A new definition for the mole based on the Avogadro constant: a journey from physics to chemistry

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The mole is the most recent addition to the set of base units that form the International System of Units, although its pre-cursor the ‘gram-molecule’, had been in use by both physicists and chemists for more than 120 years. A proposal has been published recently to establish a new definition for the mole based on a fixed value for the Avogadro constant. This would introduce consistent relative uncertainties for the molar and the atomic masses while making no change to the system of relative atomic masses (‘atomic weights’). Although the proposal would have little impact on the measurement uncertainty of practical work, it has stimulated considerable debate about the mole and the nature of the quantity amount of substance. In this paper, the rationale for the new definition is explained against the background of changes in the way the quantity amount of substance has been used, from its first use during the early development of thermodynamics through to the use of the ‘number of gram-molecules’ at the end of the nineteenth century.

Keywords: mole; amount of substance; Avogadro constant; International System of units

1. Introduction

The ideas underlying our current use of the quantity amount of substance and its base unit, the mole, have developed since the earliest times when scientists needed to quantify the observation that matter reacting chemically does not do so simply in equal masses of the samples involved.

The development of the ideas underlying the mole from the seventeenth to the nineteenth centuries has been discussed before [1]. In addition, the history of the Avogadro constant has been reviewed [2]. However, the parallel developments in the understanding of amount of substance, the quantity of which the mole is the base unit, have not been discussed in detail. This paper shows how the ‘gram-molecule’—a unit invented for practical use in the nineteenth century—was developed to become the basis for the current definition agreed for the mole in 1971. It illustrates how our understanding of the three related concepts: the mole, amount of substance and the Avogadro constant, has developed and how these changes reflect the focus of the major protagonists towards either physics

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or chemistry. The paper concludes with a discussion of whether the present way that the quantity amount of substance is used is completely consistent with the present definition for the mole, and whether this inconsistency could be removed by adopting a definition of the mole based on a fixed number of entities.

2. The gram-molecule

The ideas underlying our modern understanding of thermodynamics and kinetic theory were developed during the nineteenth century [1]. Central to these developments was the discovery that matter reacting chemically does not do so simply between equal masses of the samples involved. We now call the study of this phenomenon ‘stoichiometry’, defined as: ‘the relationship between the amounts of substance that react together, and the products that are formed’.

Another development during the nineteenth century that was central to our modern understanding of the chemical nature of matter was the observation by Avogadro that ‘equal volumes of ideal or perfect gases, at the same temperature and pressure, contain the same number of particles, or molecules’. This is now known as Avogadro’s law. It provides the motivation to formulate expressions for the quantity of a sample that reacts with another sample. The most notable example of such a formulation is the gram-molecule, which has been used to refer to both a unit and a quantity. It is informative to consider some examples of its use from the end of the nineteenth and the beginning of the twentieth centuries.

(a) Ostwald and Nernst

When Ostwald and Nernst wrote their textbooks, both published in 1893, the term gram-molecule was in common use [3,4]. A typical example of its use by these authors is ‘the pressure that one g.-molecule of a gas would exert on the walls of a vessel...’ [4]. However, the phrase makes no specific reference to either the mass of the sample or to the number of entities in it. It is simply used as a standard way to refer to the ‘size’ of the sample. These texts also include what is generally taken to be the first citation of the use of the word Mol as an abbreviation of gram-molecule, ‘...eine g.-Molekel oder ein Mol...’.

(b) Einstein

Einstein provides an example of the use of the term gram-molecule in the research he published in 1905. It is particularly interesting because it was used in the research that gave rise to one of the first determinations of what we now call the Avogadro constant. It was published at a time when the ‘atomistic hypothesis’ had become axiomatic to the study of chemistry, but was not universally adopted in the study of physics. Einstein was a supporter of the hypothesis and had an insight into how the laws of thermodynamics and kinetic theory could be brought together to give incontrovertible support for it that was observable at the macroscopic scale [5].

