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The Atomic Mass Unit, the Avogadro Constant, and the Mole: A Way To Understanding

Andrzej Barański*

Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Kraków, Poland

ABSTRACT: Numerous articles have been published that address problems encountered in teaching basic concepts of chemistry such as the atomic mass unit, Avogadro's number, and the mole. The origin of these problems is found in the concept definitions. If these definitions are adjusted for teaching purposes, understanding could be improved. In the present article, the definitions are discussed, and the following adjustments are suggested: (i) the feature that classifies carbon-12 for the definition as the standard be its abundance, (ii) Avogadro's number should refer directly to the standard nuclide sample, (iii) the definition of the mole be based on Avogadro's number, and (iv) the term *amount of substance* be replaced by the *collection* or *quantity of microentities*. It is also proposed that the definition of the mole is first presented for nuclides and then generalized for poly-isotopic elements and chemical compounds. A possible redefinition of kilogram as a multiple of the standard nuclide mass is also briefly discussed.

KEYWORDS: First-Year Undergraduate/General, High School/Introductory Chemistry, Physical Chemistry, Public Understanding/Outreach, Misconceptions/Discrepant Events, Nomenclature/Units/Symbols, Stoichiometry

Teaching and learning basic chemical concepts of the atomic mass unit, Avogadro constant, and the mole have been perennially difficult. In their review articles in 1981 and 2002, citing over a hundred references, Dierks[1] and Furió et al.[2] concluded that the concepts are confusing. Confirmed by more recent articles, the confusion apparently has not been clarified. In 2009 Mills and Milton[3] wrote "...such concepts as the quantity 'amount of substance' and its unit 'mole'...are...the subjects of widespread misunderstanding", while in 2010 Leonard[4] remarked "...beginning chemistry students...likely to be suffering from 'Avogadro anxiety' ". Important arguments to this debate were also provided by the discussion between Freeman, Gorin, Karol, and Cvitaš reported in this *Journal* in 2003−2005[5−11] and closed by the editorial note in 2005.[12] The discussion revealed the following:

- Attempts to improve the International System of Units (SI) have a profound effect on the understanding and, consequently, on the teaching of the concepts in question.
- The main controversy is the nature of a quantity, of which the mole is a unit.
- The current definitions of the atomic mass unit and of the mole, officially adopted in 1961 and 1971, respectively, are the primary sources of confusion.

The definitions are as follows:

- Definition 1: The Dalton (Da) and the unified atomic mass unit (u) are alternative names (and symbols) for the same unit, equal to 1/12 times the mass of a free carbon-12 atom, at rest and in its ground state.[13]
- Definition 2: Mole is the amount of substance of the system that contains as many elementary entities as there are atoms in 0.012 kg of carbon-12. 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 (ref 13, p 115).

Further, in 1993, the IUPAC Commission on Physicochemical Terminology recognized the term *chemical amount* as the valid synonym of *amount of substance*.[6] In 2006 (ref 13, p 115) it was approved that the *substance* in the latter term can be specified. For instance, one can talk of the *amount of benzene* (preferably C_6H_6). The term *chemical amount* was not considered in the same document. To make the concepts easier to comprehend, the currently used definitions of the atomic mass unit, the mole, and the Avogadro constant will be adjusted for teaching purposes only. Ideas, concepts, and arguments extracted from numerous relevant references will be presented, whereas references aiming at improving the SI system will be taken into account only when necessary. The article is divided into two parts. The simpler case of nuclides will be considered first.

THE ATOMIC MASS UNIT

The concept of atoms and molecules was conclusively accepted in the 20th century. The determination of their masses relative to the macroscopic standards was more difficult than relating the masses of microscopic entities among themselves. For the latter, a perfect tool, namely, mass spectrometry, became available; however, a standard mass was needed and this was the origin of the concept of the atomic mass unit.

