

On defining the mole so as to fix the value of the Avogadro constant N_A when the kilogram is defined so as to fix the value of the Planck constant h

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Introduction and Summary

The current SI definitions of the metre, second, and candela fix the values of the speed of light in vacuum c_0 , the ground state hyperfine splitting of the Cs 133 atom $\Delta\nu(^{133}\text{Cs})$, and the maximum spectral luminous efficacy K_m to have the exact values $c_0 = 299\,792\,458\text{ m s}^{-1}$, $\nu(^{133}\text{Cs}) = 9\,192\,631\,770\text{ Hz}$, and $K_m = 683\text{ lm W}^{-1}$ for radiation of frequency $\nu = 540\text{ THz}$, respectively. Further, for the reasons given in the recent paper of Mills, Mohr, Quinn, Taylor, and Williams [Metrologia **42**(2), 71-80 (2005)] and some of the other documents submitted to the 17th meeting of the CCU, it is likely that the kilogram will be redefined so as to fix the value of the Planck constant h , the ampere will be redefined so as to fix the value of the elementary charge e , and the kelvin will be redefined so as to fix the value of the Boltzmann constant k . The purpose of this note is to show how even with definitions for the six SI base units metre, kilogram, second, ampere, kelvin, and candela that fix c_0 , h , $\nu(^{133}\text{Cs})$, e , k , and K_m , it is still possible to define the remaining SI base unit, the mole, so as to fix the value of the Avogadro constant N_A . If such a definition were also implemented, it would mean that five of the seven SI base units would be tied to well recognized fundamental physical constants and that some important additional constants would be exactly known, for example, the Faraday constant F , the molar gas constant R , and the molar volume of an ideal gas V_m at a specified reference temperature T_0 and pressure p_0 . Looking to the future, it may also eventually be possible to redefine the second so as to fix the value of the Rydberg constant R_∞ , thereby allowing six of the seven SI base units to be tied to universal constants that do not refer to properties of a particular particle or atom.

Our analysis is given in some detail in the Appendix, but its main conclusions can be summarized as follows: The mole can be defined so as to fix the value of the Avogadro constant

N_A even if the kilogram is defined so as to fix the value of the Planck constant h with negligible negative consequences and many positive benefits. Simply stated, this can be done by uncoupling the definition of the mole from the kilogram as in the current definition, with the result that the molar mass of carbon 12 is no longer defined to be 12 g mol^{-1} . Nevertheless, the current definitions of the unified atomic mass unit u (also called the dalton, Da) and atomic mass constant m_u , namely, $1 u = m_u = m(^{12}\text{C})/12$, where $m(^{12}\text{C})$ is the mass of the carbon 12 atom, as well as the definition of the molar mass constant, $M_u = \text{g mol}^{-1} = 10^{-3} \text{ kg mol}^{-1}$, can remain unchanged. The relative atomic mass $A_r(X) = m(X)/m_u$ of an entity X of mass $m(X)$ can also remain unchanged, in which case $A_r(^{12}\text{C}) = 12$ as at present, and existing compilations of relative atomic masses of atoms, of molecules, and of the elements as they naturally occur remain unchanged. Indeed, the new definition can be implemented in such a way that the only consequence of the change is that the relation between molar mass and relative atomic mass, which is presently given by $M(X) = A_r(X)M_u$, would become $M(X) = (1 + \kappa)A_r(X)M_u$. The additional multiplicative factor $1 + \kappa$, where κ is experimentally determined [see Eq.(12)], is irrelevant (i.e., it exactly cancels) for molar-mass ratios in chemical reactions. Moreover, the factor is initially equal to 1, since initially $\kappa = 0$ with an uncertainty of only about 2×10^{-9} , and κ may be expected to remain equal to 0 to within about this amount indefinitely and to have an even smaller uncertainty. This means that for all practical purposes, molar mass can continue to be calculated from the product $A_r(X)M_u$, because the only effect of the factor $1 + \kappa$ would be a possible shift in the product and an additional component of uncertainty that are significantly smaller than the uncertainty of (i) practical mass measurements involving the macroscopic kilogram with which molar mass values are used; and (ii) values of $A_r(X)$ of real substances, which depend on stoichiometry, isotopic composition, impurity content, etc. Finally, we note that the fact that F , R , and V_m would become exactly known constants as a consequence of defining the mole so as to fix the value of N_A means that, with the exception of the coupling constants of the basic forces of Nature, such as the fine-structure constant α (and those constants dependent upon them), all fundamental constants not related to a specific particle or atom would be exactly known.

Appendix

1. Current definitions and relationships. The current definition of the mole reads

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.

(In this definition, it is understood that unbound atoms of carbon 12, at rest in their ground state, are referred to.)

