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Heaps of moles? – Mediating macroscopic and microscopic measurement of chemical substances

Abstract

In this paper I take a close look at the SI base quantity "amount of substance", and its unit, the mole. The mole was introduced as a base unit in the SI in 1971, and there is currently a proposal to change its definition. The current definition of the mole shows a certain ambiguity regarding the nature of the quantity "amount of substance". The proposed new definition removes the ambiguity, but at a cost: it becomes difficult to justify treating amount of substance as having its own dimension, and hence its own unit, the mole. I argue that the difficulties with amount of substance result from its role as a mediator between macroscopic and microscopic scales. To understand why amount of substance might have its own dimension, we need to connect amount of substance to mass, contra current proposals to separate them.

1. Introduction

Measurement in chemistry has long been concerned with establishing the amounts of different substances in mixtures (Brown 2013). Since 1971 *amount of substance* has been a base quantity in the *International System of Units (SI),* together with length, mass, time, electric current, thermodynamic temperature, and luminous intensity; accordingly its unit, the mole, is an SI-base unit, alongside the metre, the kilogram, the second, the ampere, the kelvin, and the candela (Bureau International des Poids et Mesures 2006). While there is little question as to the usefulness of the inclusion of the mole among the base units, its definition differs significantly from that of the other base units, and questions have been raised about the legitimacy of treating amount of substance as a quantity in its own right, much less as a base quantity. These concerns make amount of substance an interesting case study for addressing broader questions about the nature of quantities. In this paper I will look at the status of amount of substance and of the mole in their current definitions, as well as from the perspective of a proposed change in these definitions in the SI. The main aim of this paper is to understand better, why amount of substance might appear suspect or illegitimate as a base quantity and to present a cautious defense of its legitimacy.

The main reason for doubting that amount of substance is legitimately included among the base quantities of the SI is a tension between its relationship to mass on the one hand, and to number of entities on the other hand. This tension is apparent in an ambiguity in the current definition, which seems to be ambiguous between treating amount of substance as a continuous quantity and treating it as a "counting quantity". The proposed new definition, which defines the mole by fixing Avogadro's constant, seems to resolve this ambiguity in favor of treating amount of substance as a counting quantity. To do so, however, seems to undermine the status of amount of substance as a legitimate base quantity of the SI in a different manner. The problem is that counting quantities in general seem suspect as candidates for (base) quantities. One concern is that they are discrete instead of continuous. Another is that units of counting quantities seem to conflate the distinction between units and entities (Cooper and Humphry 2012). As I shall argue, however, the real problem with counting quantities is that they lack dimensions, whereas the base quantities in the SI are each supposed to have their own, independent dimension. Roughly, dimensionless quantities differ from quantities with dimensions in that the latter have units in which they are measured, whereas the former are pure numbers. If amount of substance is a counting quantity, there seems to be no reason to include it in the SI.

Defending the legitimacy of amount of substance accordingly means finding a reason for treating it as having a dimension in its own right. I argue, following suggestions by Wheatley (2011a), that we can do so if we reintroduce the connection between mass and amount of substance. This connection is present in the current definition, but missing in the proposed new definition. I argue that the deeper reason for requiring the connection between mass and amount of substance is that molar mass serves as a proxy for distinguishing different chemical substances. I conclude with the observation that the source of the ambiguity in the concept of amount of substance stems from its role as a mediator between macroscopic and microscopic scales, and between chemistry and physics. As a result the ambiguities cannot simply be removed by redefinition without undermining the role played by amount of substance.

2. What is amount of substance?

A quantity like amount of substance has long played an important role in chemistry, but for much of its history it was without a name or a clear definition (International Union of Pure and Applied Chemistry 2014, 53). This changed officially in 1971 with the inclusion of amount of substance among the base quantities of the SI, and the definition of its unit, the mole. According to the current version of the SI (Bureau International des Poids et Mesures 2006),

> The quantity used by chemists to specify the amount of chemical elements or compounds is now called "amount of substance". Amount of substance is defined to be proportional to the number of specified elementary entities in a sample, the proportionality constant being a universal constant which is the same for all samples. (114-5)

Its unit, the mole, is defined as follows:

> 1. 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".
>
> 2. 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. It follows that the molar mass of carbon 12 is exactly 12 grams per mole, $M(^{12}C) = 12$ g/mol. (115)
>
> In 1980 the CIPM approved the report of the CCU (1980) which specified that: In this definition, it is understood that unbound atoms of carbon 12, at rest and in their ground state, are referred to. (115)

Several features of these definitions are worth noting. The first is perhaps that the SI sees a need to give a definition not only for the unit, the mole, but for the quantity amount of substance as well. No definitions for length, mass, temperature, time, electric current, or luminous intensity are offered; only the units of these quantities are defined in the SI. This suggests that amount of substance is a more contentious quantity, or perhaps that there are other candidates for the relevant quantity, making it necessary to specify, which quantity is being defined as amount of substance.

A second observation is that the definition of the mole makes reference to the kilogram, thereby raising the question of how the quantity amount of substance relates to the SI base quantity mass. It seems that the mole gives us a unit for the amount of substance in a sample, and yet the mole itself is defined by specifying the size of a particular sample in terms of its mass. Both mass and amount of substance are measures of the size of a sample. How are these two measures related?

The third point to notice is that amount of substance is defined as proportional to the number of elementary entities in a sample, and that the mole, similarly, seems to be defined as a specific number of entities, namely "as many elementary entities as there are atoms in 0.012kg of carbon 12". One consequence of this definition is that for the mole, unlike for any other base units of the SI, the kind of entities measured has to be specified. Number of entities is yet another measure of the size of a sample. How is it different from amount of substance?

Observations two and three seem to point to a tension in our understanding of amount of substance, because mass is a continuous quantity, whereas number of entities is a discrete quantity. Since amount of substance seems to be related to both, we find two competing interpretations of amount of substance.

According to the first interpretation, the mole is the unit of a continuous quantity, amount of substance, just like the metre is the base unit of the continuous quantity length. Amount of substance would be treated as in no way different from the other base quantities in the SI. This seems to fit with the use of the quantity in most chemical measurement contexts. Measurements are made on large samples, which makes "counting" the elementary entities in the sample impractical, if not impossible. While amount of substance may be discrete at the atomic level, at the level of chemical measurement it is treated as continuous, and hence amount of substance should be understood as a continuous quantity (Wheatley 2011b).

Against this interpretation, however, one might point to the definition of amount of substance as proportional to *the number of specified elementary entities* in a sample. The definition, at least prima facie, suggests that amount of substance is not a continuous quantity in the sense in which length is a continuous quantity, but that it is instead a "count" of the elementary entities in the sample. This is the view expressed in the IUPAC definition of amount of substance:

> It is the number of elementary entities divided by the Avogadro constant. Since it is proportional to the number of entities, the proportionality constant being the reciprocal Avogadro constant and the same for all substances, it has to be treated almost identically with the number of entities. Thus the counted elementary entities must always be specified. (International Union of Pure and Applied Chemistry 2014, 78)

Here amount of substance is clearly defined as a discrete quantity, since N, the number of entities in a sample, and N_A, Avogadro's constant, are (very large) integers. The ratio of two integers is a *rational* number, not just any real number. By contrast, we treat quantities like length as though they are mapped onto the real line, not just the rational numbers. But whereas the set of rational numbers is countable, the set of real numbers is not. So if continuous quantities are ones that can be mapped onto the real numbers, amount of substance looks like it might fail to be continuous in this sense (Wheatley 2011b).[1]

Considerations like these have led to a second interpretation of the quantity amount of substance. According to this interpretation, amount of substance is a "counting quantity", different in character from the other base quantities of the SI. This special status explains why, in the case of amount of substance, the entities in question have to be specified (as per the second clause in the definition of the mole), and it does justice to the impression that amount of substance is a way of measuring the size of a sample by giving

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[1] There are complications, of course. In practice, our measurements are confined to measuring ratios, not reals.

the number of entities in it. Specifying the amount of substance of a sample, on this view, is akin to describing the size of a population in terms of the number of individuals.

A disadvantage is that the majority of chemical measurements are not actually cases of counting—for most chemical cases, the samples will simply be too large to make counting the entities a viable option. For most cases of measurement in chemistry, then, amount of substance would be a counting quantity only in a strictly conceptual sense—for all practical purposes it will be treated as a continuous quantity, simply because the numbers involved are so large. In the fourth section we will look further at general arguments why accepting counting quantities might seem problematic.