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Einstein’s argument [6] started with the formula derived by van’t Hoff for the osmotic pressure \( \Pi \) in a solution at temperature \( T \),

\[
 \Pi V = zRT, \tag{2.1}
\]

which introduced the gas constant \( R \) and the variable \( z \). He explained it with the phrase ‘Let \( z \) gram-molecules of a non-electrolyte be dissolved in a volume \( V \).’ Subsequently, he set \( z = n/N \) ‘where there are \( n \) suspended particles present . . . and . . . \( N \) signifies the actual number of molecules contained in a gram-molecule’. (When Einstein’s argument was re-worked by Langevin [7], he also used the same terminology.) The argument leads to the derivation of the Stokes–Sutherland–Einstein formula, which can be re-arranged to give

\[
aN = \frac{RT}{6\pi\eta D}, \tag{2.2}
\]

where \( N \) is the ‘actual number of molecules contained in a gram-molecule’, \( a \) is the radius of the particles, \( \eta \) is the viscosity of the solution, \( T \) is the temperature, \( R \) is the ideal gas constant (Einstein does not explain this symbol in his text) and \( D \) is the diffusion coefficient, which can be measured by microscopic observation of the mean square displacement of a particle in time \( t \) using \( D = \bar{x}^2/2t \).

In a publication the following year [8], Einstein reworked an argument from his doctoral dissertation to derive a formula for the change in viscosity of a solution when molecules of radius \( a \) were dissolved in it. In the first step, he developed a formula that linked the change in viscosity to the total volume of molecules dissolved per unit volume of solution. This formula could be re-organized to give

\[
a^3N = \frac{3M}{10\pi\rho} \left( \frac{\eta^*}{\eta} - 1 \right), \tag{2.3}
\]

where \( M \) is the molecular weight of the dissolved molecules, \( a \) is the radius of the particles, \( \rho \) is the mass of the dissolved substance per unit volume of solution, \( \eta \) is the viscosity of the solvent and \( \eta^* \) is the viscosity of the solution.

In both cases, the gram-molecule is introduced to the argument in order to quantify the number of molecules in a sample. The combination of formulae (2.2) and (2.3) enabled him to determine the actual number of molecules contained in a gram-molecule \( (N) \), achieving a value of \( 6.56 \times 10^{23} \) [8].

\[(c)\] Perrin

In 1909, Perrin [9] made further measurements of the Brownian motion of particles, which, together with the formulae derived by Einstein, enabled him to determine a value of \( 6.7 \times 10^{23} \) for \( N \) [2]. Perrin explained clearly how he used the gram-molecule:

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. [9]
He then went on in the same publication to propose that ‘This invariable number \(N\) is a universal constant, which may appropriately be designated the Avogadro constant. If this constant be known, the mass of any molecule is known’ [9,10].

These examples illustrate two conceptually different approaches to the use of the gram-molecule. One of them (by Einstein) uses it to refer to a number of molecules and the other (by Perrin) uses it to refer to a mass of material specified according to its atomic weight.

3. Advances in the determination of the Avogadro constant

Einstein expressed his gratitude to Perrin for his work, ‘I would have thought it impossible to investigate Brownian motion with such precision; it is fortunate for this material that you have taken it up’ [11].

The next important advance in the history of the Avogadro constant was the development of a new method that was based on entirely different physics. It required the use of X-ray crystal diffraction (XRCD) to measure the dimension of the unit cell in a crystal and a measurement of the atomic weight of the material. These gave the density of the unit cell of the crystal (expressed in unified atomic mass units), which by comparison with a measurement of the density of the crystal as a whole (expressed in kilogram) enabled the determination of the Avogadro constant. This is the same method that is used today.

The first application of the method was to single crystals of calcite [2]. The major limitation of the method at that time was in the determination of the length of the unit cell of the crystal. The X-ray wavelengths were measured with respect to Siegbahn’s x-unit, which was defined in terms of the grating spacing of a cleavage plane of ‘purest calcite’. In this way, the precision of the measurement exceeded the accuracy with which the absolute values were known (in the International System (SI) unit of metre). In the mid-1960s, Bearden [12] published a re-evaluation of all X-ray data and corrected the wavelengths (as far as possible) to five standard lines. These changes in the value of Siegbahn’s x-unit, together with a small change owing to the adoption of the \(^{12}\text{C}\) scale for relative atomic masses in place of the \(^{16}\text{O}\) scale, resulted in relative changes of 450 ppm (corresponding to six standard uncertainty intervals) in the accepted values of the Avogadro constant over the period from 1953 to 1965.

The next major improvement in the uncertainty of the Avogadro constant came with the first measurement based on a pure crystal of silicon [13]. The application of the XRCD methods to a silicon crystal, together with the use of an X-ray method capable of giving a value for the lattice constant in the SI metre, was a breakthrough. The uncertainty of the result was then dominated by the determination of the chemical purity of the artefact and the measurement of its atomic weight. For the first time in the history of the Avogadro constant, the major limitations in its measurement were chemical rather than physical.