Definition 1 of the unified[14] atomic mass unit (u) originates from the agreement between physicists and chemists concerning the carbon-12 scale, reached in 1961.[15] However, the assignment of the atomic mass equal to 12 u to the nuclide of the mass number 12 in this definition creates a potential danger of misunderstanding. A student may think, erroneously, that the essential feature of carbon-12 is the mass equal to 12 u. This is why Feynman et al.,[16] Tro,[17] and Kotz et al.[18] defined the standard atom as having six protons and six neutrons in its nucleus. By contrast, Brescia et al.[19] referred to carbon-12 as "the most common carbon isotope" and Gorin,[6] as "predominant carbon

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isotope". The isotopic abundance is seen by chemists simply as an intensity of mass spectrometry peaks, and this is why I propose that the atomic mass unit is defined as exactly 1/12 of the mass of the atom of the most abundant carbon isotope. Linking the unit u with mass spectrometry is a common and useful practice, as shown in numerous textbooks.[17−22] This inspired me to propose the following imaginary experiment:

> Imagine a time-of-flight mass spectrometer.[19] Prepare samples of all nuclides of all elements and introduce them simultaneously to the spectrometer. The total number of nuclides in these samples is equal to r, the value of r not being essential. The recorded spectrum consists of r peaks, and for each peak the value of time t_i is known. Thus, a series of values is obtained: $t_1, t_2, ..., t_s, ..., t_r$. The kinetic energies of ions of all the nuclides inside the spectrometer are equal, hence $(r - 1)$ proportions can be written:
>
> $$\frac{m_i}{m_s} = \frac{t_s^2}{t_i^2} \tag{1}$$
>
> where $i = 1, 2, ..., r$ for $i \neq s$ and m_s is the atomic mass of the nuclide chosen as the standard.
>
> The values of m_i are unknown, but note that if the standard mass is known then the remaining masses can be calculated easily. By virtue of definition, the mass of the most abundant carbon isotope is assigned 12 u. Its peak is the greatest one among all the carbon peaks. Having this atomic mass defined, the atomic masses of the other nuclides can be calculated immediately.

THE MOLE AND THE AVOGADRO CONSTANT

Experimental Roots of the Mole Concept

The mole concept is useful in science for the following reasons: (i) Samples of the order of grams or milligrams are commonly used in macroscopic experiments. They contain a huge number of atoms, normally greater than 10^{20}. (ii) It is frequently convenient to use samples with given proportions of atoms or molecules. Stoichiometric calculations and preparation of solutions of given concentrations, as well as the application of the ideal gas law to characterize gas samples are examples taken from elementary chemistry.[23] In specific cases, the numbers of entities need to be equal.

The Existing Definition of the Mole and the Problem of Amount of Substance

With reference to the discussion in this *Journal* mentioned earlier,[5−12] the relations are examined between the terms seen in definition 2: *amount of substance* (AoS) and the itemized microscopic entities, namely, *atoms*, *molecules*, *ions*, *electrons*, and so forth. The term *substance is* applicable to characterization of elements and chemical compounds, that is, the type of matter with a uniform, well-defined composition (even at microscopic level). This enables us "to specify the number of identical, individual units that comprise it".[5] For substances, the term AoS is acceptable under the condition that the stoichiometric variability of chemical compounds can be ignored.

A mole of electrons, also named the Faraday constant, amounts to the charge of 96,485 coulombs, and it cannot be labeled *substance*. The same statement applies to *einstein*, as remarked by Karol:[7] " ...spectroscopists unit, the einstein... defined as a mole of radiation quanta ... definitely not being a substance under accepted terminology". Hence, for these two cases, the term AoS is not applicable.

The majority of matter in the universe has no definite composition. Rocks, plasma, or biomass cannot be named *substances*. Consequently, the mole concept is not applicable, for instance, to a piece of wood. This is why the term *amount of matter*, although embracing electrons and quanta as well as elements and chemical compounds, is also not an acceptable candidate for the quantity of which the mole is a unit, when applying definition 2. The amount of matter, whether measured by mass or volume, quantifies a system adequately, if the composition of the system is irrelevant.

