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ABOUT MOLES AND “AMOUNT OF SUBSTANCE”

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Abstract : Some areas of physics, such as statistical physics, generally consider particle numbers to be dimensionless. This is not consistent with the definitions of the mole and the “amount of substance” in the international system. Possible improvements are considered in this article, in particular the definition of a new unit to count individual particles.

Résumé : Certains domaines de la physique, comme la physique statistique, considèrent usuellement sans dimension les nombres de particules. Ceci n'est pas cohérent avec les définitions de la mole et de la “quantité de matière” dans le système international. Des améliorations possibles sont envisagées dans cet article, en particulier la définition d'une nouvelle unité pour compter les particules individuelles.

Introduction

The notion of “amount of substance” dates from before the time when the scientific community was convinced of the corpuscular nature of said substance. Over time, the successive definitions of the mole have been drafted in such a way as to clarify this notion as knowledge improves. The definition of 2019 (discussed in what follows) increasingly highlights an inconsistency in the system of units, with respect to the “amount of substance”.

1. The definition of 2019

Many books mention the legal definition of the mole (IUPAC[1], CGPM[2] et BIPM[3]) [1-4] :

- The mole (symbol mol) is the unit of amount of substance of the international system (SI). One mole contains exactly $6{,}02214076.10^{23}$ elementary entities.
- This number (called “Avogadro's number”) corresponds to the fixed numerical value $N_A = \{\mathcal{N}_A\}$ of the Avogadro's constant $\mathcal{N}_A$, when expressed in mol^{-1}.
- The amount of substance (usually symbol n) of a system is a representation of the number of elementary entities. An elementary entity can be an atom, a molecule, an ion, an electron, or any other particle (photon...) or specified group of particles.

◊ remark: the notation of the Avogadro's constant is personalized here to facilitate the following discussion.

This definition of 2019 has the advantage of being in very clear progress compared to the previous ones, which tried to “define” at the same time in an intuitive way the unit “mole” and the “amount of substance” it is used to measure.

[1] International Union of Pure and Applied Chemistry (en français : Union internationale de chimie pure et appliquée).
[2] Conférence générale des poids et mesures (in English: General conference on weights and measures).
[3] Bureau international des poids et mesures (in English: International bureau on weights and measures).

It would in fact have been preferable to define the physical quantity before the unit used to measure it :

> • first of all, the “amount of substance” (or “amount of matter”) of a system is proportional to the number of specific elementary material entities that this system contains (the type of entities must therefore be specified, otherwise one does not know what is counted) ;
>
> • then, the mole is the amount of substance of a system containing exactly $6{,}02214076.10^{23}$ elementary entities (which defines the unit mole by fixing the coefficient of proportionality).

However, it can be understood that, as regards a list of definitions of units, the CGPM deemed it preferable to start by indicating the unit, then to specify only after the notion of amount of substance.

2. Minor ambiguities which may remain

Questions may arise about the choice of the expression “amount of substance”.

2.1. Concerning the “substance”

This word was chosen for historical reasons, when it was not yet clear that matter was made up of atoms and molecules.

In practice, one can also count particles such as photons, yet generally considered not to be “matter”.

We could also count stars in a study on a galactic scale, but the mole would be of little interest in this case since it is (by historical construction) a unit specially adapted to chemistry, or to physical phenomena where atomism occurs in a comparable way. One could even generalize by counting length standards to measure distances. This would not be of any interest since there are other more suitable units.

2.2. Concerning the “amount”

Is there the same amount of substance in a mole of iron atoms and in a mole of copper atoms?

> • yes if we define “substance” as being “atoms” because there are as many iron atoms in a mole of iron atoms as there are copper atoms in a mole of copper atoms;
>
> • no if we define “substance” as being “elementary particles” (protons, neutrons, electrons...) because there is not the same quantity of these particles in both cases.

The mention of the chemical element is also insufficient: it is necessary to avoid using expressions such as “amount of sulfur” without specifying whether it is the amount of sulfur atoms or the amount of octasulfur molecules. In a given sample, the “amount” depends on the “substance” considered. In an expression “one mole of H_2 molecules”, “one mole” indicates the “amount” and “H_2 molecules” designates the “substance”.