The most recent advance in the application of the XRCD method has been by the use of a single silicon crystal that is highly enriched in the isotope \(^{28}\text{Si}\). This approach was foreseen by Deslattes as the best way to minimize the uncertainty owing to the measurement of the atomic weight [13], and is described elsewhere [14].

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4. The ‘chemical mass unit’, ‘number of moles’ and amount of substance

Although improvements in the experimental methods of physics during the twentieth century enabled the determination of the Avogadro constant with ever decreasing uncertainty, it is difficult to find evidence of any similar interest in formalizing the term gram-molecule. Stille, in his text on metrology [15], provided a detailed explanation of how the term Mol was in use at that time. He explained that it was being used in two conceptually different ways. The first was as a ‘chemical mass unit’ through the quantity equation

\[ 1 \text{ mol} = \{A_r(X)\} \text{ g}, \quad (4.1) \]

where \( A_r(X) \) represents the numerical value of the atomic weight of X.

The second way in which the term Mol was used was referred to by Stille as Molzahl (literally translated ‘number of moles’), defined by the equation

\[ l = \frac{N}{L}, \quad (4.2) \]

where \( l \) is the number of moles (Molzahl), \( N \) is the number of entities and \( L \) is Loschmidt’s number. Equation (4.2) is given using current notation in the following section.

In Stille’s text, Molzahl is a dimensionless quantity. He advocated its retention in this form rather than the introduction of an alternative German term Stoffmenge (literally ‘amount of substance’) as a new base unit with an associated definition for the term Mol of the ‘Stoffmenge that contains as many entities as there are in \( A_r(O) \) g of atomic oxygen’.

One of the advocates of a firm metrological basis for chemical science at this time was Guggenheim, who argued that ‘it can sometimes be useful in dimensional analysis to regard the number of atoms as having dimensions different from a pure number’ [16]. He proposed that the term ‘amount of substance’ be used as the name for the quantity for which the mole is the unit, and justified its choice with reference to the German noun Stoffmenge [17].

5. The 1971 definition of the mole

In 1970, the International Union of Pure and Applied Chemists (IUPAC) published a definition for amount of substance:

The amount of substance is proportional to the number of specified entities of that substance. The proportionality factor is the same for all substances and is called the Avogadro constant. [18, p. 7]

The text also emphasizes that the term ‘number of moles’ should not be used [19]. While this remark is supported by the example that the term ‘number of kilograms’ would not be used, it takes no account of the view of Stille about

\[ 1 \text{ Equation (4.1) appears in Stille’s text. It provides a practical expression for the formulation of the mol, but it is not strictly a quantity equation.} \]

\[ 2 \text{ Stille used the term ‘Loschmidt’s number’ to refer to the numerical value of the Avogadro constant. Modern usage reserves the term Loschmidt’s number for the number of particles in 1 cm}^3, \text{ and refers to the numerical value of the Avogadro constant as the Avogadro number.} \]

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the *Molzahl* referred to above.\(^3\) Hence, equation (4.2) would be written in the current notation as

\[
\{n\} = \frac{N}{\{N_A\}},
\]

(5.1)

where \{n\} is the numerical value of \(n\), \(N\) is the number of entities and \{\(N_A\)\} is the numerical value of \(N_A\).

In 1971, the General Conference of Weights and Measures [22] endorsed the principal of the definition for the mole as previously approved by the International Unions for Chemistry and for Physics,

> The mole is the amount of substance of a system that contains as many elementary entities as there are atoms in 0.012 kilogram of carbon 12.

When the mole is used, the elementary entities must be specified and may be atoms, molecules, ions, electrons, or other particles, or specified groups of such particles.

[22, p. 115]

The definition resolved any confusion arising from the use of both the gram-molecule and the kilogram-molecule as units and between the use of a scale based on either \(^{13}\)C or \(^{16}\)O. It made a number of practical units such as the gram-atom, gram-equivalent, equivalent, gram-ion and gram-formula obsolete [19]. It also introduced dimensional analysis to chemistry, which is now considered essential for the efficient use of the many different quantities used to express composition [23]. However, the form of definition that was chosen [24] split the wording that had been used by the International Unions into two sentences, thus, introducing the qualifying condition for the use of the mole, which we discuss in the following section.

### 6. Difficulties with the 1971 definition of the mole

Before moving on to discuss the case for a revision to the definition of the mole, it is necessary to emphasize that, although a limited number of views were published on the topic prior to the proposals to re-define four base units of the SI, there has never been any significant momentum generated for a change. Nevertheless, the opportunity to re-define four base units and to re-word the remainder including the mole, into a consistent form has now generated some momentum in favour of such a change.