Moreover, it seems that the synonym *chemical amount* proposed in 1993 is a step back compared to AoS. *Amount of substance* is based on the well-defined term *substance*. Besides, considerations concerning the *chemical amount* provoke associations with diffuse boundary between physics and chemistry and encourage more clever students to ask embarrassing questions, such as "Is the electron a physical or a chemical entity?" The modifications of the definitions approved in 2006, already mentioned in the introduction, make their understanding easier, but emphasize the ambiguity of definition 2.

To constructively shift this discussion, one can focus attention on the term *numerosity* as seen in the article by Price and De Bievre.[24] To conclude the discussion, it would seem sufficient to adjust the definition advocated by IUPAC (cited after Milton and Mills[25]) "Amount of substance is a quantity proportional to the number of specified elementary entities in a sample. The proportionality constant is the same for all substances, and is the reciprocal of the Avogadro constant." For the adjustment, I propose that *amount of substance* is replaced by *collection* or *quantity of microentities*, the term very similar to "a collection of a number of specified elementary entities", as seen in Leonard.[26] The exemplary adjusted definition would then be: *The collection of microentities is a quantity proportional to the number of specified microentities. The proportionality factor is the reciprocal of the Avogadro constant.*

AVOGADRO'S NUMBER

The essential feature of the definition 2 is its flexibility. When modified, it can be used to define Avogadro's number, N. Thus, two possibilities result. Either the definition of the mole is followed by the definition of N or vice versa, the definition of Avogadro's number is followed by the definition of the mole. In this article the latter case is chosen, that is, the definition of Avogadro's number involves the direct comparison with the carbon-12 standard (see ref 27) as it seems that this order facilitates understanding. Accordingly, definition 2 can be adjusted to be as follows:

- Definition 3: Avogadro's number is the number of atoms in 0.012 kg of carbon-12.

Then, definition 3 implies directly:

$$\begin{aligned} N &= (\text{mass of the sample})/(\text{mass of the single atom}) \\ &= 12\ \text{g}/12\text{u} = 1\ \text{g/u} \end{aligned} \tag{2}$$

Note that a measurement is a comparison with the standard and there are two standards for the measurements of mass: kilogram and the atomic mass unit. For practical purposes, the fractions of kilogram, gram, and milligram are preferred by chemists. The ratio of two standards cannot be chosen arbitrarily but must be determined experimentally. This is clearly shown by eq 2. The

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unit u must be expressed in kilograms,[13] then Avogadro's number is dimensionless.

The value of N was determined independently many times by several experimental methods over the period of about 150 years. Uncertainty of the determinations has been reduced significantly.[27] The most recent value of the redetermined Avogadro's number, published in January 2011, is $6.02214078(18) \times 10^{23}$.[28] However, in teaching, most commonly a value of 6.022×10^{23} is used.

It seems that Rutherford's method of the determination of Avogadro's number, applied in 1909 (for a description see ref 19, pp 137−139), is most suitable for teaching purposes. It is because the conceptual simplicity makes the experiment easy to grasp. In the experiment, a known number of alpha particles were emitted by radium owing to which the number of helium atoms resulting from their catching of electrons was also known. The volume of the helium was then measured yielding the number of helium moles. The resulting Avogadro's number is the ratio of the number of atoms to the number of moles.

Avogadro's number can also be determined by students in an electrolysis experiment; for a description see the article by Ceyhun and Karagölge.[29]

THE MOLE CONCEPT

The mole can be defined as follows:

- Definition 4: *The number of any objects equal to Avogadro's number is the mole.*

Thus, the numbers of $N = 6.022 \times 10^{23}$ atoms or molecules or ions or electrons are examples of moles. By this definition, the value of N has a unit, the reciprocal mole (mol^{-1}). This value is the Avogadro constant denoted N_A.[30] In the case of elements and chemical compounds, the quantities, of which the mole is a unit, are *collections of atoms* and *collections of molecules*, respectively. In the case of electrons, however, the quantity is *charge*, the term shorter than the *collection of electrons*. In the case of alpha particles, the quantity will be the *collection of alpha particles*. *Mole* is a term similar to *dozen* or *score*. These units are undoubtedly useful if the counted objects are identical, such as unused pencils, matches, nuclides, or electrons. A generalization of the mole concept for similar objects will be discussed in the next section.