Before doing so, let's have a look at the role played by amount of substance in the laws of nature, to understand better why the quantity itself might be useful. This is important, since in addition to being ambiguous between counting and continuous quantities, amount of substance might also seem superfluous, especially if it has to be treated "almost identically with the number of entities".

The quantity amount of substance occurs in the ideal gas law and in stoichiometric relations specifying the relations among reacting molecules (Milton and Mills 2009). In both cases the quantity was known to play a role before it was determinately defined, and before the mole was introduced as its unit. Indeed a quantity like amount of substance had been introduced in 19th century chemistry to describe the definite proportions by which substances reacted, even before the atomic conception of matter became widely accepted.[2] The law of definite proportions states that elements in a given compound always combine in the same proportion by mass. For example, the ratio of oxygen to hydrogen in water is 1/8 by mass (because oxygen is significantly heavier than hydrogen). It is surprising, therefore, how tightly the quantity amount of substance now seems bound to a conception of matter as consisting of individual entities, and for the quantity to look like a "counting quantity" that is proportional to the number entities in a sample.

The ideal gas law can be written either as (1) $PV = nRT$, where P is the pressure of a gas, V is the volume, T is temperature, R is the molar gas constant and n is amount of substance. Or it can be given as (2) $PV = Nk_BT$, where $k_B = R/N_A$ is the Boltzmann constant, N is the number of entities, and N_A is Avogadro's constant. The first formulation makes use of the quantity amount of substance, while the second instead gives the number of entities, and accordingly relates it to Avogadro's constant instead of just the molar gas constant R. The same law of nature, it seems, can be expressed either using the quantity amount of substance, or a count of the number of entities in the gas sample! Surely this suggests that the quantity amount of substance is closely related to the number of entities?

While the stoichiometric relations point to a close relationship between amount of substance and mass, the thermodynamic law suggests that amount of substance and number of entities are de facto interchangeable. The two main places where amount of substance occurs, then, pull in opposite directions when it comes to the task of disambiguating amount of substance. We shall encounter this tension again below. The two types of relations in which amount of substance occurs prominently have one commonality, however. Both stoichiometric relations and thermodynamics connect macroscopic and microscopic descriptions of the world. More specifically, in both cases we start out with law-like descriptions of macroscopic phenomena, e.g., reactions between substances measured in bulk or the behavior of gases, of which we are later given theoretical accounts in terms of their microscopic constituents, i.e., molecules and atoms. This suggests that the role played by the quantity amount of substance in laws of nature is

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[2] Ostwald, for example, uses the expression "Gramm-Molekulargewicht" or "Mol" in his 1893 textbook (Ostwald 1893, 120).

that of a mediator between macroscopic measurements, and microscopic measurements describing these chemical and thermodynamic phenomena in terms of molecular interactions. This explains to some extent why the definition of the mole as its unit seems to contain surprising ambiguities—something we should expect to be carefully avoided in a work like the SI. On the macroscopic level the description of the phenomena is presented in terms of macroscopically continuous quantities like mass, volume, pressure, and temperature. An explanation of the macroscopic relations is offered in terms of microscopic entities (atoms, molecules), which are typically too small and too numerous to count. Amount of substance plays the role of a mediator between these two descriptions, and so it is perhaps unsurprising that its definition exhibits a tension between the macroscopically continuous quantity mass and the discrete microscopic quantity number of entities. If the ambiguity indeed results from the function of amount of substance, we might also suspect that it cannot easily be removed by changing the definition. In the next section we will see how the proposed new definition aims to resolve the ambiguity. In sections four and five we will see that doing so comes at a significant cost.

3. The new definition of the mole

The ambiguities outlined in the previous section have rarely posed a serious problem for practical chemistry. However, recent efforts to redefine many of the base units of the SI, including considerations to redefine the mole, have sparked controversies among metrologists and drawn attention to the problems with the existing definitions, including in particular the definition of the mole (e.g., Leonard 2007; Milton 2009; Lorimer 2010).