Although there have never been any coordinated views in favour of such a change, the view that the mole is in some respects different to the other base units of the SI has been proposed by several authors. The argument centres on two points. The first concerns the inter-play between the two views that the mole is, on the one hand, simply a number of entities and, on the other hand, it is simply a mass of material. These views correspond to the conceptually different approaches of the number of moles and the chemical mass unity articulated by Stille. As they both have a sound basis, we should recognize that they have different uses, and they should be allowed to coexist. The wording of the 1971 definition conveys elements of both approaches.

\(^3\)The previous publication [20] recommended the term ‘number of moles’ and made no reference to the ‘amount of substance’. The same recommendation was made in the report of The Symbols Committee of the Royal Society [21].
The second aspect in which the mole is different to the other base units of the SI is in the presence of a ‘qualifying condition’ about its use as the second sentence of the definition [25]. While such a qualifying condition does not appear in the definitions of the other SI base units, it is only a statement of something very obvious—that a sample of a mixture can only be fully characterized by stating the amount of all of the components present. In practice, this condition need not be any different to the observation that a complete specification of the size of an object requires measurement of its length in many different directions.

7. A definition of the mole based on a fixed number of entities

The proposal made in 1995 [26] and subsequently clarified in 2009 [27] was for a definition of the mole based on a fixed number of entities. This is expressed in the form: ‘The mole is the unit of amount of substance of a specified elementary entity, which may be an atom, molecule, ion, electron, any other particle or a specified group of such particles; its magnitude is set by fixing the numerical value of the Avogadro constant to be equal to exactly $6.02214 \times 10^{23}$ when it is expressed in the unit mol$^{-1}$.’

It is stated here in an explicit unit style to give a presentation that is consistent with the proposed revised definitions for the other base units. The value chosen for $N_A$ will be the best available at the time that the definition is finally ratified.

A consequence of moving to a definition of the mole based on a fixed number of entities rather than a fixed mass of a specified material is that there must be some changes to the way the definition is expressed mathematically. The molar mass constant is fundamental to the present definition of the mole and to its use, as illustrated by the formulation of the present definition with the following expression:

$$M(^{12}\text{C}) = A_r(^{12}\text{C})M_u.$$ (7.1)

The present definition sets the molar mass constant $M_u$ equal to $10^{-3}$ kg mol$^{-1}$ exactly. Therefore, all of the quantities in equation (7.1) are exact, as $A_r(^{12}\text{C})$ is fixed as the basis of the conventional scale of atomic weights (relative molecular masses).

If the mole is re-defined on the basis of a fixed number of entities, then the mass of a mole of $^{12}\text{C}$ would still be given by

$$M(^{12}\text{C}) = N_A m(^{12}\text{C}).$$ (7.2)

However, as $m(^{12}\text{C})$ is the mass of a carbon atom, which must continue to be an experimentally determined quantity, then $M(^{12}\text{C})$ will become an experimentally determined quantity. Therefore, $M_u$ must also become an experimentally determined quantity with a relative uncertainty of $1.4 \times 10^{-9}$ [27]. This would be too small to have any significance in practical work. It is a practical consequence of fixing $N_A$ that $M_u$ becomes an experimentally determined quantity.

However, a re-definition of the unit mole should take account of our best understanding of the quantity for which it is a unit. Considering again the distinction made by Stille (§4), we can see that this proposed definition moves from the mole as defined by equation (4.1) to something that is conceptually
much closer to the number of moles as defined by equations (4.2) and (5.1). It would lose its explicit connection to mass, which is considered axiomatic by many chemists.

8. Difficulties with the proposed new definition of the mole

Even in the short time since the proposal for a new definition for the mole was published, various counter views have been published. One of the objections to the proposal to re-define the mole based on a fixed value of the Avogadro constant uses the argument that \( N_A \) is not truly a fundamental constant in the same way that, for example \( c \), \( h \) and \( e \) are. This argument is difficult to sustain in the absence of a consensus view on what is truly a ‘fundamental constant’. Different views have been published, for example, that the fundamental constants are solely those which are dimensionless (e.g. those that are entirely independent of any choice of unit system) or the view that they are the ‘minimum set’ of constants from which all others can be derived. While many prominent scientists have contributed to this debate [16,28,29], there is no consensus.