The definition of the mole exposes the importance of the Avogadro constant. This constant is a scaling factor between atomic-scale entities, such as atoms and molecules, and a mole—the macroscopic base unit in the SI system.[31]

Consider a sample consisting of N nuclides of A with the atomic mass M_A u and another sample consisting of N nuclides of B with the atomic mass M_B u. By virtue of eq 2, the total mass of the first sample is equal to $N \times M_A$ u or M_A grams. Similarly, the mass of the second sample is equal to $N \times M_B$ u or M_B grams. The mass of a mole of atoms or molecules expressed in grams is called the molar mass. A comprehensive characterization of this important term is presented in the article by DeMeo.[32]

The considerations outlined above hint how to count atoms by weighing. To prepare a sample consisting of 1 mol of aluminum atoms (aluminum is a monoisotopic element!), the atomic mass of aluminum should be known (equal to 27 u) and a piece of aluminum wire weighing 27 g should be cut. Obviously, any fraction of mole can be prepared in this way. The idea of counting by weighing outlined above works well when all objects are identical or at least similar. Similarity means here that the value of average mass of objects is reasonable information. This remark is essential for understanding the mole concept in the case of poly-isotopic elements.

Finally, a quote by Lorimer[33] is highlighted: "...the mole is often thought of by chemists as an Avogadro's number of entities." The definition in question can be found, for instance, in one of chemistry textbooks available in Poland since 1999, written by Kluz and Łopata[34] and addressed to young school students aged 13−14 years.

GENERALIZATION

DeMeo[32] describes the following situation: for a poly-isotopic element E both the atomic masses of its constituent isotopes E_1, E_2, ... and their percentage abundances are known. Hence, the abundance-weighted average mass expressed in atomic units is E_{av} and consequently, the molar mass of element E is E_{av} grams. The mole of E can be considered as consisting of N identical *non-existing* atoms with atomic mass equal to E_{av} u each. This concept is useful in stoichiometry. However, during spectrometric measurements, one should remember that a mole of atoms consists of different nuclides E_1, E_2, ... with slightly different (except hydrogen) atomic masses M_{E1}, M_{E2}, ... and sometimes extremely different abundances.

In the above situation, the mole concept has been applied to the ensemble of similar objects characterized by an average value reasonably determined. In this generalization, the word *reasonably* is pivotal. What does it really mean? The definition is difficult to propose; however, various examples may be helpful. A dozen eggs bought in a shop can be *reasonably* characterized by the average mass of an egg. Likewise, a mole of atoms of a poly-isotopic element is a *reasonable* concept. However, an average mass of a dozen animals may not be *reasonable* for instance, for a zoo manager preparing transportation of 12 different animals, such as tigers, butterflies, elephants, and parrots.

Further, an element that exists in the form of diatomic molecules is a slightly more complicated case. It is obvious that molar masses of O_2, N_2, and Cl_2 are equal to the doubled molar masses of O, N, and Cl. However, the effect of isotopic composition in this case is more pronounced than in the case of single atoms (see ref 22). Two stable isotopes of nitrogen and three stable isotopes of oxygen are known. Hence, a nitrogen molecule and an oxygen molecule can be formed from two atoms in three and six combinations, respectively. Consequently, three types of nitrogen molecules and six types of oxygen molecules exist. The molecular masses differ slightly within each group.

For chemical compounds, the mole concept is principally identical to that of polyatomic elements. If for some reason the molecular mass is unavailable, it can be calculated from the chemical formula of a compound, and then the average atomic masses of the elements are used. An example is instructive: The formula of a simple amino acid called glycine is H_2N-CH_2-COOH. The molecule consists of 5 hydrogen atoms, 2 carbon atoms, 2 oxygen atoms, and 1 nitrogen atom. The average atomic masses of these elements are multiplied by 5, 2, 2, and 1, respectively, and summed up. Thus, the molecular mass of glycine equal to 75.07 u is obtained. Correspondingly, a mole of glycine is 75.07 g. If we take into consideration that there are also two stable isotopes of carbon and two stable isotopes of hydrogen, we see that a huge number of glycine molecules can be distinguished. The isotope effect outlined above is observed as contributing to the broadening of vibration spectroscopy