The discussion over the redefinition of the mole arises in the context of a massive overhaul of the SI system. Initially several of the definitions of the SI base units made reference to particular prototypes, and later particular physical systems, to define the unit in question. The new strategy is to define units in terms of fundamental constants. Most famous among these is perhaps the definition of the metre, which started out as a prototype based definition, but has since been replaced by a definition in terms of the speed of light:

> "The metre is the length of the path travelled by light in vacuum during a time interval of 1/299 792 458 of a second.
>
> It follows that the speed of light in vacuum is exactly 299 792 458 metres per second c_0 = 299 792 458 m/s" (Bureau International des Poids et Mesures 2006, 112).

This new definition exemplifies the strategy behind the proposed redefinition of several other SI-units. Instead of using a prototype, or a process in a particular physical system, the new definition makes use of a *fundamental constant*, the speed of light in a vacuum, c_0. By fixing that constant to an exact value of 299 792 458 m/s, the metre is defined to be a fixed length. Defining a unit by fixing a constant is made possible by the fact that constants typically have characteristic units in which they are expressed. Speed is given as meter/second, which permits fixing the length of the metre by fixing the value of a particular constant speed, the speed of light in the vacuum. One consequence of this definition is that the speed of light in vacuum can no longer be empirically determined; its value is now known exactly by definition.

Following this model, the *Bureau International Des Poids et Mesures* (BIPM) is currently considering redefinitions of other base units, including the mole. The idea is to replace existing definitions by fixing a relevant fundamental constant to an exact value.[3] The most important such change is the redefinition of the kilogram, which to this day is defined in terms of the prototype kept in Paris. However, given that the current definition of the mole is tied to the current definition of the kilogram, changing the definition of the kilogram would seem to require changing the definition of the mole as well (Mills et al. 2006). Several candidates for the redefinition of the mole have been proposed, but a key idea is to fix Avogadro's constant to a determinate value:

> The mole, symbol mol, is the SI unit of amount of substance. One mole contains exactly 6.022 140 76 × 10^{23} elementary entities. This number is the fixed numerical value of the Avogadro constant, N_A, when expressed in the unit mol^{-1} and is called the Avogadro number.
>
> The amount of substance, symbol *n*, of a system is a measure of the number of specified elementary entities. An elementary entity may be an atom, a molecule, an ion, an electron, any other particle or specified group of particles. (*Draft of the Ninth SI Brochure - Dated 05 February 2018)*

According to this definition, the mole is explicitly defined in terms of a fixed value for Avogadro's constant, and accordingly the value of Avogadro's constant can no longer be empirically determined, but is known with certainty. In this way the proposed definition is like the definition of the metre in terms of the speed of light. In several other respects, however, the proposed redefinition of the mole is different. For as Avogadro's constant is fixed to a precise value, *other constants* in turn become empirically measurable again. First and foremost this is true for the molar mass of carbon $M(^{12}C)$. The molar mass of a substance is defined as the ratio of mass to amount of substance: $M(B) = m/n_B$. The mole is defined as the number of entities in 0.012kg of carbon-12, thereby setting the molar mass of one mole of carbon-12 to be equal to exactly 12 grams. The proposed redefinition makes the molar mass of carbon-12 empirically determinable, and hence not known exactly. This is important, since carbon-12 is used as the reference mass for the unified atomic mass scale, with the atomic mass constant $m_u=m_a(^{12}C/12)$. Since other constants, like the molar mass constant M_u, are defined in terms of m_u, they too become empirically determinable on the new definition, while they are fixed by the current definition. Unlike in the case of the metre, then, where the redefinition simply meant giving up the exact knowledge that a particular prototype is one meter long,[4] the proposed redefinition of the mole exchanges the empirical determinability of Avogadro's constant for the empirical determinability of the molar mass of carbon-12.

In light of this one might wonder why the new definition does not simply keep a fixed molar mass of carbon-12, instead of switching to Avogadro's constant. The reason brings us back to the problems we discussed in section two: the molar mass constant definitionally connects the mole to the kilogram, and thereby amount of substance to mass. A definition in terms of Avogadro's number is supposed to break that link, allowing for independent definitions of the kilogram and the mole (Mills et al. 2006). One important consequence of the redefinition of the mole would therefore be a disambiguation between the two interpretations of amount of substance given above. With the new definition of the

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[3] There are actually several proposals for the exact reformulations of the definition. Common to all is the idea of relying on fundamental constants; the proposals differ in how explicit this reliance is supposed to be, and how the constants are to be used.

