The Mole is Not an Ordinary Measurement Unit

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Abstract In this paper it is argued that the SI system has not carefully enough taken into account the differences that exist between stoichiometry and physics, and because of this neglect forced the kind-of-quantity amount of substance into a false form. The mole is not a unit such as the metre, the kilogram, and the second. It is a "unit" only in the sense in which purely mathematical scaling factors can be called units.

Keywords Mole · SI system · Avogadro number · Avogadro constant · Stoichiometry

Introduction: discrete entities and continuous properties

Atoms and molecules are *naturally discrete* entities, but in the SI system [1] the dimension (or kind-of-quantity) amount of substance has nonetheless been forced to conform to a structure that fits only *naturally continuous* kinds-of-quantity, i.e., quantities such as length, mass, time duration, and so on. This is a mistake; even though an explainable one. In the SI system, unhappily, the mole is regarded as a unit of the same kind as the metre, the kilogram, and the second. The main difference can be stated thus: in order to count or estimate numbers of a discrete kind-of-quantity no measurement unit has to be introduced, but a continuous kind-of-quantity cannot possibly be used to measure or count anything before a conventional unit has been imposed on it (sect. 6. 3 of [2], [3]). Discrete kinds-of-quantity are, if I may speak so, their own units, but continuous kinds-of-quantity are not.

One consequence of the difference is the following. It is a matter of convention whether we should regard 1 kg as the standard unit and 1 g as a submultiple of this unit, or regard 1 g as the standard unit and 1 kg as a multiple unit. But it is *not* a matter of convention whether we should regard 1 molecule H_2O as a unit and 1 dozen molecules H_2O as a multiple unit, or regard it the other way round. Here, the "standard unit" must be the naturally discrete entity, the molecule H_2O. We cannot understand what a dozen of water molecules is before we know what one water molecule is. Whereas 1 kg may be either a standard unit or a scaling factor, 1 dozen is always and everywhere nothing but a scaling factor for a pre-given standard unit.

The SI metrologists should stop regarding the mole as a unit needed in order to measure/count amount of substance, and instead regard it as being nothing but a scaling factor such as the dozen and the gross. Such scaling factors are not in themselves bound to any specific kinds of entities. In principle, they can be applied everywhere where there are discrete entities. As y dozen entities is equal to 12 y entities and y gross entities is equal to 144 y entities, we get the following equalities:

$$y \text{ mole entities} = (6.022\,14 \times 10^{23})\, y \text{ entities} = (\text{the Avogadro } \textit{number}) \text{ times } y \text{ entities} = A_N\, y \text{ entities.}$$

What this view means for the so-called Avogadro *constant* is explained in the fourth section below.

My proposal, it should be noted, has nothing at all to do with the discussion whether or not the concrete international kilogram prototype at BIPM should be replaced by an abstract theoretical definition of 1 kg.

Stoichiometry and physics

There is quite a difference between stoichiometry and what is typical of physics [4–8]. Stoichiometric formulas, e.g.,

‘$N_2 + 3H_2 \rightarrow 2NH_3$’ and ‘$2H_2 + O_2 \rightarrow 2H_2O$’,

differ not only from the very complex equations of modern physics, they differ radically even from very simple physical laws such as Galilei’s law for falling bodies and Newton’s second law, i.e.,

‘$d = g\, t^2$’ (the distance fallen is proportional to the square of the time elapsed; g is a constant), and
‘$F = m\, a$’ (force equal mass times acceleration), respectively.

There are three interconnected differences between stoichiometric formulas and simple physical laws that I will highlight: the kinds-of-number difference, the kinds-of-unit difference, and the kinds-of-quantity difference. When these differences are clearly seen, the gap between the mole on the one hand, and the metre, the kilogram, and the second on the other, becomes glaring.

The *kinds-of-number difference* is simple to state: stoichiometric formulas take only integers (as in the examples) and rational numbers as values, whereas physical laws typically allow real numbers, and often also complex numbers, as values.

Let me next present the *kinds-of-unit difference*. In stoichiometric formulas we find specific numbers connected to discrete kinds of entities, whereas in physical laws we find quantity variables and physical constants. The laws ‘$d = g\, t^2$’ and ‘$F = m\, a$’ are not purely arithmetical statements, and must not be identified with ‘$z = g\, y^2$’ and ‘$z = y\, u$’. The symbol d is not a variable for pure numbers, it is a variable for the quantity distance; t is a variable for the quantity time duration; and so on, for F, m, and a. However, all these kinds-of-quantity have to be thought of as having *some* (even though no specific) unit by means of which they are connected to the real numbers; otherwise the identity sign of the physical laws makes no sense. The laws are in this sense unit-independent, but not unit-less.