An important consequence of this definition is that one mole of any specified entity X contains the exact same number of entities. The Avogadro constant N_A is defined as this exact number of entities per mole, and its current recommended value is $N_A = 6.022\,1415(10) \times 10^{23} \text{ mol}^{-1}$ [1.7×10^{-6}]. [Here and throughout this note, all values of fundamental constants are 2002 CODATA recommended values—see P. J. Mohr and B. N. Taylor, *Rev. Mod. Phys.* **77**(1), 1-107 (2005).]

The molar mass $M(X)$ of a specified entity X is the mass of one mole of X, and thus it follows from the above definition of the mole that the molar mass $M(^{12}\text{C})$ of the carbon 12 atom is $M(^{12}\text{C}) = 0.012 \text{ kg mol}^{-1}$ exactly. It is convenient to introduce the molar mass constant M_u , defined by

$$M_u = 10^{-3} \text{ kg mol}^{-1}, \quad (1)$$

in order to have the compact notation

$$M(^{12}\text{C}) = 12M_u. \quad (2)$$

It also follows from the definitions of molar mass and N_A that for any entity X

$$M(X) = N_A m(X), \quad (3)$$

where $m(X)$ is the mass of entity X. The molar mass of an entity is an important quantity, because it may be used to determine the amount of substance of the entity in a given sample.

The masses of atoms and molecules are most conveniently and accurately expressed not in the SI unit of mass, the kilogram, kg, but in the unified atomic mass unit u (also called the dalton, Da). A non-SI unit, it is defined according to

$$1 \text{ u} = m_u = \frac{m(^{12}\text{C})}{12}, \quad (4)$$

where m_u is called the atomic mass constant. The relative atomic mass $A_r(X)$ of an entity X, which is a dimensionless quantity, is then defined as

$$A_r(X) = \frac{m(X)}{m_u}, \quad (5)$$

which together with Eq. (4) gives $A_r(^{12}\text{C}) = 12$ exactly.

Equation (3) with $X = ^{12}\text{C}$, together with Eqs. (2) and (4), yield

$$M_u = N_A m_u, \quad (6)$$

and Eqs. (3), (5), and (6) lead to the following well-known expression for the molar mass of an entity X:

$$M(X) = A_r(X)M_u. \quad (7)$$

2. New definitions and relationships. Because the current definition of the mole depends on the kilogram, and we assume that the kilogram will be defined so as to fix the value of h and that the other SI base units will be defined as discussed in the Introduction and Summary, it is not possible to define the mole so as to fix the value of the Avogadro constant N_A while retaining its dependence on the kilogram. However, if one defines the mole so as to fix the value of N_A in a way that is independent of the kilogram, then there is no inconsistency between the definitions of the kilogram and mole. Such a definition of the mole might read

1. The mole is the amount of substance of a system that contains exactly $6.022\,141\,5 \times 10^{23}$ elementary entities; 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.

Clearly, this definition (i) retains the basic definition of the Avogadro constant as the number of entities per mole; (ii) fixes the value of the Avogadro constant to have the exact value $N_A = 6.022\,141\,5 \times 10^{23} \text{ mol}^{-1}$ without placing any restrictions on the kilogram; (iii) retains the basic relationship between the molar mass of an entity X and the mass of the entity as given in Eq. (3); and (iv) is more readily understood because of its simplicity than is the current definition while at the same time makes clear that the mole is a measure of a number of specified entities and has nothing to do with mass. Also, the new definition has no direct effect on the definitions of the molar mass constant, unified atomic mass unit, atomic mass constant, and the quantity relative atomic mass, as defined in Eqs. (1), (4), and (5). However, it does affect Eqs. (6) and (7), because they depend on the exact relation $M(^{12}\text{C}) = 12M_u$, which is a consequence of the current definition of the mole but is not necessarily true for the new definition. Thus, since

Eqs. (6) and (7) are not necessarily consistent with both the current definitions of the quantities that appear in them and the new definition of the mole, it is necessary to reconsider the definition of molar mass, or relative atomic mass, or even in principle the molar mass constant, in order to obtain new expressions consistent with the new definition of the mole. We address this issue in detail in the following two sections, although for simplicity we do not consider the possibility of redefining more than one of these quantities at the same time. As we shall see, the issue can be resolved quite satisfactorily.

