

# On the dimensionality of the Avogadro constant and the definition of the mole

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## Abstract

There is a common misconception among educators, and even some metrologists, that the Avogadro constant  $N_A$  is (or should be) a pure number, and not a constant of dimension  $\mathbf{N}^{-1}$  (where  $\mathbf{N}$  is the dimension amount of substance). Amount of substance is measured, and has always been measured, as ratios of other physical quantities, and not in terms of a specified pure number of elementary entities. Hence the Avogadro constant has always been defined in terms of the unit of amount of substance, and not vice versa. The proposed redefinition of the mole in terms of a fixed value of the Avogadro constant would cause additional conceptual complexity for no metrological benefit.

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## 1. Introduction

The Avogadro constant  $N_A$  is fundamental for connecting measurements made on macroscopic systems with those made on the atomic scale [1]. Jean-Baptiste Perrin was the first to coin the name “Avogadro’s constant” in his monumental 1909 paper *Brownian Motion and Molecular Reality* [2]. Although Perrin was not the first to estimate the size of molecules, the precision of his results effectively silenced the remaining sceptics of atomic theory and earned him the 1926 Nobel Prize in Physics [3]. It is worth briefly quoting from Perrin’s paper:<sup>1</sup>

“It has become customary to name as the gram-molecule of a substance, the mass of the substance which in the gaseous state occupies the same volume as 2 grams of hydrogen measured at the same temperature and pressure. Avogadro’s proposition is then equivalent to the following:

*‘Any two gram-molecules contain the same number of molecules.’*

This invariable number  $N$  is a universal constant, which may appropriately be designated *Avogadro’s Constant*. If this constant be known, the mass of any molecule is known: [...] The weight of a molecule of water, for example, is  $18/N$ ; that of a molecule of oxygen is  $32/N$ , and so on for each molecule. Similarly the weight of the oxygen atom, obtained by dividing the gram-atom of oxygen by  $N$ , is  $16/N$ ; that of the atom of hydrogen is  $1.008/N$ , and so on for each atom.”

“This invariable number  $N$ ” soon became known as “Avogadro’s number” [3] and treated as a quantity of dimension one, i.e. a pure number.

<sup>1</sup> The passage appears on pp 16–17 of the original article: the English translation is by Frederick Soddy, of isotope fame, and was published in 1910 by Taylor & Francis, London.



The error of incorrectly treating a physical constant as a pure number is hardly unprecedented in metrology. It also occurred in the conception of the electrical and magnetic units in the CGS system, where the electric constant  $\epsilon_0$  and the magnetic constant  $\mu_0$  were treated as dimensionless and equal to unity. This led to two systems of units, incoherent with one another and where, for example, electric resistance could have the dimensions of velocity.

In the case of the Avogadro constant, this error has had many consequences. The impression left on many students, and indeed reinforced by many educators and textbooks, is that the mole is simply a shorthand notation for some very large number – six hundred sextillion ( $6 \times 10^{23}$ ) to the first significant figure. A few of these students go on to become eminent metrologists, and there was significant opposition to the inclusion of the mole as a base unit in the International System of Units (SI) [4,5] as it was supposedly redundant to the kilogram. A recent proposal for the redefinition of certain SI base units [5] refers to the mole as a “counting unit”, even though the demonstration that it is impractical to count a number of the order of  $6 \times 10^{23}$  is a classic exercise in high-school chemistry lessons.

There have been several recent proposals to redefine the mole in terms of a fixed value of the Avogadro constant [5–8]. It would be most unwise to consider the redefinition of the mole without first addressing the misconceptions surrounding both the current definition and indeed the very concept of amount of substance.

## 2. Amount of substance

The concept of amount of substance is one of the most fundamental principles in chemistry: it predates Dalton’s atomic theory and, arguably, even Lavoisier’s concept of the elements.<sup>2</sup> The law of definite proportions is usually attributed to Joseph Proust [9], although the term “stoichiometry” had already been coined by Richter in 1792 [10,11].

Wherever lies the priority, it is clear that these earlier chemists had realized that mass was not a sufficient defining property in chemical reactions, and that the ratios of reacting masses also had chemical significance. By a judicious choice of one of the components as a reference point, the ratios become very close to simple fractions. Dalton combined this empirical observation with Lavoisier’s concept of the chemical element to create his atomic theory.

To illustrate these early concepts of amount of substance, let us take a generic chemical reaction between substance E and substance F to form the desired substance G:



The practical problem is to find the ratio of masses  $m(E)/m(F)$  that will react together: from that ratio, the masses of the individual reactants can be calculated for any given situation. Wenzel (1777) gave values of  $m(E)$  and  $m(F)$  for each reaction, which was already an innovation in affinity tables. Richter realized that the ratios  $m(E)/m(F)$  could be reduced to (relatively) simple fractions, at least among a related set of reactions such as acid–base reactions, by choosing a particular value for one reactant Q [11]. By defining a factor  $\chi(X) = m(X)/m(Q)$ , which can be determined by the multiplication of other empirical mass ratios, it is easy to see that

$$m(E)/m(F) = \chi(E)/\chi(F) \quad (2)$$

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<sup>2</sup> There is some disagreement as to whether Carl Friedrich Wenzel’s 1777 work *Lehre von der Verwandtschaft der Körper* (“Lessons on the Affinity of Bodies”) constitutes a discovery of the law of definite proportions, as Berzelius believed it did [10]: Wenzel’s use of mass ratios is only implicit in his work. Henry Cavendish was certainly aware of the principle of equivalent weights and, from his notebooks, it can be calculated that he used 100 pennyweights (155 g) of marble ( $\text{CaCO}_3$ ,  $M_r \approx 100$ ) as his standard for his conductivity experiments (1777): see [12]. Cavendish, however, never published his work on equivalent weights.

Dalton introduced two major innovations in this system. Firstly, he envisaged that reactants E and F might be combinations of different chemical elements: if E, for example, is actually a 1:1 combination of A and B then, by conservation of mass,

$$\chi(E) = \chi(A) + \chi(B) \quad (3)$$

Having reduced the system of factors down to the level of the elements, Dalton then made the non-trivial choice to refer all masses to the mass of hydrogen, the lightest of the elements [13]. With this, the system of factors for the chemical elements became the system of atomic weights.<sup>3</sup>

Virtually simultaneously with Dalton's work, Joseph-Louis Gay-Lussac realized that the law of definite proportions could be extended from ratios of masses to ratios of volumes of gases at a given temperature and pressure [14]. By the end of 1809, and through empirical observations, the chemical concept of amount of substance had been defined as a series of ratios of measured macroscopic quantities: it would wait another 150 years to be named [4].