Table 1. Comparison of the Current and Proposed Definitions

Topic	Current Definition	Proposed Definition
Atomic mass unit	Definition 1: The Dalton (Da) and the unified atomic mass unit (u) are alternative names (and symbols) for the same unit, equal to 1/12 times the mass of a free carbon-12 atom, at rest and in its ground state.[13]	The Dalton (Da) and the unified atomic mass unit (u) are alternative names (and symbols) for the same unit, equal to 1/12 times the mass of the free atom of the most abundant carbon isotope, at rest and in its ground state.
Mole	Definition 2: Mole is the amount of substance of the system that contains as many elementary entities as there are atoms in 0.012 kg of carbon-12. 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.[13]	Definition 3: Avogadro's number is the number of atoms in 0.012 kg of carbon-12. Definition 4: The number of any objects equal to Avogadro's number is the mole.

bands. However, the discussion of this effect is beyond the scope of this article.

In a chemistry course, I suggest that the concepts could be taught in the following order. First, the concept of molar mass is almost obvious for nuclides, also the abundance-weighed atomic mass is an easy issue. Once familiar with these two concepts, a student will be able to understand the more difficult concept of molar mass of poly-isotopic elements and of chemical compounds. This scheme of teaching was adopted, for instance, in the textbook by Tro[17] where two separate subchapters were proposed: "Atomic Mass: The Average Mass of an Element's Atoms" and "Molar Mass: Counting Atoms by Weighing Them".

THE POSSIBILITY OF A NEW DEFINITION OF MOLE AND KILOGRAM

A measurement is a comparison with the standard. This is why the reliability of the standards is of pivotal significance for science. The standards should be "invariant under translation in space and time – even on an astronomical scale".[35] Similar to the successful cases of time and length,[7] attempts have been undertaken[33] to replace the mass standard—the only SI unit that is still defined by an artifact (the platinum–iridium cylinder kept at the Bureau International des Poids et Mesures in Sèvres, France). Other metallic mass standards in various countries have been compared with the Sèvres standard over the period of over 100 years, and stability of this standard has been questioned. This is why "the unit of mass needs to be redefined".[36]

A few possibilities of the replacement of the standard were discussed in the critical review article by Leonard;[4] the simplest case suitable for incorporation into an introductory chemistry course is presented. Equation 2, of key importance, can be easily transformed into

$$1\ \mathrm{kg} = 10^3 \times N \times \mathrm{u} = 10^3 \times N \times \{m_a(^{12}\mathrm{C})/12\} \qquad (3)$$

where $m_a(^{12}\mathrm{C})$ denotes the mass of carbon-12 atom. As Leonard[4] points out "any two of Avogadro's number, kilogram, and atomic mass unit (Da in the Leonard text) may be defined independently; then the third is determined by equation (3)". The kilogram and u are presently defined; thus, Avogadro's number is determined from eq 3.

Intensive work has been done to change this situation. The value of the Avogadro constant has been determined experimentally a number of times with an effort to minimize the uncertainty of determination. Once the criteria assumed for the relative standard uncertainties, as well as other criteria, are met,[37] the Conférence Generale des Poids et Mesures (CGPM)[38] will select the best estimate ($N_{A,best}$) as the value of the Avogadro constant, a value which, by definition, has no uncertainty. The approval of the $N_{A,best}$ by CGPM will imply that the kilogram is determined by eq 3 as the multiple of the mass of carbon-12 atom, because the definition of u remains unchanged.