An advantage of the 2019 definition is to clearly indicate that it is about counting the number of elementary entities of a specified type. In reality, the expression “amount of substance” is deliberately general, insofar as it is intended to count “elementary” entities which may a priori be arbitrary, but which must therefore be clearly specified.

3. Comparison with electric charge

The situation is different in the case of electric charge, for which we count particles with particular properties: some particles are not counted because they have no charge, others have charges that compensate each

other... In a given sample, one cannot find two different “amounts of charge” according to the way in which one would choose to count them (unless changing the unit).

From another point of view, since the electric charge is quantized, it would be possible to choose the unit in such a way as to define the charge as a relative integer number, which could be considered to be without physical dimension.

◊ remark: the choice of the physical dimension of the electrical units involves an arbitrary one, moreover used by the CGS systems (centimetre-gram-second) to bring them back to the units already defined in mechanics.

The situation of the mole is in a way analogous to the faraday unit, charge of one mole of protons (or mole of elementary charges): $1\ \mathcal{F} = N_A\ q_p \approx 96500$ C, while noting q_p the charge of the proton.

◊ remarks:

- the elementary charge is often denoted e, when there is no ambiguity with the exponential, so that $q_p = +e$;
- this corresponds to a Faraday constant $\mathcal{F} = \mathcal{N}_A\ e \approx 96500$ C.mol^{-1}.

The choice was made to attribute a specific physical dimension to the quantities of electric charge, the unit of which is fixed by the elementary charge $e = 1{,}602176634.10^{-19}$ C (exactly).

4. Physical dimension of the “amount of substance”

4.1. Validity of the proposed dimension

Under these conditions, there is no difference between the concepts of “amount of iron atoms” (in moles) and “number of iron atoms” (in “units”). It's just a different way of counting them. Thus, the mole would only be a “counting unit” of elementary entities, that is to say a cardinal number: “a mole” is for $N_A = 6{,}02(...).10^{23}$ what “a pair” is for 2, or “a million” for 10^6.

This aspect can cause ambiguities. Considering that: 1 mole of H atoms = N_A H atoms (like a dozen of atoms = 12 atoms), one would obtain by simplifying: 1 mole = N_A (without unit). This would also give $\mathcal{N}_A = 6{,}02(...).10^{23}$ mol^{-1} = 1, particularly abnormal!

This kind of problem arises from the fact that we have considered as equal an amount of substance and a number of atoms without physical dimension. The unit of Avogadro's constant comes from the fact that we usually calculate the number of constituents using the relation $N = \mathcal{N}_A\ n$. With N without unit and n in moles, this needs $\mathcal{N}_A$ in mol^{-1}. To improve consistency, it would be necessary to give the same dimension to all the numbers of atoms of the same type, whether or not they are counted in moles: changing the counting unit must keep unchanged the physical dimension [4].

But in fact, there is a number of areas of physics, such as statistical physics, where the numbers of particles are generally considered dimensionless [5], for example the study of diffusion phenomena and Fick's law. The calculations are then made with a “particle concentration” or “particle density” $n^* = N/V$ (generally denoted by n, but one must avoid ambiguity with a number of moles), therefore the unit is of the type m^{-3}. How to reconcile the two approaches?

One possible method would be to consider the amount of substance as dimensionless, the mole being a simple “counting unit” like “dozen” or “thousand”, with the possibility of using the prefix “mol” in a way similar to “kilo” or “Yotta” (for 10^{24}). It would be a kind of “yochi” playing for chemistry a role analogous to “kibi” for the binary pseudo-thousand ($2^{10} = 1024$).

This would require some rectifications to the current notation conventions, as indicated in the previous remark regarding $\mathcal{N}_A$, but these details will not be specified here since this is not the orientation of the CGPM's proposals.