[4] Since the metre was redefined in 1960 as 1 650 763.73 wavelengths of the orange-red emission line of krypton-86, strictly speaking the definition in terms of the speed of light makes not only the length of the prototype empirically determinable, but also a particular physical wavelength.

mole a new definition of amount of substance has been proposed, and it seems to make it clear that amount of substance is entity based:

> Amount of substance is a quantity that measures the size of an ensemble of entities. It is proportional to the number of specified entities and the constant of proportionality is the same for all substances. The entities may be atoms, molecules, ions, electrons, other particles, or specified groups of particles. (Milton and Mills 2009, 334)
>
> The amount of substance, symbol n, of a system is a measure of the number of specified elementary entities. An elementary entity may be an atom, a molecule, an ion, an electron, any other particle or specified group of particles. (*Draft of the ninth SI Brochure - Dated 05 February 2018*, 17)

This definition suggests that amount of substance is indeed a counting quantity; it measures the size of an enumerable aggregate. One advantage is that the new definition avoids the ambiguities of the old definition, as well as making it clear how amount of substance differs from mass. Doing so comes at the cost of accepting that amount of substance is not a continuous quantity at all. The same is true for the mole, which will now be defined explicitly as the amount of substance corresponding to a specific number of entities. Ambiguities regarding the definitions of amount of substance and the mole would hence be removed in the new definitions. But while the new definition makes amount of substance less ambiguous, it threatens to undermine its status as a legitimate quantity in other ways.

4. Problems with counting quantities

Our initial concerns about amount of substance had to do with the ambiguity involved in its definition, which left it unclear whether we should understand amount of substance as a discrete quantity or a continuous quantity. The new definition would resolve this ambiguity by apparently defining amount of substance as a counting quantity. However, counting quantities are by no means uncontroversial, although it is not easy to say exactly what seems to be wrong with "counting quantities". I will begin with a discussion of Cooper and Humphry's (2012) arguments that counting quantities are not really quantities. Then I show that these arguments are insufficient to establish that counting quantities are not quantities, by comparing amount of substance to electric charge. I conclude this section by suggesting that the problem with counting quantities is their lack of dimensions.

Cooper and Humphry (2012) suggest that there are two interrelated problems with counting quantities: formal concerns and ontological concerns. Formally, counting quantities are represented by natural numbers, whereas continuous quantities are represented by real numbers. This formal difference corresponds to an ontological difference between quantities that are only finitely divisible, and those that are infinitely divisible. Cooper and Humphry suggest that this means that while the unit of a continuous quantity is a particular *determinate property*, a counting quantity is an *enumerable aggregate*, and its unit is an *entity*. For example, length is a continuous quantity, and its unit, the metre, is a particular determinate length, which some objects instantiate. Determinate amounts of continuous quantities are infinitely divisible. By contrast, amount of substance is not infinitely divisible. While its unit, the mole, is divisible, it is ultimately defined in terms of specific entities. This requires specification of the kind of entity involved, e.g., molecules of methane, or atoms of zinc. These specific entities cannot be further divided, at least not without changing the nature of the entity. According to Cooper and Humphry, there are then two related ontological differences between continuous quantities and enumerable aggregates. First, continuous quantities are infinitely divisible, whereas the entities making up an aggregate are not. Second, the "units" of aggregates are (ultimately) entities, whereas the units of continuous quantities are determinate properties. A failure to recognize these ontological differences has resulted in "considerable confusion" (Cooper and Humphy, 2012, 400) in metrological definitions.

It seems to me, however, that Cooper and Humphry are a bit too quick in their dismissal of "counting quantities". It would seem to be an empirical question whether quantities like length and mass are ultimately best represented by the real line. After all, current approaches to quantum gravity consider the possibility that quantities like length might be discrete (see (Hagar 2014) for discussion). Deciding a priori that quantities must be continuous seems to preclude important developments in physical theorizing.[5] Indeed, it is very much concerns arising from developments in physical theories that prompt the redevelopment of the SI (Mills et al. 2006, 228), and amount of substance is not the only discrete quantity in the new SI .