The modern definition of amount of substance is slightly different, at least at first sight. Amount of substance  $n$  has been defined as a physical quantity that is proportional to the number of (specified elementary) entities  $N$ , where the proportionality constant is the same for all samples [15,16].

$$n \propto N \quad (4)$$

This definition can be traced back to Avogadro's famous hypothesis in 1811 that equal volumes of gas at equal temperature and pressure contain equal numbers of molecules [17]. However, Avogadro's hypothesis (now Avogadro's law) was almost completely ignored in the first half of the nineteenth century: it relies on an acceptance of atomic theory that was far from universal at the time. On the other hand, the laws of constant and multiple proportions *were* generally accepted among chemists, and were a sufficient basis for the research on atomic weights and stoichiometry [18,19].

It is not necessary to know the value of the proportionality constant in equation (4) for purely macroscopic measurements. The proportionality constant is  $1/N_A$ , and this is one way to define the Avogadro constant independently of a system of units, but more than a hundred years passed from the discovery of the rules of stoichiometry to the first precise measurement of  $N_A$ . Even today, chemists have little use for the definition in equation (4): instead, the "chemical" definition of amount of substance [20] is

$$n = m/M = m/M_u A_r \quad (5)$$

This is simply a restatement of the nineteenth-century concept in modern terminology, but it can be seen to be equivalent to equation (4) if we assume

$$m \propto N \quad (6)$$

which is simply Dalton's atomic theory. The definition of the Avogadro constant becomes

$$N_A = M(X)/m(X) = M_u A_r(X)/m(X) \quad (7)$$

where  $m(X)$  is the mass of any individual entity X. Equation (7), with X as the electron, is the method used to calculate  $N_A$  in the CODATA adjustments of the values of fundamental physical constants [21]: the electron mass  $m_e$  can be calculated from spectroscopic data

<sup>3</sup> Throughout this article, the term "relative atomic mass" is reserved for the relative masses of individual nuclides, while the term "atomic weight" is used for the mean of the relative atomic masses of the isotopes of a given element weighted according to their amount fractions in a given sample or in normal terrestrial samples. Only relative atomic masses (as defined here) can be expressed as absolute masses in daltons (atomic mass units): no physical chlorine atom, for example, has a rest mass of 35.453(2) Da. See [4] for further discussion of the distinction. Unfortunately, relative atomic mass and atomic weight share the same symbol  $A_r$ , which is used here for the (weighted mean) relative mass of any elementary entity.

through the Rydberg constant  $R_\infty$ , while the electron relative entity mass  $A_r(e)$  can be measured, giving

$$N_A = M_u A_r(e) / m_e = c_0 \alpha^2 M_u A_r(e) / 2 R_\infty h \quad (8)$$

Equation (7) gives a clear, practical definition of the Avogadro constant that is independent of the system of units:  $N_A$  is the ratio of the molar mass to the mass of a single entity, whatever unit of molar mass we choose.

### 3. Historical unit of amount of substance

Amount of substance was not only anonymous in the nineteenth century, it was also without a clear unit with which to measure it.<sup>4</sup> This did not seem to bother the early chemists, who were working in terms of series of ratios (mass ratios, volume ratios, heat capacity ratios, etc.), although explanations of stoichiometry often used examples where the numerical value of the reacting mass in grams was equal to the atomic or molecular weight (or a simple multiple thereof) [22]. It became problematic when chemical measurements had to be related to measurements in physics, in the mid-nineteenth century.

The combination of Boyle's law and Charles' law gives

$$pV = R_{sp} T \quad (9)$$

where  $R_{sp}$  is a constant now known as the specific gas constant, because it is defined in terms of unit mass (although it is also 'specific' to each individual gas). The well-known derivation of the proportionality between  $pV$  and  $T$  from classical mechanics was developed (independently) by August Krönig [23] and Rudolf Clausius [24] in 1856–1857. Clausius noted that  $R_{sp}$  for different gases was inversely proportional to the density of the gas [25], although he does not seem to have considered the matter any more than that. Gas densities (at constant pressure and temperature) were known to be proportional to molecular weight from the work of Gay-Lussac and Dumas: had Clausius thought to multiply his specific gas constants by the molecular weight of each gas,<sup>5</sup> he would have obtained the modern molar gas constant  $R$ .

Amount of substance  $n$  is not a 'natural' base quantity in kinetic theory, despite its appearance in modern versions of the ideal gas equation

$$pV = nRT \quad (10)$$

The related quantity that appears most often in the equations of kinetic theory is the number density of molecules. Hence it is understandable that, when Josef Loschmidt made the first estimate of the size of gas molecules in 1865 [26], it was interpreted in those terms.<sup>6</sup> The term "Loschmidt constant" is still used to refer to the number density of molecules in an ideal gas at a (specified) standard temperature and pressure: it has also been used, particularly in German-language works, as a synonym for the Avogadro constant [27], hence the alternative symbol  $L$  for  $N_A$ .

<sup>4</sup> The discussion as to whether the "equivalent" or "equivalent weight" was a true measurement unit of amount of substance is beyond the scope of this article. Suffice it to say that it was not a *simple* unit, and that its shortcomings were well apparent by the mid-nineteenth century [18].

<sup>5</sup> In modern terms, this statement is dimensionally inhomogeneous, as one should multiply by the molar mass (and not the molecular weight) to obtain the molar gas constant. However, the distinction between molecular weight and molar mass was not clear in Clausius' time, and the statement would have seemed dimensionally reasonable.

<sup>6</sup> Loschmidt did not give an explicit value for the constant that now bears his name, but the calculation of the number density was quickly seen as a trivial extension of his method to estimate molecular size.

The description of the colligative properties of dilute solutions presented greater problems, as can be seen from François-Marie Raoult's 1882 paper on the general law of freezing-point depression [28]. When Raoult refers to "the lowering of the freezing point caused by one molecule dissolved in 100 grams of liquid," he is obviously not using the term "molecule" in its usual sense, but rather in the sense that we would use the term "mole" (he even uses the symbol "mol"). Yet Raoult also uses the term "molecule" in its usual sense, as in "the physical molecules, which act here, can be formed of two, and exceptionally, three, chemical molecules" (describing the dimerization of short-chain carboxylic acids and the anomalous behaviour of water) [28]. This duality of meanings for the same word is obviously confusing, although it found its way into late nineteenth century textbooks without comment, even on translation [29]. The matter was clarified by the introduction of the term "gram-molecule", which was still a relative novelty at the time of Perrin's experiments [2].

