $M_u = (1 + \kappa)$ g·mol^{-1} [4, 5, 20]. Thus, the new SI is based on introducing a special new constant M_u, which should, however, vary from time to time subject to changes in the constants contained in it. Furthermore, a change in the molar mass constant

$$M_u' = M_u(1 + \kappa), \tag{1}$$

where $M_u = 1$ g·mol^{-1}, means that the molar mass of carbon-12 now comes to depend on the values of other fundamental physical constants, such as the fine structure constant α and the Planck constant h. This kind of dependence for M_u' leads to a need for repeated changes in a large number of values of molecular masses given in handbooks, textbooks, instructions, and data bases of various kinds. From a physical standpoint, this implies a false conclusion regarding the constancy of the mass of a given atom or molecule and its dependence, for example, on α. Thus, for example, the mass of the carbon atom must obey the formula

$$m(^{12}\mathrm{C})N_\mathrm{A} = 12M_u(1 + \kappa), \tag{2}$$

since, in terms of the new SI with the kilogram defined on the basis of a fixed value of the Planck constant and the independent definition of the mole on the basis of a fixed value of the Avogadro constant, it is necessary to avoid the constant M_u and replace it with the variable M_u' from Eq. (1), which contains

$$\kappa = 2R_\infty hN_\mathrm{A}/(A_r(e)\alpha^2 cM_u) - 1.$$

This happens because there is a known relationship between the speed c of light in vacuum, the molecular constant M_u, the relative atomic mass $A_r(e)$ of the electron, and the fine structure α, Avogadro N_A, and Rydberg R_∞ constants:

$$R_\infty/(A_r(e)\alpha^2) = M_u c/(2hN_\mathrm{A}).$$

Here $M_u = 10^{-3}$ kg/mol and $M_u = M(^{12}\mathrm{C})/12$, where $M(^{12}\mathrm{C})$ is the molar mass of carbon. At present, the constants c and M_u are fixed, while $A_r(e)$, R_∞, and α are determined experimentally to high accuracy (on the order of 10^9 or higher). If N_A is fixed, then a certain specified variable mass of the carbon atom results. In addition, in various areas of science and industry, the change in status of M_u that occurs when the kilogram is defined on the basis of the Planck constant h leads to more complexity in obtaining accurate measurements of the amount of a substance, such as the molar mass of any element X, which equals

$$M(X) = A_r(X)M_u', \tag{3}$$

where M_u' is the variable “molecular mass constant” introduced in Eq. (1) which will now depend on the relative experimental uncertainties at a level of 10^{-9}. These corrections cannot be neglected here, since the values of $A_r(X)$ are known with an accuracy of 10^{10} or better. This situation is unsatisfactory.

It is, however, possible to use another version of the redefinition of the kilogram which retains a relation of succession with the current SI. This version is based on fixed values of the Avogadro and molecular mass constants. Here it is desirable that the following quantitative criteria for succession and possible temporal instability be satisfied [23]: the consistency of new prototypes with the international kilogram prototype must be confirmed with a relative standard uncertainty on a level of $2\cdot10^{-9}$ and a possible temporal instability over a year on a level of $5\cdot10^{-10}$ or less. These quantitative criteria for consistency of new prototype kilograms with the international prototype kilogram and their stability follow from the required maximum accuracy for determining the Planck and Avogadro constants and maintenance of succession with the current SI, as well as a fixed temporal instability of the copy of the international prototype kilogram over 100 years [24].

Then the new kilogram 1 kg^* (here and in the following the units defined with a fixed value of N_A are indicated by *) can differ from the international prototype kilogram by no more than $2 \cdot 10^{-9}$ in terms of the relative standard uncertainty in accordance with the above criterion; thus, in formulas containing the Avogadro constant, determined to an accuracy of order 10^8, and the new kilogram, it is possible to set 1 kg^* = 1 kg. As opposed to Eq. (3), this is permissible for calculating molar masses, since the next relationship involves a quantity determined with an accuracy of order 10^8, and in this case, as opposed to Eq. (2), we have

$$m(^{12}C)N_A = 12M_u, \tag{4}$$

where M_u is the known molar mass constant, equal to 10^{-3} kg/mol, which is defined in terms of the existing SI.