3. Preferred approach to the calculation of molar mass. Obviously, the new definition of the mole does not alter the relationship between the molar mass of an entity X , the Avogadro constant, and the mass of the entity as given in Eq. (3). However, because of the new definition, the molar mass in Eq. (3) is changed to $\tilde{M}(X) = \tilde{N}_A m(X)$, where $\tilde{M}(X)$ is the molar mass of X when the mole is defined so that the Avogadro constant has the fixed value \tilde{N}_A . On the other hand, the Avogadro constant N_A in Eq. (6) cannot be replaced by the fixed value \tilde{N}_A without either changing the definition of M_u or m_u given in Eqs. (1) and (4), or including an additional correction factor in Eq. (6). We make the latter choice here and write

$$(1 + \kappa)M_u = \tilde{N}_A m_u, \quad (8)$$

where

$$\tilde{N}_A = (1 + \kappa)N_A, \quad (9)$$

and so the updated version of Eq. (7) is

$$\tilde{M}(X) = (1 + \kappa)A_r(X)M_u. \quad (10)$$

The factor $1 + \kappa$ can be evaluated from the definition of the Rydberg constant, $R_\infty = c_0\alpha^2 m_e/2h$, where α is the fine-structure constant and m_e is the mass of the electron, and the exact relation $M(^{12}\text{C}) = 12M_u$ given above based on the current definition of the mole, which together yield

$$N_A = \frac{c_0\alpha^2 A_r(\text{e})M_u}{2R_\infty h}, \quad (11)$$

and hence

$$1 + \kappa = \frac{\tilde{N}_A}{N_A} = \frac{2R_\infty \tilde{N}_A h}{c_0\alpha^2 A_r(\text{e})M_u} = 1 + 0.0(1.9) \times 10^{-9}. \quad (12)$$

The numerical value of the multiplicative factor $1 + \kappa$ is based on the 2002 recommended values of the relevant constants under the assumption that the kilogram and mole are defined so as to fix the value of the Planck constant h and Avogadro constant \tilde{N}_A to have their 2002 values but with no uncertainties, and also on the expectation that within the next year the relative standard uncertainty of the fine-structure constant $u_r(\alpha)$ will be reduced to about 9×10^{-10} from its present value of 3.3×10^{-9} . [If the latter value of $u_r(\alpha)$ is used, the relative standard uncertainty $u_r = 1.9 \times 10^{-9}$ in Eq. (12) becomes $u_r = 6.7 \times 10^{-9}$.] The important points concerning the factor $1 + \kappa$ are that it will initially be equal to one when the new definition of the mole is adopted, should never deviate from unity by more than a few parts in 10^9 , and its uncertainty should be sufficiently small that it can be considered negligible in calculating molar mass for use in the determination of amount of substance, since amount of substance determinations in the real world rarely, if ever, have relative standard uncertainties that approach 1×10^{-6} . Thus, for all practical chemical measurements, which is where the mole is used, molar mass should still be obtainable from the product $A_r(\text{X})M_u$ as in Eq. (7).

4. Other approaches to the calculation of molar mass. Equation (10), our preferred approach, is essentially one of three straightforward ways of adhering to a useful overall guiding principle, namely, that because Eq. (7) is so familiar and widely used, it would be helpful to retain an expression of the same general form for calculating molar mass when the mole is redefined so as to fix the value of the Avogadro constant. Although we prefer the solution offered by Eq. (10) for reasons that will soon become apparent, and therefore have included only it in the above Introduction and Summary, there are two other possible approaches that should be mentioned. In fact, all three possibilities may be summarized as follows:

Use a new equation for molar mass. This is the preferred approach as given by Eq. (10).

Define a new atomic mass constant. Equation (8) can be written in the form of Eq. (6) by defining a new atomic mass constant given by

$$m'_u = m_u / (1 + \kappa). \quad (13)$$

However, in this approach all existing compilations of relative atomic mass $A_r(\text{X})$ would no longer be valid and would have to be converted to compilations of $A'_r(\text{X}) = (1 + \kappa)A_r(\text{X})$.

Further, the relative standard uncertainty $u_r = 1.9 \times 10^{-9}$ of the factor $1 + \kappa$ is larger than that of some values of $A_r(X)$ and thus would increase the uncertainties of these values, in some cases by more than an order of magnitude. Finally, the compilations would have to be revised every time CODATA issued a new set of recommended values, because the value of $1 + \kappa$ [see Eq. (12)] will likely change slightly from one least-squares adjustment to the next due to slight changes in the recommended values of R_∞ , α , and $A_r(e)$. By way of comparison, such slight changes from unity are inconsequential in the first approach. Thus, we believe our preferred approach is the better of the two.

Define a new molar mass constant. Equation (8) can be written in the form of Eq. (6) by defining a new molar mass constant given by

$$M'_u = (1 + \kappa)M_u. \quad (14)$$

However, as already noted above, since the molar mass constant is simply a special name and symbol for the unit gram per mole, symbol $\text{g mol}^{-1} = 10^{-3} \text{ kg mol}^{-1}$, it would be inconsistent with the general practice in the International System of Units (SI), where there are 22 SI units with special names and symbols, to incorporate into the molar mass constant an experimentally determined multiplicative factor. Thus, we again believe that our preferred approach is advantageous.

Finally, we note that Eq. (8) can be written as $1 \text{ u} = m_u = (1 + \kappa)M_u / \tilde{N}_A$, which is to be compared to the corresponding relation from Eq. (6) based on the current definition of the mole, $1 \text{ u} = m_u = M_u / N_A$.