But was the gram-molecule a unit of amount of substance? The definition cited by Perrin [2] suggests a volume, whereas the name – and definitions of the type "molecular weight multiplied by grams" – suggest a mass. On the other hand, it was obviously a measurement concept that was different from mass or volume, a quantity of a different kind, or there would have been no need for a separate unit. The unit did not arise out of philosophical speculation, but to resolve a practical problem: the description of colligative properties. But it arose in a period when "absolute" measurements were referred to a three-dimensional system of quantities, usually (but not necessarily) the CGS system.

The problems of forcing all measurements into this artificially restricted system were most apparent in the electrical and magnetic units: the abohm, or emu of electrical resistance, had the dimensions  $\mathbf{LT}^{-1}$  ( $\mathbf{L}$  = length;  $\mathbf{T}$  = time) and the statfarad, or esu of capacitance, had the dimension  $\mathbf{L}$ , not to mention the fractional dimensions of most electrical and magnetic units in the two CGS systems [30]. As Giovanni Giorgi pointed out in 1901, the system could be "rationalized" by including an electromagnetic dimension to the system of quantities, and hence assigning dimensions to constants that had been considered as having the dimension one, and by the consequent simplification of the corresponding quantity equations [31]. It is Giorgi's system that now forms part of the International System of Quantities.

Just as the electromagnetic dimension was long ignored in quantity systems such as CGS, so was the dimension of amount of substance. The unit of amount of substance could appear to have the dimension of mass, volume, pressure, or even specific heat capacity. But, while the need for an electromagnetic dimension is now widely accepted, the dimensionality of the mole, and hence of the Avogadro constant, is still the matter of some debate [4].

#### 4. Quantization of amount of substance

The discontinuous nature of matter is now generally accepted as a physical reality and not simply as a convenient heuristic. One can speak of one uranium atom, or three methanol molecules, but not of half a uranium atom or two-thirds of a methanol molecule. Much of chemistry is concerned with theories of behaviour at the molecular scale, but only a few measurements can truly be said to be made on individual atoms or molecules. A statement such as "trimolecular reactions in the gas phase are rare" refers to reactions involving exactly three molecules, and not one, two or four, however many times the reaction would have to repeat itself to produce an observable amount of product.

Herein lies another of the confusions concerning amount of substance, the mole and the Avogadro constant. Counting out three molecules is a measurement of a number of molecules, a discontinuous quantity of dimension one. But the mole is also defined in terms of the

number of carbon atoms in 12 grams of carbon 12: surely this is also a discontinuous quantity of dimension one?

The misconception can be illustrated by means of an analogy. Electric charge is also a quantity that is quantized at microscopic scales. For observable particles, the electric charge must be an integer multiple of the elementary charge  $e$ . From the 2006 CODATA recommended values [21]

$$e = 1.602\,176\,487(40) \times 10^{-19} \text{ C} \quad (11)$$

$$1 \text{ C} = 1/e = 6.241\,509\,65(16) \times 10^{18} \text{ elementary charges} \quad (12)$$

At the atomic scale, electric charge can be considered to be a count of elementary charges, and so a quantity of dimension one, but that does not make the coulomb a “counting unit”, a shorthand for a large number of elementary charges. Electric charge at the macroscopic scale is not measured by counting elementary charges. Instead, a quantity that is proportional to the number of elementary charges is measured, such as a mass of silver deposited by electrolysis or a force between two conductors multiplied by the time the current flows.

By convention, quantities such as mass, force, length and time are considered to be continuous, that is they can take any real numerical value and, perhaps more importantly, they can be differentiated. They may be quantized, and hence discontinuous, at a sub-microscopic scale – and some theories suggest that they are – but such a scale is far below the scale of our measurements. Electric charge is discontinuous on a scale that is within our ability to measure, but still below the scale of most practical measurements. Hence, the *macroscopic* quantity electric charge is conventionally assumed to be continuous, allowing us to write quantity equations such as

$$dW = (q/C) dq \quad (13)$$

where  $dW$  is the infinitesimal work involved in changing the charge on a capacitor of capacitance  $C$ , whose plates hold the charges  $+q$  and  $-q$ , by the infinitesimal amount  $dq$ .

As for amount of substance, it is defined by equation (5) in terms of mass  $m$ , (weighted mean) relative entity mass  $A_r$ , and a proportionality constant, the molar mass constant  $M_u$ , whose numerical value we are free to choose to define our measurement unit. All of these are continuous quantities, and so equation (5) defines amount of substance as a continuous quantity. This allows us to write quantity equations such as

$$\mu = (\partial U/\partial n)_{S,V} = (\partial G/\partial n)_{T,p} \quad (14)$$

where  $\mu$  is the chemical potential of a species and  $U$  and  $G$  are the internal energy and the Gibbs energy of a system respectively.

It is often assumed that one can substitute

$$n = N/N_A \quad (15)$$

into any equation involving amount of substance, but this is not true. One cannot substitute equation (15) into equation (14) because  $N$  is a discontinuous quantity and so non-differentiable: instead, one must use equation (5). This is (in modern terms) how Gibbs originally defined chemical potential in 1876 [32], lacking a well-defined quantity dimension of amount of substance.

Above, it was said that equations (4) and (5) were equivalent definitions of amount of substance, but now we see that this is not strictly true because equation (4) defines the continuous  $n$  in terms of the discontinuous  $N$ :

- either we admit that  $n$  is discontinuous, and hence lose the power of differential calculus in analysing the effects of changes in the amount of one species relative to the others;

- or we limit the applicability of equation (4), and hence the applicability of equation (5) as well, assuming we wish them to stay as equivalent definitions.

The latter seems to be the more desirable solution, and is implicit in the use of the macroscopic quantity electric charge in differential equations. An explicit version for the macroscopic quantity amount of substance might be:

Amount of substance  $n$  is a continuous quantity that is nevertheless proportional to the number of entities  $N$ . As a consequence, the quantity amount of substance should only be employed if the quantity  $1/N$  can be treated as a differential  $dn/n$  under the conditions of measurement.

The quantity  $1/N$  is the fractional change in the number of entities when  $N$  changes by one entity.

## 5. Counting

The age of the universe is about 13.75 billion years, that's about  $4.3 \times 10^{17}$  seconds: you would need to count more than a million atoms a second to count the atoms in 12 grams of carbon 12, even if you literally had "all the time in the universe."