While electric current is continuous at the macroscopic scale, at the microscopic (or better, the subatomic) level we find elementary charges, which are discrete. Just as in the case of chemical measurement, it is impractical in most cases to measure currents by "counting" the flow of elementary charges, but that does not mean that charge is not discrete. The proposed redefinition of the ampere, the unit of electric current, makes reference to elementary charges:

> The ampere, symbol A, is the SI unit of electric current. It is defined by taking the fixed numerical value of the elementary charge *e* to be 1.602 176 634 $\times 10^{-19}$ when expressed in the unit C, which is equal to A s, where the second is defined in terms of $\Delta\nu_{Cs}$. (*Draft of the ninth SI Brochure - Dated 05 February 2018,* 15)

The proposed new definition of the ampere is in some respects similar to the redefinition of the mole. The ampere is defined by fixing a particular value for elementary charge (in particular units), which in effect means taking electric current as the flow of discrete elementary charges and defining the ampere as corresponding to the flow of 1/ 1.602 176 634 $\times 10^{-19}$ elementary charges per second (*Draft of the ninth SI Brochure - Dated 05 February 2018,* 15). Is amount of substance relevantly similar to electric current?

If both electric current and amount of substance are quantities that are continuous at the macroscopic scale, but discrete at the microscopic scale, then amount of substance is no longer the odd one out, and objections against "counting quantities" have to address the fact that the need to introduce non-continuous quantities might simply arise from the existence of discrete structures in nature. If so, the fact that we traditionally map quantitative attributes onto the real numbers turns out to be the result of our epistemic access to the world, which needs to be supplemented by an improved understanding of nature at the microscopic scale.

But this still leaves the second problem, concerning the difference between determinate properties and entities. A length of one meter is a determinate property of particular objects, for example of meter sticks, bookshelves, and so forth. By contrast, molecules or atoms are entities, not properties of something else. So if amount of substance provides a count of entities, then it does indeed seem as though amount of substance is metaphysically different from mass or length. Units of quantities were supposed to be determinate properties, whereas "units" of counting quantities seem to be entities. At first

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[5] Cooper and Humphry concede this point in principle, but offer no discussion.

glance the latter seems to be the case for amount of substance and the mole according to the new definition. If the mole is just a determined number of elementary entities, namely 6.022 140 76 × 10^{23} , doesn't that mean that a unit in this count is just one such entity?

We need to be careful. The unit of amount of substance is not a specific entity, but proportional to a particular number of entities: according to the old definition as many entities as are contained in a gram of carbon-12, according to the new definition 6.022 140 76 × 10^{23}. The unit itself, then, is not simply an entity, but a *number of entities*. Arguably the mole is even a determinate property: a specific cardinality of a set of entities. Amount of substance, even on the "counting quantity" interpretation, would be the size of a sample of a substance understood as its cardinality, and its unit would be a determinate cardinality to which samples can be compared. A mole is not a single elementary entity, it is really a particular value of the cardinality of a set of entities. Cardinality is a *property* of a set of entities, not an entity. So in specifying a particular number of entities as the unit of amount of substance, the new definition of the mole does not obviously conflate the distinction between entities and properties.

One might still feel uneasy about the definition of the mole, while finding the definition of ampere less problematic. The reason is that "elementary charge" is somewhat ambiguous in its current usage. Usually it is used to refer to fundamental units of charge, based on the idea that charge is quantized. But occasionally it is used to refer to the carriers of unit charges, e.g., electrons and protons. This ambiguity does little harm in practice, but it allows the definition of the ampere and the definition of the mole to look more similar than they really are. For in the case of the ampere, the definition really only means that we think of charge as a discrete quantity; hence we can define current as the number of discrete unit charges per second. The entities carrying these charges are "counted" in virtue of carrying units of charge, not in virtue of being entities. By contrast, in the case of the mole we are "counting" entities *qua entities*, not in virtue of these entities carrying a particular attribute. In the case of charge, we "count" entities like electrons, because each electron *carries the same amount of charge*. By contrast, in the case of amount of substance we "count" entities because they are entities of a particular kind: atoms of gold, ions of sodium, molecules of water… . Elementary particles are (typically) carriers of mass, charge, and spin, and they can be sorted into different *kinds* depending on the typical values they have for these attributes: electrons have characteristic mass, charge and spin, and protons have different ones. For each elementary entity, then, there are quantities in terms of which we can describe the entity in question, and which we take to be attributes of the entity. Where entities are thought to carry "unit" amounts of such a quantity, we can use the entities as a proxy measure by counting the entities that carry unit amounts of the quantity. Amount of substance, by contrast, is not a measure of an attribute by way of counting a kind of entity that carries it, but a measure of the size of a sample in terms of the number of entities.