Of course, using the established units, we can make the physical law-equations mentioned more like the stoichiometric formulas; we can reformulate them as ‘$z \text{ m} = g\, y^2 \text{ s}^2$’, and ‘$z \text{ N} = y \text{ kg x } u \text{ m/s}^2$’, respectively. Nonetheless, at least two differences remain. First, z, y, and u are *variables* for numbers, not specific numbers as in the stoichiometric formulas. Second, the units used (m, s, N, kg, m/s^2) can be exchanged for other units (yards, hours, etc.), but the stoichiometric formulas contain no similar conventionality. The naturally discrete entities of stoichiometry are their own metrological units, whereas the properties and relations that are typical of physical laws by convention must be ascribed a unit. In other words: stoichiometry works with natural units, physics normally with artificial units.

Both the kinds-of-unit difference and the kinds-of-number difference are connected with, and emerge from, the difference between naturally discrete quantities and naturally continuous quantities that I mentioned in the first section. This is the *kinds-of-quantity difference* between stoichiometry and physics. Note that negative electrostatic charge is a naturally continuous quantity in spite of the fact that, with today’s knowledge, all such charges must be regarded as multiples of the invariant charge of the electron. For other reasons, physics must allow electric charge to take also non-integer values.

Entities that are naturally discrete can be said to be their own counting units, and they need for their counting only the natural numbers. Counting always involves making some sense of the term “next”. Starting with number one, the *next* number is two, and so on. In a continuum, however, “the next” is impossible to use. Why? Answer: because between *any* two points, however close to each other in a continuum, there is always a third point. It is a category mistake to try to apply the term “the next point” in a continuum. This is the reason why continuous kinds-of-quantity must have a measurement unit externally imposed on them before they can be used in measurements.

Direct and indirect counting

When as children we were taught arithmetic, we were at the same time taught applied arithmetic. Or, rather, the other way round: we were taught pure arithmetic by means of applied arithmetic. One toy plus one toy equals two toys, and 1 + 1 is equal to 2. Everyone who knows pure arithmetic also knows much about its tacit application rules. Therefore, as soon as we have what we regard as discrete entities, we know in principle how to apply some arithmetic to them. From this perspective, there is no theoretical problem of how to count discrete entities such as molecules and atoms, only practical problems. But the latter can be huge, since it can be a matter of counting/measuring huge aggregates of unobservable discrete entities.

One part of the practical problem is very easily solved. The impracticality of using very large numbers is solved by the introduction of special names for large numbers. And starting from this perspective, the mole can be regarded as a name for sets that have the Avogadro number of entities as elements. And this is in my opinion also how the mole ought to be conceived [2]; and I am not alone [8]

The hard part of the problem is of course that the entities of interest for physics and chemistry are not directly perceivable like the ordinary discrete things around us. However, if each entity on its microscopic level has a kind of property – let's think of mass – that also exist on the macroscopic level, and we in some way or other think we know the value of the mass for a single such unobservable entity, then we can indirectly count numbers of such entities by measuring the mass of the whole aggregate. The rest is mere calculating. If we are interested not in the actual number of entities in the aggregate, but only in the relative number of entities in relation to another aggregate, it is enough to measure relative mass. This fact has been of great importance in the history of chemistry.

Sometimes in the philosophy of measurement [9], a distinction is made between direct measurement (measuring something with something of the same kind; length by a metre stick) and indirect measurement (measuring something by means of something of another kind; velocity by means of clocks and metre sticks). What I have said in the last paragraph brings out into the open a similar distinction between *direct* and *indirect counting.* In indirect counting one either measures properties and then calculates what numbers of entities there are, or one measures property ratios and calculates the relative number of entities. Indirect counting comes naturally also outside of science. Children who play Memory (with cards) realize immediately, that there is no need to count all the pairs of cards of the players in order to see who has won. It is enough to make piles, one for each player, and check who has the highest one. This means that there is nothing in principle wrong in defining the mole as a scaling factor that is equal to the number of a certain kind of atoms in an aggregate with a specific mass. Wrong, though, is to regard it as an ordinary conventional measurement unit instead of as a scaling factor or a multiple unit that necessarily has to be related to some discrete kind of entity.

The mole and the Avogadro constant

I think there are a number of factors that can explain why, hitherto, a majority of metrologists have reached the false conclusion that the mole should be not just a number functioning as a scaling factor, but an artificial conventional metrological unit on a par with the other SI units. Here, however, I will only mention one such factor. I have become convinced that the problem of the mole has one of its roots in the fact that there is a famous law – the ideal gas law – that can be regarded as combining variables for continuous quantities (pressure, volume, and temperature) with a variable for discrete entities, numbers of molecules in a gas.