Comparisons such as this are commonplace in elementary textbooks of chemistry (see, e.g., [33]). They are intended to illustrate the practical impossibility of realizing the mole by counting elementary entities, although this author fears they often have the opposite effect. In fact, such comparisons say nothing at all about the mole: all they say is that atoms are very small and that there are an awful lot of them. Thankfully for practical chemistry, the mole is not defined as a count of elementary entities, and never has been.

The definition of the mole, as approved by the 14th Conférence Générale des Poids et Mesures (CGPM) in 1971, is as follows [15]:

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".

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.

To avoid a possibly ambiguity in the measurement of relative atomic masses, the Comité International des Poids et Mesures (CIPM) recommended the following interpretation in 1980 [15]:

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

The mass equivalent of the bond energy of graphite at 298 K is  $7.9014(50) \times 10^{-9}$  g mol<sup>-1</sup>, or 0.65 parts per billion compared to the total mass [34]: this is obviously insignificant for chemical purposes, but comparable to the uncertainty in the most precisely measured relative atomic masses.

To realize the mole, it is not necessary to know the number of atoms in 12 grams of carbon 12: it is merely necessary to show that the number of specified entities in the realization is identical (to within standard measurement uncertainty) to the number of atoms in 12 grams of carbon 12. Three examples of realization methods are discussed in the current *Mise en pratique* [20], which does not mention the term "Avogadro constant" once.

Nevertheless, references to the mole as a “counting unit” have always been around, and continue to be published [4,5]. The International Avogadro Coordination (IAC) does not “count atoms” in its silicon spheres, as Becker *et al.* put it [5] and as Andreas *et al.* imply in the title of the latest IAC report [35]. The IAC compares a measurement of the {220} distance (equal to  $a/\sqrt{8}$ , where  $a$  is the unit cell parameter) to a measurement of the diameter of the macroscopic sphere to *deduce* the number of silicon atoms in the sphere, assuming that crystal defects can be accounted for. If what the IAC does is counting, then the word “counting” has been redefined as an exact synonym of “measurement”.

Perhaps, to avoid confusion, the scientific community needs a specific definition of “count”. The following is proposed for the purposes of this paper, although it may be too restrictive for application across all fields of measurement:

A count is a measurement method for the number of specified entities in which the discontinuity in the measurement result when the number of entities changes by one entity is, or would be, significant compared to the uncertainty of the measurement result, discounting the contribution to the uncertainty from any correction for systematic measurement error.<sup>7</sup>

Under this definition, Millikan’s oil-drop experiment [37] is a count of elementary charges (or charge number) on the oil drops, while Perrin’s determination of the Avogadro constant [2] is not a count but rather a measurement of number density (a continuous quantity).

## 6. $N_A$ as a fundamental constant

The situation of the Avogadro constant among physical constants is somewhat paradoxical. On the one hand, it is treated as the defining quantity of amount of substance, and rare is the text that introduces that concept without emphasizing that there are (about)  $6 \times 10^{23}$  atoms in 12 grams of carbon 12. On the other hand, there is a widespread feeling that  $N_A$  is a ‘different kind’ of constant from the speed of light or the Planck constant. For example, Andres *et al.* [38] state that “Avogadro’s constant [*sic*] is an arbitrary number that has nothing to do with a ‘true invariant of nature’ or a fundamental constant.” and “ $N_A$  is nowhere provided by nature”; Leonard [7] states:

There is a common misconception that the Avogadro constant is one of the fundamental constants of nature, in the same category as the speed of light, the Planck constant and the invariant masses of atomic-scale particles. Although the absolute mass of any specified atomic-scale entity is an invariant universal constant of nature, the Avogadro constant relating this to a macroscopic quantity is not. Rather, it is a man-made construct, designed by convention to define a convenient unit relating the atomic and macroscopic scales.

And yet, the purpose of current experiments to measure  $N_A$  (such as the IAC) is that such measurements, in our current system of units, are determinations of the Planck constant [21], the quantum of action and of angular momentum.

As discussed above, this author contends that the confusion arises from defining amount of substance to be proportional to the number of entities to the exclusion of other definitions that are at least as valid. Amount of substance is intimately linked to the concept of atomic weights, and hence, in modern terms, to the relative masses of the various elemental entities.

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<sup>7</sup> Underlined terms are defined in the 3rd edition of the *International Vocabulary of Metrology* (VIM3) [36]. Note that definition does not require the entities to be counted “one-by-one”, nor does it imply that the final measurement result has no uncertainty, merely that the result must be an integer and that the uncertainty must have a discontinuous element.

Since 1960, the conventional scale of relative atomic masses has been defined in terms of the mass of a carbon 12 atom, with  $A_r(^{12}\text{C})$  being fixed as 12 [39]. There is a certain feeling that this definition in itself is somewhat arbitrary, so let us consider the consequences of redefining the quantity to a more “fundamental” base point: specifically, defining  $A_r^*$  so that the relative mass of the electron is fixed as 1. The most obvious difference between the two sets of values is that  $A_r^*$  values will be about 1823 times larger than current  $A_r$  values.

At the same time, let us define the new unit of amount of substance – we shall call it the whale, symbol whl – in terms of the kilogram instead of the gram, so that the new molar mass constant  $M_u^*$  becomes 1 kg/whl instead of 1 g/mol. Hence the whale is about 1.8 million times larger than the mole. What is the value of the Avogadro constant in reciprocal whales? Using braces  $\{\}$  to denote the numerical values of the respective quantities:

$$\{N_A\}^* = \{M_u^*\} \{A_r^*(e)\} / \{m_e\} = 1 / \{m_e\} \quad (16)$$

“Avogadro’s number”  $\{N_A\}^*$ , the numerical value of the Avogadro constant under this system, would be simply the reciprocal of the numerical value of the electron mass in kilograms:  $N_A = 1.097\,769\,293(55) \times 10^{30} \text{ whl}^{-1}$ .

Of course, “Avogadro’s number” would still depend on our choice of unit of mass, even under this hypothetical system. But that is true for any physical constant that is associated with a measurement unit. The numerical value of the speed of light is just as correctly 173.144 632 674(3) as it is 298 792 458, the former value being in astronomical units per TDB day [40]. *A numerical value of a physical quantity is meaningless without reference to the appropriate measurement unit.* The appropriate measurement unit might simply be the number 1, but this is not the case for the Avogadro constant. The value of “Avogadro’s number” changes with the unit of amount of substance, and so is fundamentally meaningless as a pure number, without reference to the unit of amount of substance. The Avogadro constant has the dimension  $\mathbf{N}^{-1}$ , where  $\mathbf{N}$  is the dimension amount of substance, and not simply the dimension  $\mathbf{1}$ .