The question at stake here is actually—is the Avogadro constant suitable to be used as the basis for a definition of an SI base unit? Clearly, the Avogadro constant (and its precursor ‘the number of molecules in a gram-molecule’) has been in widespread use for nearly 150 years. In addition, the determination of the best value for \( N_A \) is now inextricably linked to the process of the least-squares fitting of the fundamental constants [30,31]. It has become ‘fundamental’ to chemistry, and has a unique and important role in the language and practice of physics and chemistry.

9. Realizing the mole

Each of the base units of the SI has an agreed text associated with it specifying how it should be realized in practice. Each of these is known as a *mise en pratique* [32], and the mole is no exception. However, the statement of how the mole should be realized is much more general than the equivalent statements for the other base units. In essence, it specifies that a method with a well-defined measurement equation in which all of the quantities involved are expressed in SI units should be used. The important features of how such primary methods can be used have been the subject of discussion [33]. To a large extent, the generality of the *mise en pratique* for the mole lies behind the ubiquity of its use [34].

The most widely used primary method for the realization of the mole is the process of weighing pure material and evaluation of the amount of substance according to the equation

\[
n = \frac{m}{M(X)} = \frac{m}{A_r(X)M_u}, \tag{9.1}
\]

where \( n \) is the amount of substance (mol), \( m \) is the mass of pure material (kg), \( M(X) \) is the molar mass of \( X \) (mol kg\(^{-1}\)), \( A_r(X) \) is the atomic weight (relative molecular mass) of \( X \) and \( M_u \) is the molar mass constant (mol kg\(^{-1}\)).

In some respects, equation (9.1) is a specification of the 1971 definition of the mole, but it is not the only method by which the mole is realized. It will still be
valid if a revised definition of the type discussed in §7 were to be introduced, but
$M_u$ would have become an experimentally determined quantity with a very small
uncertainty.

In some respects, the essence of the proposed definition is better summarized by

$$n = \frac{N}{N_A},$$

(9.2)

where $N$ is the number of specified entities in the sample. This is the same as the
quantity $\text{Stoffmenge}$ discussed by Stille (see §4), and the underlying numerical
values are related by equation (5.1). It is also equivalent to equation (9.1), as can
be shown by the substitution

$$N = \frac{m}{A_r(X)M_uN_A}.$$  

(9.3)

This illustrates another interesting feature of the new definition of the mole—that
the amount of substance corresponding to one entity would be $\{N_A\}^{-1}$ exactly.
While the need to quantify such a small amount of substance may not have been
required in the past, it has been suggested that it may be useful in emerging
applications in the biological sciences.

10. Conclusion

In summary, we have reviewed how our present use of the quantity amount of
substance has developed from the practical quantity the gram-molecule. Among
early published uses of the term, it appears that some users intended it to refer
to a number of entities, but others intended it to refer to a mass of material. The
distinctions between these conceptually different uses of the term are subtle and
have only been explained clearly by Stille [15]. It is a mistake to assert that the
amount of substance has solely the character of one, to the exclusion of the other.

Any proposals that are debated for a future definition of the unit or the
quantity amount of substance must recognize that the present terms are in
extremely widespread use. There have always been some differences between the
mole and the other base units. One of these is that the underlying quantity—
amount of substance—has the character of both a mass of material (the most
natural realization for chemistry) and a number of entities (the most natural
approach in physics). The present definition specifies the mass of a mole of a
particular pure substance, but not the number of entities. If a revised definition
is adopted based on a defined number of entities, the alternative position would
exist in which the number of entities is specified exactly, but the mass is not.
Different communities of users will view such a change differently, which will
again raise the discussion between the relative merits of the chemical mass unit,
the number of moles and the amount of substance discussed in §4.

When considering the merits of a revised definition for the mole, it should not
be forgotten that there is very little initiative for such a change from any of the
communities of users of the mole. Notwithstanding this, the proposal that all
of the base units should be revised into a new consistent form has developed
some momentum in its own right, which might be sufficient to carry such a
change through [35].
In the same way that the determination of the Avogadro constant with ever decreasing uncertainty was a challenge for the highest accuracy physical experimentation [36,37] its uncertainty is now dominated by measurements of the purity and the atomic weight of a single crystal—all issues for chemical measurement. It has moved from presenting challenges at the leading edge of physics to the leading edge of chemistry. Therefore, a change in the definition of the mole may be seen as taking it in the opposite direction and bringing it closer to the established approaches of physics and further from its ubiquitous implementation in chemical measurement.

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References

16 Guggenheim, E. A. 1942 Units and dimensions. Phil. Mag. 33, 479–496.