The mole is a collection containing $N_{A,best}$ microentities.[39] This definition of the mole is similar to that proposed by Tro in his textbook:[17] "A mole is the amount of material containing 6.02214×10^{23} particles". A sequence of six digits in the Avogadro constant used in this definition is also seen in four recent values of N_A published in 2006–2011 (ref 28, Figure 5). Understandably, the value $N_{A,best}$ is expected to be more accurate. In teaching, however, a four-digit Avogadro constant, $6.022 \times 10^{23}\ \mathrm{mol}^{-1}$, is commonly used. In this context, the definition of Tro simulates a future situation when, upon the approval by CGPM, the uncertainty of the N_A value will be equal to zero. It would be beneficial if students were able to understand the way of thinking they would be facing during many years of their professional activity.

SUMMARIZING REMARKS

The controversial issues tackled in this article are almost invisible in the quoted chemistry textbooks. The current definition of the mole (definition 2) is typically given in brief, which is why the elementary entities are not always itemized and *amount of substance* is sometimes lacking. In fact, the latter term is frequently mentioned only marginally. The number of moles of substance is often referred to as the "amount" of the substance.[17] The same is also true of the term *chemical amount*. This is "...the formal name for the quantity for which the units are moles... However, almost universally, chemists talk informally in terms of the 'number of moles'" (ref 21, p 65).

The above situation can be accounted for by the obvious fact that authors of introductory chemistry textbooks cannot discuss the unclear matter in detail. A long list of shortcomings of the current definition of the mole was presented by Leonard in the article dated 2007, the first shortcoming in the list being: "The indirect nature of definition makes it somewhat difficult to comprehend".[26] The implications are obvious too. Teachers facing the lack of information are unable to clarify the doubts of students, as evidenced by the tests proposed, performed, and described by Furió et al.[40] Finally, the conclusion is obvious too. The source of shortcomings should be removed by adjusting the basic definitions. This will initiate a chain of corrections. For such adjustments, in the present article it is suggested that

- the description *the most abundant carbon isotope* be used for the definition of the standard nuclide,

- the already defined Avogadro's number be used for the definition of the mole,
- in the currently accepted definition of the mole, the term *amount of substance* be replaced by the term *collection* or *quantity of microentities*.[26]

In this manner the internal inconsistency of the definition (definition 2) would be eliminated, that is, the term *amount of substance* would no longer be connected with the terms *mole of electrons* and *mole of quanta*. The current and the proposed definitions have been compared in the Table 1.

I also propose that in teaching:

- it is exposed that *Avogadro's number is equal to the quotient gram/atomic mass unit*, as suggested by Leonard[4] and DeMeo,[32]
- the difference between *Avogadro's number* and *the Avogadro constant* is discussed,
- the definition of the mole is first presented for nuclides, to be further generalized for poly-isotopic elements.

As outlined in this article, the redefinition of kilogram and the mole is a challenging metrological task. For its realization, a more exact value of Avogadro's number is needed, which will be followed by a lengthy formal procedure. The same, however, is not true of teaching. The new definition of the mole or the current one, if adjusted, can be included into elementary courses of chemistry even now.

AUTHOR INFORMATION

Corresponding Author

*E-mail: baranski@chemia.uj.edu.pl.

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$$N_A = \text{the Avogadro constant} = N\ \text{mol}^{-1}$$

The name of the particle, for example, *Si atom*, must be added too on the basis of the definition of the mole (see definition 2). This can be illustrated when taking into account the conversion of a number of moles (e.g., 2.1 mol of argon atoms) into a number of particles, that is, a number of argon atoms. For this purpose, a number of moles must be multiplied by the proper conversion factor.

$$2.1 \text{ moles} \times (\mathbf{6.022{\times}10^{23}} \text{ argon atoms})/\mathbf{mole} = 1.265 \times 10^{24} \text{ argon atoms}$$

In the above equation, the Avogadro constant is printed in bold type. The addition of the name *argon atoms* is consistent with definition 2.
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(38) The article by Freeman[5] characterizes 10 or so International Organizations involved in solving metrology problems, for example, choice of standards, defining units, adjustments of the values of the fundamental physical constants.

(39) For comparison, see the following text cited after ref 33: "The effect of this definition is that the mole is the amount of substance of a system that contains $6.02214179 \times 10^{23}$ specified elementary entities". Explanation of the metrological need for nine-digit Avogadro constant is beyond the scope of this article.

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