If one accepts that the absolute masses of individual atoms and subatomic particles are fundamental invariants of nature, as Andres *et al.* and Leonard do, then one must also accept that the Avogadro constant is also a fundamental invariant of nature. That is a common working definition of a “fundamental constant”, and it is beyond the scope of this paper to discuss other definitions of the term (see, e.g., [41,42]).

## 7. Relative atomic mass and $M_u$

In the International System of Units, the Avogadro constant is given by the quantity  $0.012 \text{ kg mol}^{-1}$  divided by the mass of an unbound carbon 12 atom at rest and in the ground state. At first sight, this might seem somewhat arbitrary as a definition, and indeed it arises from the apparently arbitrary definition of the mole. It is true that the molar mass constant  $M_u$  and the relative atomic mass of carbon 12  $A_r(^{12}\text{C})$  are unit-defining constants, and so their numerical values can be chosen at will, subject to the constraints of a coherent system of units. However their current values are anything but arbitrary, but rather are closely linked to the practical measurement of amount of substance.

### 7.1 Relative atomic mass

The relative atomic mass of an entity X,  $A_r(X)$ , is the ratio of the mass of that entity,  $m(X)$ , to one-twelfth of the mass of a carbon 12 atom,  $m(^{12}\text{C})/12$ .

$$A_r(X) = 12m(X)/m(^{12}\text{C}) \quad (17)$$

Relative atomic mass is measured in a way that is very similar to its formal definition. The most precise measurements are made using Penning-trap mass spectrometers, where individual ions are confined in a “trap” consisting of perpendicular electric and magnetic fields (see, e.g., [43]). The ions travel in a circular trajectory within the trap, and emit cyclotron radiation whose frequency is proportional to the mass-to-charge ratio. If one could precisely measure the electric and magnetic fields, one would have a measure of absolute mass, but this is impractical. Instead, another ion is used as a mass standard and the ratio of the two cyclotron frequencies is calculated, giving the ratio of the two mass-to-charge ratios. The practical question, therefore, is to find the optimal mass standard for precise measurements.

The optimum standard depends on the range of mass-to-charge ratios that one wishes to measure, as the most precise measurements will be of ratios that are close to one. If one considers singly charged ions, as in conventional mass spectrometry, the optimum mass standard (the one that gives the ratios nearest to one for all ions) will have a mass number close to the square root of the highest mass number to be measured. Nitrogen 15 and oxygen 16 are optimal standards for singly charged ions and for measurements across the whole periodic table, with  $15^2 = 225$  and  $16^2 = 256$ , while the proton is too light, and the electron far too light, to be a practical standard.

However we are not limited to singly charged ions, nor are we equally interested in all relative atomic masses across the periodic table. For high-precision measurements, it is convenient to use a completely ionized nuclide as the mass standard, as this removes any uncertainty due to the electronic state of the ion. Several stable nuclides – such as  $^2\text{H}$ ,  $^4\text{He}$ ,  $^6\text{Li}$ ,  $^{10}\text{B}$ ,  $^{12}\text{C}$ ,  $^{14}\text{N}$ ,  $^{16}\text{O}$  and  $^{20}\text{Ne}$  – give ions with  $m/z \approx 2 m_u/e$  on complete ionization; all other stable nuclides, with the exception of  $^1\text{H}$  and  $^3\text{He}$ , give ions with  $m/z > 2 m_u/e$ , although complete ionization is increasingly impractical with increasing atomic number. These nuclides give ions that lie close to the centre of the range of accessible  $m/z$  values for most elements.

Using the proton (or the  $^1\text{H}$  atom) as the basis for  $A_r(\text{X})$  might seem more “logical” at first sight, but it is an objectively worse choice in practical terms:  $m/z$  for the proton is inevitably at one end of the scale of values to be measured, rather than in the middle as is desired for maximum precision of ratio measurements. The effect can be seen in the relative uncertainties in  $A_r(\text{X})$  values, as illustrated in Table 1, where the relative uncertainty in  $A_r(^1\text{H})$  is an order of magnitude higher than the relative uncertainties in the most accurately known relative atomic masses. The relative uncertainty in  $A_r(\text{e})$  is higher still, at  $u_r = 4.2 \times 10^{-10}$  [21].

**Table 1.** Values of the relative atomic masses of various atoms, taken from [21]. Apart from  $A_r(^2\text{H})$ , these are the values of the 2003 atomic mass evaluation [44].

Atom	Relative atomic mass $A_r(\text{X})$	Relative standard uncertainty $u_r$
$^1\text{H}$	1.007 825 032 07(10)	$1.0 \times 10^{-10}$
$^2\text{H}$	2.014 101 778 040(80)	$4.0 \times 10^{-11}$
$^4\text{He}$	4.002 603 254 153(63)	$1.6 \times 10^{-11}$
$^{16}\text{O}$	15.994 914 619 56(16)	$1.0 \times 10^{-11}$
$^{28}\text{Si}$	27.976 926 5325(19)	$6.9 \times 10^{-11}$
$^{40}\text{Ar}$	39.962 383 1225(29)	$7.2 \times 10^{-11}$
$^{87}\text{Rb}$	86.909 180 526(12)	$1.4 \times 10^{-10}$
$^{133}\text{Cs}$	132.905 451 932(24)	$1.8 \times 10^{-10}$

The value of the electron relative atomic mass  $A_r(e)$  does enter into the calculation of other  $A_r$  values. Physical carbon 12 atoms cannot be used practical mass standards, as they are rather difficult to prepare “unbound, at rest and in their ground state”, and even more difficult to weigh. In using the  $^{12}\text{C}^{6+}$  ion as the practical mass standard, account must be taken of the mass of the six electrons in a neutral carbon atom, and also of the mass equivalent of their binding energy (taken as the sum of the six ionization energies). The practical realization of the unbound carbon 12 atom at rest and in its ground state can be expressed as

$$A_r(^{12}\text{C}) = 12 = A_r(^{12}\text{C}^{6+}) + 6A_r(e) - E_b(^{12}\text{C})/m_u c_0^2 \quad (18)$$

which gives

$$A_r(^{12}\text{C}^{6+}) = 12 - 6A_r(e) + E_b(^{12}\text{C})/m_u c_0^2 = 11.996\,709\,626\,4108(14) \quad (19)$$

The relative standard measurement uncertainty is  $1.2 \times 10^{-13}$ , and the residual uncertainty in  $A_r(^{12}\text{C}^{6+})$  is almost entirely due to the uncertainty in  $A_r(e)$ . By comparison, the relative uncertainty in the atomic mass constant  $m_u$ , which relates these mass ratios to the kilogram, is  $5 \times 10^{-8}$  [21].