4.2. Generalization of a dimension

Another possible approach, strongly suggested by the new definition of 2019, would consist in defining an elementary “amount of substance” corresponding to each of the corpuscles among a large number N, in the same way as we define an elementary electric charge. It is indeed with this notion “corpuscular entity among a set N” that the considered physical dimension is associated. Thus, if we adopt the principle of assigning a physical dimension to the numbers of atoms counted in moles (which follows from the definition of the mole and the amount of substance), it would be necessary to give the same dimension to all the numbers of atoms of the same type, even if they are not counted in moles. In homage to Jean Perrin, who did a lot for atomism, we could define the perrin (symbol Pn) as an “elementary” unit of amount of substance.

◊ remark: be careful, such a unit thus suggested has (at least for the moment) nothing official...

Several consequences would follow:

♦ Thus, the particle concentrations in $Pn.m^{-3}$ would have the same dimension as the molar concentrations in $mol.L^{-1}$ (only a different unit).

♦ The current “Avogadro's constant” would be $\mathcal{N}_A = 6{,}02(...).10^{23}\ mol^{-1} = 1\ Pn^{-1}$, but would become useless, because:
- the number N being measured in perrins, the relation $N = \mathcal{N}_A\, n$ would correspond to $\mathcal{N}_A$ en $Pn.mol^{-1}$ therefore dimensionless; in practice $\underline{\mathcal{N}}_A = 6{,}02(...).10^{23}\ Pn.mol^{-1} = 1$ (symbol underlined here to avoid ambiguity);
- and so one could directly write $n = 0{,}1\ mol = 6{,}02(...).10^{22}\ Pn = N$ (simple change of unit of amount of substance), just as one writes for a length $L = 1\ km = 1000\ m$;
- the Avogadro's number (without unit) would intervene only to define the mole : $1\ mol = N_A\ Pn$.

♦ Molar masses (amount of mass per amount of substance) would then have a slightly different interpretation. For example $M(^{12}C) = 12\ g.mol^{-1} = \dfrac{12}{6{,}02(...).10^{23}}\ g.Pn^{-1}$ would be both the mass per mole of atoms and the mass per atom.

◊ remark: with the definitions of 2019, the value $M(^{12}C) \approx 12\ g.mol^{-1}$ is no longer an exact value.

♦ In another area, to count radioactive decays, we use the becquerel (symbol Bq), homogeneous to the hertz as long as the number of decays is considered dimensionless. With this number measured in perrins, we would obtain $1\ Bq = 1\ Pn.s^{-1}$.

♦ In thermodynamics, the constant R of ideal gases would also correspond to the numerical value of the Boltzmann's constant $k_B = 1{,}380649.10^{-23}\ J.K^{-1}$ (exact value since 2019), knowing that currently this constant is such that $R = \mathcal{N}_A\, k_B$, but with a different unit:

$$R = 8{,}31(...)\ J.mol^{-1}.K^{-1} = \frac{8{,}31(...)}{6{,}02(...).10^{23}}\ J.Pn^{-1}.K^{-1} = \underline{k}_B.$$

◊ remarks:
- for comparison while avoiding ambiguity with k_B, we use here the notation $\underline{k}_B$, but this symbol would be useless with the proposed notations since it would correspond to R;
- many expressions exist in which currently R plays a macroscopic role and k_B (in its “classical” use) an analogous microscopic role, according to $n\,R = N\,\underline{k}_B$; with $n = N$ it is normal that $R = \underline{k}_B$ (with the new notations).

On the other hand the constant intervening in the expression of the entropy $S = k_B \ln(\Omega)$ should be unchanged (the multiplicity intervenes in the number of configurations Ω). But from another point of view, according to the preceding remark, is it quite normal that a constant of "microscopic nature" thus intervenes in the expression of the entropy of a macroscopic system? Noting that R would become a constant "per amount of substance", valid as well on the macroscopic as on the particle scale, k_B would then appear simply as a "bare" constant unrelated to the amount of substance.

Conclusion

With the new definition in 2019, the notion of "mole" has obviously progressed. Noting that there may still be some imperfections in the consistency, we can propose new improvements. Several choices are possible. However, these are in no way obligatory: the traps in the use of the mole, due to a lack of consistency in the definitions, are easy to circumvent; it is currently used in a very practical and efficient manner.

References

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