From Eq. (4), we may conclude that for fixed values of M_u and N_A one also obtains a fixed value of $m(^{12}C) = m(^{12}C)^*$. This conclusion is entirely acceptable from a physical standpoint, since the mass of a carbon atom is a natural invariant. Thus, we obtain the following definition of the unit of mass: *the kilogram*, the unit of mass, is the exact mass $\{N_A^*\}$/0.012 of free carbon-12 atoms in a state of rest and in their quantum mechanical ground state.*

The great advantage of this definition of the unit of mass is that it simultaneously leads to a new definition of the unit of the amount of a substance: *the mole*, the unit of the amount of a substance, contains $\{N_A^*\}$ structural elements of the given substance.*

N_A^* must be taken to be the most accurate experimental value of N_A obtained, for example, in the international Avogadro project, which lies within the following limits with a confidence of 68% (the 1σ interval) [3]:

$$\{N_A^*\} = (6.02214066 \ldots 6.02214102) \cdot 10^{23}.$$

Since the fixed Avogadro number $\{N_A\}$ must be divided by 12 [23], we can choose

$$\{N_A^*\} = 602214087869325727188096.$$

These definitions of the kilogram and mole are consistent with the existing definitions of these units in the SI and with the relationship that exists between them. Therefore, in this case we can retain the existing values $M(^{12}C)$ = 12 g/mol and M_u = 1 g/mol. Thus, given the condition that the mole is already defined, we can, with retention of the existing relationship between the mole and the kilogram in the current SI, provide the following short definition of the kilogram [23]: *the kilogram* is the unit of mass such that the molar mass of carbon-12 is equal to 12 g/mol.*

Note that one consequence of a consistent fixing of the Avogadro N_A and molar mass M_u constants, which leads to a coupling between the number of carbon atoms specified by the kilogram and the number of these atoms that specifies a mole, is the fixing of two other constants: the mass of the carbon atom m_C^* and the natural unit of the amount of a substance [20],

$$1 \text{ ent} = \{N_A\}^{-1} \text{ mol}.$$

Thus, when we fix the Avogadro constant $N_A = N_A^*$, we obtain a mutually unique correspondence between the mole and the new unit of the amount of a substance, 1 ent, which in this case is the fractional unit of the amount of a substance. Similarly, when $M(^{12}C)$ and N_A are fixed, we have single fixed value of $m(^{12}C)^*$ and, thereby, a fixed value of the amu or dalton:

$$Da^* = m(^{12}C)^*/12.$$

We note that it has also been proposed [25] that a fixed value of $M(^{12}C)$ be retained, but with simultaneous fixing of the Planck constant h. Then the Avogadro constant remains unfixed and the current definition of the mole is retained. Nevertheless, there is another possibility – simultaneous fixing of N_A and $M(^{12}C)$ [23]. In that case, the Planck constant must be included in the class of electromagnetic quantum constants, which also includes the electronic charge e, and the Josephson

K_J and von Klitzing R_K constants. A consistent determination of the exact values of these constants is possible only after creation of a quantum standard for current [13] and a redefinition of the kelvin, kilogram, and mole.

Conclusions. The developers of the new SI recognize that key aspects of this system are extremely confusing. Besides the unresolved questions relating to the published scientific criticisms of the new SI and the subsequent scientific discoveries which could greatly improve the proposed changes, this certainly raises doubts about the validity of an urgent restructuring in the proposed form.

Thus, it is proposed that Resolution 1, adopted at the 24th CGPM, should be made more precise at the 25th CGPM, and that the Consultative Committee for Units (CCU) should revive the discussion on a review of the SI taking other points of view into account in order to correct the inadequacies that have been pointed out. It is best that observers and additional experts be admitted to the sessions of the CCU devoted to these questions [26]. There is no rigorous need for urgent adoption of the new SI, which, in particular, requires the introduction of a new constant κ and contains a number of poorly thought out definitions. If these things are not done, then later corrections to the new SI will involve great expenditures of time and money.

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