The choice of carbon 12 as the basis of the relative atomic mass scale may be the result of a historic compromise between chemists and physicists [39], but it is not an arbitrary choice. There are other choices that would work equally well with current measurement techniques, such as oxygen 16, but that does not mean that *any* choice would work equally well. The atomic mass of hydrogen 1 or, particularly, the electron mass (see, e.g., [5,45]), would be bad practical choices for the basis of a relative atomic mass scale, whatever their philosophical attraction.

### 7.2 Molar mass constant, $M_u$

The molar mass constant  $M_u$  relates the relative atomic mass  $A_r$  to the molar mass  $M$ .

$$M = M_u A_r \quad (20)$$

In the International System of Units,  $M_u$  has the defined value of  $1 \text{ g mol}^{-1}$ . This simple value, fixed by definition, makes  $M_u$  one of the most gloriously ignored of physical constants, and several commentators have called for its use to be made more explicit (see, e.g., [46]). It is, however, essential for writing dimensionally homogenous quantity equations involving relative atomic masses, such as equations (5), (7) and (8) in this article.

The chemist’s method for calculating molar mass could be expressed as

$$M = \{A_r\} \text{ g mol}^{-1} \quad (21)$$

that is (the numerical value of) the atomic (or molecular) weight in grams per mole: examples of this usage, if not the terminology, can be found in mid-nineteenth century texts explaining the principle of stoichiometry.

Outside the SI, we are not restricted to measuring amount of substance in moles, and chemical engineers in the United States sometimes use the “pound-mole” (lb-mol.) with  $M_u = 1 \text{ lb. lb-mol.}^{-1}$  and  $M = \{A_r\} \text{ lb. lb-mol.}^{-1}$  (see, e.g., [47]). However, whatever the units of mass and amount of substance used, the numerical value of the molar mass constant  $\{M_u\}$  is always equal to one: this is implicit in the use of equations such as (21) to calculate molar masses, which are what chemists and chemical engineers actually measure out.

While the numerical value of  $M_u$  is constrained to unity by more than 200 years of chemical practice, its magnitude depends on the units chosen to express it. In particular, it depends on the unit of mass which is chosen: once the choice of unit of mass has been made, and within the constraint that  $\{M_u\} = 1$ , the unit of amount of substance is defined.

### 7.3 Criteria for a unit of amount of substance

Milton and Mills [8] consider it a question of semantics whether the current definition of the mole fixes the molar mass of carbon 12 atoms or the molar mass constant. This raises the question as to whether the molar mass constant is a sufficient definition for a unit of amount of substance.

A unit of amount of substance can only be used in practice if it is associated, explicitly or implicitly, with a convention for the expression of relative atomic masses. Hence if one measurement refers relative atomic masses to  $A_r(^{16}\text{O}) = 16$  while another refers them to  $A_r(^{12}\text{C}) = 12$ , the two units of amount of substance will be incoherent with one another. For this reason, the current definition of the mole is explicitly linked to the  $A_r(^{12}\text{C}) = 12$  scale of relative atomic masses, drafted, as it was, shortly after a change in the conventional basis for relative atomic mass scales.

Nevertheless, such associations can also be implicit in unit definitions. The candela is implicitly associated with a standard luminosity function, and the ampere is implicitly associated with the use of four-dimensional rationalized equations for electromagnetic quantities. These associations do not appear in the unit definitions, but have been collected together in the International System of Quantities. Other associations and assumptions can be found in the *Mises en pratique*; for example, that the metre is a unit of proper length.

If we assume that the current definition of the mole fixes the numerical value of the molar mass constant, we are assuming that the quantity relative atomic mass is adequately defined. On the basis of that same assumption, the molar mass constant is sufficient to define a unit of amount of substance.

## 8. Redefinition of SI base units

Proposals to redefine the kilogram in terms of a fundamental constant, instead of the current artefact standard, have been made for at least 35 years [48]. They gained urgency with the results of the third periodic verification of mass standards (1988–1992), which suggested an instability in the masses of the current standards that was at least an order of magnitude greater than expected [49].

At its 94th meeting in 2005, the International Committee for Weights and Measures (CIPM) agreed to examine similar proposals to redefine the kelvin, the ampere and the mole [50], such as Leonard's proposals to redefine the mole in terms of a specified numerical value for the Avogadro constant [6,7]. The Consultative Committee for Amount of Substance: metrology in chemistry (CCQM) has expressed its "preference" for a redefinition of the mole of the type that Leonard proposes, although it notes that discussion within the wider chemical community has so far been minimal [51]. The principle of a redefinition of the mole in terms of  $N_A$  has also been supported by the IUPAC Interdivisional Committee on Terminology, Nomenclature and Symbols (ICTNS) and the IUPAC Executive Committee [52].

Jeannin [53] has analyzed the question in terms of a straight choice between a fixed numerical value for  $N_A$  and a fixed numerical value for  $M_u$ : he concludes that most chemists would prefer a fixed numerical value for  $M_u$ . Andres *et al.* [38] have argued that there is "no rationale for the redefinition of the mole," which they describe as a "counting unit".

### 8.1 The current link between the mole and the kilogram

Several authors [7,54,55], and also the ICTNS [52], have commented on the supposed desirability of breaking the link between the kilogram and the mole in the current definition of the latter. This is a strange position to take: the metre has been defined in terms of the second

since 1983 without obvious problems, and it is widely proposed to redefine the kilogram and the ampere in terms of the second.<sup>8</sup> As for the proposed redefinition of the kelvin based on

$$E = kT \quad (22)$$

the unit of temperature would be defined in terms of the second, the metre *and* the kilogram.

The second is something of a special case, as it can be realized far more precisely than the other SI base units (see also [57]). But the uncertainty in the realization of the kilogram is not “transmitted to the mole”, as Leonard contends [7]: the current definitions of the mole and the kilogram are exact. Uncertainties in the realization of the kilogram are transmitted to *realizations* of the mole, where they are (with the exception of the IAC results) completely negligible. The main residual uncertainty in routine realizations of the mole is the uncertainty in the purity of the substance being measured, although relative uncertainties of less than  $10^{-6}$  can be obtained in ideal circumstances [20]. The residual uncertainty in highly precise realizations of the mole is still (usually) the uncertainty in the atomic weight of the sample,<sup>9</sup> and practical realizations will still rely on mass measurements, as does the IAC, whatever the definition.