Let us first look at the law in the form '$p\ V = n\ R\ T$'. Normally, as I have said, quantity variables are unit-independent but not unit-less. In the equation above this is certainly true of p, V, and T, but not necessarily of n. This symbol might be regarded as a variable for numbers of moles, not for a certain kind-of-quantity. Whereas physical laws can be said to have variables that are searching for a unit, here we find a variable, n, that when understood as a unit can be said – conversely – to be a unit searching for a kind-of-quantity. And so it became linked to amount of substance. The mistake is not to try to find a kind-of-quantity to a pre-presented unit, but to regard from the start the mole as surely being an ordinary measurement unit. It comes out in the open if the following statement is accepted as true (sect. 6 of [2]):

> The law '$p\ V = n\ R\ T$' and the similar law with the Boltzmann constant, '$p\ V = N\ k\ T$', are not two different laws that happen to be similar, but are two empirically equivalent formulations of one and the same law.

The Boltzmann formulation (in which N is a variable for number of molecules) neither has nor needs a concept of mole or some transformation of it; a fact that immediately indicates that there might be something odd in assuming that the mole must be an ordinary unit. Let's take a closer look.

From the equivalence of the law formulations, it follows that $n\ R$ is equal to $N\ k$. Since n is a variable for moles and N a variable for a discrete kind-of-quantity, molecules, we can regard the gas constant R as being a *constant per mole of a gas*, and the Boltzmann constant k as being a *constant per molecule of a gas*. And now the Avogadro constant (N_A) enters the scene as a conversion factor between the gas constant and the Boltzmann constant: '$R = N_A\ k$'. The first thing now to be noted is, that the Avogadro constant, the name notwithstanding, cannot possibly be regarded as a constant of nature such as the Planck constant and the velocity of light in vacuum [2, 8]. However, this is exactly how it is regarded in the so-called "New SI" (p 3 in [10]). If the ideal gas law were not "ideal", then the gas constant and the Boltzmann constant could be seen as two different ways of apprehending the same real constancy of nature, but the Avogadro constant would nonetheless be no more than a conversion number between these "real" constants. This being noted, the remaining problem is: should N_A be regarded as some kind of *conversion factor for ordinary conventional units* or as necessarily being *only a scaling factor*.

Traditionally it is claimed, that since R is equal to N_A k and R is a constant per mole of a gas, we must regard N_A as being the Avogadro number (A_N) per the unit mole of a gas ($N_A = A_N$ mol^{-1}). But there is another both simpler and better possibility. Using the Avogadro number, we can exchange the expression '$R = N_A\ k$' for '$R = A_N\ k$'. But then, in the name of consistency, since R is a constant per mole of a gas, k a constant per molecule of a gas, and A_N a pure number, the mole cannot here be understood as being a measurement unit. In terms of the SI brochure's notion of "dimension" [1], the left-hand and the right-hand sides of the equality '$R = A_N\ k$' must have the same dimension; but it hasn't if the mole (in "per mole") on the left-hand side is an ordinary measurement unit. However, if the mole is regarded as only a purely mathematical scaling factor for molecules, this dimensional requirement is met. If one frees oneself from the view that the mole *must* be an ordinary measurement unit, then much of the fuzz around the mole disappears.

I urge all metrologists to take a step back and, without any preconceptions, ask themselves: is the mole an ordinary conventional measurement unit, or is it nothing but a scaling factor in relation to pre-given units?

According to my analysis, the whole essence of the mole is captured by this equality:

'y mole entities $E = A_N\ y$ entities E' (where E represents an arbitrary discrete kind of entity).

This equality, however, does *not* also capture the essence of the Avogadro number. As all pure numbers, A_N can take on other functions; and so this number has. In the equality 'y g = $A_N\ y$ Da', it functions as a *conversion factor* for two different conventional units of mass, the gram and the dalton; it functions here exactly the way 1.09 functions in the expression 'y m = 1.09 y yard'. We can choose whether to make kilogram, gram, dalton, or something else our standard unit for mass, but we cannot choose whether the concept "mole entities E" or the concept "entities E" should be the primary concept. It must be the latter.

SI and the New SI

In the presently valid SI brochure [1], the unit mole is defined in such a way that it holds true: y mole entities $E = A\ y$ entities E; where A is an experimentally determined specific number. It is the number of a certain kind of atoms in an aggregate with a specific mass; and it has been shown to equal 6.022 14 x 10^{23}. The New SI [10] takes the experimental determination away. Its proposal implies that the following should be regarded as true by definition: 'y mole entities $E = A_N\ y$ entities E' (A_N = 6.022 14 x 10^{23}). If the main reason behind the proposal is that the Avogadro constant is regarded as a constant of nature like the Planck constant (which is central to the re-definition of the kilogram), then the proposal rests (as shown in the former section) on a mistake. Otherwise, I can only say that the things I have tried to make clear in this paper apply equally to both the old and the new mole. In both cases, the mole is falsely presented as being an ordinary conventional measurement unit on a par with the other base units of the SI system. *I propose that the mole should be regarded as nothing but a scaling factor or multiple unit for discrete entities, i.e., for entities that by nature are their own counting units.*

If this proposal is accepted, a natural further change would be to rename "amount of substance"; in the future it ought to be called "(number of) elementary entities" or simply "entities" [2, 11].

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