### 8.2 Quantum metrology and fundamental constants

Andres *et al.* [38] note that “the argument ‘quantum metrology’ is not applicable to the mole,” and is worth emphasizing this point: that the question of defining a fixed numerical value for  $N_A$  can be approached independently of the discussions concerning the proposed redefinitions of the kilogram and the ampere. However, fixing the numerical values of  $h$  and  $e$  would have benefits far beyond the field of electrical measurements, as the measurement uncertainties in many other fundamental constants would be reduced or even eliminated.

As Andres *et al.* [38] point out, definitions in the International System of Units are cultural goods, reproduced in countless handbooks and student texts: they should not be changed without positive reasons, because there will always be a cost in any change. The question to ask is: what would be the additional benefit, in terms of measurement uncertainties in fundamental constants, from also fixing the numerical value of  $N_A$ ?

There are three non-trivial fundamental constants in the 2006 CODATA adjustment whose values depend on the  $N_A$ : the Faraday constant  $F$ , the atomic mass constant  $m_u$  and the Boltzmann constant  $k$ . As it is also proposed to redefine the kelvin in terms of a fixed numerical value for  $k$ , the Boltzmann constant should be replaced in this list by the molar gas constant  $R$  and the molar volume of an ideal gas  $V_m$ . The effects on measurement uncertainties of fixing the values of various unit-defining constants are shown in Table 2.

<sup>8</sup> The mole can also be defined in terms of the second: the mole is the amount of polonium 210 atoms that has an activity of  $3.491\,419(49) \times 10^{16}$  becquerels. However, such definitions are completely impractical, not least because of the measurement uncertainty in radioactive decay constants – here,  $u_r = 1.4 \times 10^{-5}$  for  $\lambda(^{210}\text{Po})$ , which is the most precisely known of the half-lives quoted in NUBASE 2003 [54].

<sup>9</sup> The latest IAC report [35] greatly reduces the uncertainty in the atomic weight of the silicon used, leaving the largest components of the residual uncertainty in  $N_A$  as the contributions of surface layers and the measurement of the volume of the sphere. Nevertheless, in order to achieve this result, the IAC needed to prepare 5 kg of silicon enriched to about 99.9994% in  $^{28}\text{Si}$ , and also to develop new methods for measuring the enrichment, feats that can hardly be considered routine even in the context of high-precision metrology.

**Table 2.** Relative measurement uncertainties ( $10^9 u_r$ ) in various physical constants under the current definitions of the SI base units and under three possible redefined systems: redefinition of the kilogram and the ampere, with additional redefinition of the kelvin or of the kelvin and the mole.  $m(K)$  = mass of the International Prototype Kilogram;  $\mu_0$  = magnetic constant;  $T_{\text{tp}}(\text{H}_2\text{O})$  = triple point of Vienna Standard Mean Ocean Water (VSMOW).

	current	kg-A	kg-A-K	kg-A-K-mol
$N_A$	50	1.4	1.4	0
$h$	50	0	0	0
$e$	25	0	0	0
$F$	25	1.4	1.4	0
$m_u$	50	1.4	1.4	1.4
$R$	1700	1700	1.4	0
$k$	1700	1700	0	0
$V_m$	1700	1700	1.4	0
$m_e$	50	1.4	1.4	1.4
$\alpha^2$	1.4	1.4	1.4	1.4
$A_r(\text{e})$	0.42	0.42	0.42	0.42
$M_u$	0	0	0	1.4
constants	$m(K)$	$h$	$h$	$h$
with fixed	$\mu_0$	$e$	$e$	$e$
numerical	$T_{\text{tp}}(\text{H}_2\text{O})$	$T_{\text{tp}}(\text{H}_2\text{O})$	$k$	$k$
values	$M_u$	$M_u$	$M_u$	$N_A$

The choice is quite straightforward:

- either we choose zero measurement uncertainty, instead of  $u_r = 1.4 \times 10^{-9}$ , in  $N_A$ ,  $F$  and  $R$  (and hence  $V_m$ ) in return for  $u_r = 1.4 \times 10^{-9}$  in  $M_u$ ;
- or we say that  $u_r = 1.4 \times 10^{-9}$  in  $N_A$ ,  $F$  and  $R$  is already practically insignificant, and so there is no additional benefit from reducing it further by changing the definition of the mole.

The residual uncertainty of  $u_r = 1.4 \times 10^{-9}$  represents the uncertainty in  $\alpha^2$ , the square of the fine structure constant: as  $\alpha$  is a quantity of dimension **1**, this fundamental measurement uncertainty cannot be removed by any redefinition of the system of units.

By far the most precise direct determination of  $N_A$  is the ongoing IAC project. The latest IAC result has  $u_r = 3 \times 10^{-8}$  [35], still more than an order of magnitude greater than  $u_r(\alpha^2)$ . The best practical determination of  $F$  is by silver coulometry, and gives a relative uncertainty of  $1.3 \times 10^{-6}$  [21,58,59], almost three orders of magnitude higher than  $u_r(\alpha^2)$ .<sup>10</sup> The current value of  $R$  comes from direct measurements of the speed of sound in argon, and has  $u_r = 1.7 \times 10^{-6}$  [21,58,60,61]: although there are ongoing efforts to measure  $k$  directly [62,63], rather than to determine it by

$$k = R/N_A \quad (23)$$

these have yet to reach the necessary precision even to supersede the value obtained from equation (22) [64,65].

<sup>10</sup> Indeed,  $u_r(\alpha^2)$  is more than an order of magnitude lower than the current relative uncertainties [44] in  $A_r(^{107}\text{Ag})$  and  $A_r(^{109}\text{Ag})$ , the two naturally occurring isotopes of silver.

In short, any additional reduction in the measurement uncertainty of fundamental constants by the redefinition of the mole in terms of a fixed numerical value of  $N_A$ , over and above that achieved by fixing the numerical values of  $h$ ,  $e$  and  $k$ , would be *completely insignificant at the practical level*. Measurement techniques will have to improve in precision by one to three orders of magnitude before  $u_r(\alpha^2)$  becomes significant for the direct experimental determination of these quantities, even discounting any future improvements in the determination of the fine structure constant.

Proponents of a redefinition of the mole in terms of a fixed numerical value for  $N_A$  point out that the consequential measurement uncertainty of  $u_r = 1.4 \times 10^{-9}$  in the molar mass constant  $M_u$  would also be practically insignificant [5,7,46], given that the most precise realizations of the mole have relative measurement uncertainties of the order of  $10^{-8}$ – $10^{-6}$ . However, as noted above, this is not a reason in itself to change the definition.

### 8.3 Atomic mass constant

As shown in Table 2, the measurement uncertainty in the atomic mass constant  $m_u$  would be unaffected by any redefinition of the mole.

$$m_u = m(^{12}\text{C})/12 = M_u/N_A \quad (24)$$

It is not possible to fix all three of  $h$ ,  $M_u$  and  $N_A$  in a single coherent set of units, as to do so would be equivalent to fixing a defined value for the dimensionless fine structure constant  $\alpha$  (see [6,54]). A simpler explanation of the problem is to look at the definition of the atomic mass constant rather than its practical determination:  $m_u$  is defined as one-twelfth of the mass of an unbound carbon 12 atom at rest in its ground state [66]. The only way to have a fixed value of  $m_u$  is to define the carbon 12 atom as the mass standard, and hence the kilogram as the mass of a fixed number of carbon 12 atoms, leaving the Planck constant as an experimentally determined quantity. Comparing the mass of the carbon 12 atom against *any* other mass standard will lead to a measurement uncertainty and hence an uncertainty in the value of  $m_u$ .

### 8.4 Ease of comprehension

It is in no way clear how a definition for the mole in terms of a fixed number of entities would be “conceptually simpler” than the current definition in terms of a fixed numerical value for  $M_u$ , equivalent to a fixed molar mass for carbon 12. The conceptual difficulties are just shifted one step down the line. The proposed redefinition suggests that amount of substance is measured by counting elementary entities, when this is obviously and completely impractical. Chemists would, of course, continue to measure amount of substance in terms of mass ratios, but educators would have to convince their students that these mass and mass-ratio measurements are equivalent to “counting” numbers of entities of the order of  $6 \times 10^{23}$ , an extra complexity in teaching this fundamental aspect of chemistry.

Physics teaching wouldn’t have it any easier either. It is generally assumed in elementary physics that the ideal gas equation (10) can be rewritten as

$$pV = NkT \quad (25)$$

but this assumes that  $N$  can tend to one. If  $N = 1$ , the system is a “particle in a box”; the well-known result is that the energy (equal to  $pV$ ) is quantized. Does that mean that temperature is quantized? That depends on the definition of temperature, of course, but equation (24) is only generally valid – on the basis of the normal definitions of the physical quantities therein – if  $N$  is large. These are exactly the situations where equation (10) would also be valid: equation (10) also provides a more accurate description of the measurements to be made, given the current status of determinations of the Boltzmann constant and the impossibility of counting large numbers of molecules.

### 8.5 Alternative wordings

The current definition of the mole and its description in the SI brochure are singular among the seven base units. The definition of the mole appears to have been mixed in with an attempt at a “definition” of the quantity amount of substance: if the various organs of the Metre Convention do not see it necessary to define “luminous intensity”,<sup>11</sup> it is hard to see why they should try to define “amount of substance”.

The first part of the current definition of the mole is an unhappy mix of equations (4) and (5) as definitions of amount of substance: it talks of “as many elementary entities”, i.e. a number, while explicitly fixing the molar mass of carbon 12 atoms. The second part of the definition attempts to define “elementary entities” by example, a job that is surely better left to textbooks or to the *Mise en pratique*. The clarification issued by the CIPM in 1980 arises from a real practical need, and so deserves to be included in the formal definition. Within these constraints, the current definition could be redrafted as follows without any change in meaning:

The mole is the amount of unbound carbon 12 atoms, at rest and in the ground state, that has a mass of 0.012 kilograms.

*La mole est la quantité d’atomes non liés de carbone 12, au repos et dans l’état fondamental, qui a la masse de 0,012 kilogrammes.*

There are also suggestions to make the defining constants explicit in the definitions of SI base units. Along these lines, the definition of the mole could be written

The mole, the unit of amount of substance, is defined such that the molar mass of unbound carbon 12 atoms, at rest and in the ground state, is equal to 0.012 kilograms per mole.

*La mole, l’unité de quantité de matière, est définie telle que la masse molaire d’atomes non liés de carbone 12, au repos et dans l’état fondamental, soit égale à 0,012 kilogrammes par mole.*

As discussed above, the true defining constant of the unit of amount of substance is the molar mass constant  $M_u$ . In line with the desire to increase the visibility of this constant, a fixed-constant definition of the mole would be

The mole, the unit of amount of substance, is defined such that the molar mass constant is equal to 0.001 kilograms per mole.

*La mole, l’unité de quantité de matière, est définie telle que la constante de masse molaire soit égale à 0,001 kilogrammes par mole.*

Substituting “one unit of mass” for “0.001 kilograms” in this last definition gives the definition of the “unit of amount of substance” that has, in practice, served chemists for more than 200 years.

## 9. Conclusions

The Avogadro constant has always been defined as the number of molecules (or other practically indistinguishable entities) *per unit of amount of substance*, whether that unit of was called the gram-molecule, the gram-atom or the mole. The confusion with the use of “Avogadro’s number” as a pure number appears to arise from comparison with equations in kinetic theory, and may have been aggravated by the terminology in the German-language

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<sup>11</sup> Luminous intensity is the physical quantity measured by the candela. It can be briefly described as the “brightness” of light as perceived by human eyes, and so is distinct from radiant intensity, a quantity measured in watts per steradian without correction for the spectral selectivity of human vision.

literature in the first half of the twentieth century: this does not make it any more correct, in either historical or metrological terms.

Amount of substance is a physical quantity that is quantized at the molecular scale but practically continuous at the macroscopic scale: it is not unique among physical quantities in this characteristic. At any macroscopic scale, amount of substance has never been measured by counting elementary entities; indeed, it is simple to show that such a count would be completely impractical. The macroscopic measurement of amount of substance relies on the assumption of practical continuity and not on the value of the Avogadro constant; historically, it did not rely on the acceptance of (or even conception of) atomic theory.

The current debate on the redefinition of the kilogram and other SI base units is an excellent opportunity to *explicitly reject* a redefinition of the mole, the unit of amount of substance at the macroscopic scale, in terms of a fixed value for the Avogadro constant. Such a redefinition would offer no practical benefits to chemists or metrologists, but would detach the definition of the unit of amount of substance from its practical realization. It would also destroy the defined relationship between molar mass and atomic weight and add extra conceptual complexity to the teaching of basic chemistry.

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