This is also why, in the case of the mole, we need to specify the kind of entity being "counted", whereas for the ampere we do not. In the case of electric current we are interested in charges, not their carriers, whereas for amount of substance we want to know which entities we are counting. If we found, against our current theoretical expectations, particles with less than unit charge, this would suggest that we might have to change what we consider to be unit charge. By contrast, if we decide to count ions instead of molecules, we've simply switched the type of entity we are counting. These closely connected differences between charge and amount of substance suggest that the important contrast between counting quantities and other quantities in the SI is not that counting quantities are discrete while the other quantities are continuous. Even a discrete quantity like charge seems to differ from counting quantities.

While counting quantities do not seem problematic in virtue of being discrete, there nonetheless seems to be a difference between charge and amount of substance. The challenge is to articulate just what that difference is. Both can be understood as properties, even determinate properties, if we understand amount of substance as a kind of cardinality. Cardinality is not a physical property in quite the way that charge is, and it is perhaps debatable whether cardinality can be thought to apply to concrete entities directly, or only indirectly by applying to sets of them. Nonetheless, it is a property, and so the Cooper-Humphry objection regarding units and entities does not apply as stated. It does point in the right direction, though.

The problem with "counting quantities" is that it is unclear what, if any, their dimensions are. Cardinalities are usually thought to be pure numbers, that is, numbers without units specifying dimensions. This is held to be true of counting quantities in general—they all are either said to have dimension one or no dimensions at all.[6] This is the viewpoint of the SI, which states that "[s]uch counting quantities are also usually regarded as dimensionless quantities, or quantities of dimension one, with the unit one, 1"(Bureau International des Poids et Mesures 2006, 106). Number of molecules is explicitly mentioned as an example of such a counting quantity. Number of entities, then, is regarded by the SI as a counting quantity, and hence as being dimensionless or as being of dimension one.

What about amount of substance? As a base quantity of the SI, with its own unit, it would seem to be a dimension in its own right, as is held by the SI for all base quantities (105). But on the new definition it seems very unclear how amount of substance could have its own dimension, given that amount of substance is now tied so closely to number of entities. If amount of substance is a counting quantity, as the new proposed definition suggests, then should we not expect that its dimension is the same as that of other counting quantities? And if the mole is merely a specific number of entities, namely $6.022\ 140\ 76 \times 10^{23}$, then this does not seem to warrant speaking of amount of substance as a dimension with unit mol. Instead it seems to suggest that amount of substance is just a convenient way for converting very large numbers (of the order of 10^{23}) to more usable numbers, by diving the number of entities by Avogadro's constant. Avogadro's constant is given in units 1/mol by the SI, which of course means that the equation $n=N/N_A$ will have units of mol on both sides. But this does not justify why we should accept a new dimension for amount of substance; it merely makes sure that the claim that it has its own dimension is consistent. Avogadro's constant cannot be said to have units 1/mol unless amount of substance has units of mol, but that does not provide reasons for thinking that either of them does indeed have these units. If amount of substance is interpreted as a counting quantity, then it seems quite mysterious how it can be understood as having its own dimension, instead of being merely a cardinality. Moreover, given the close ties between amount of substance and number of entities, it is difficult to see how they could have *different* dimensions, even if we thought they were not dimensionless.[7] So it seems the claim that amount of substance is a counting quantity (a kind of cardinality) and the claim that it is its own dimension are in tension with one another.

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[6] While all counting quantities are dimensionless or of dimension one, we should not assume that all dimensionless quantities are counting quantities. Quantities are "dimensionless" when they are the result of the ratio of two like dimensions, e.g., [mass]/[mass], or [length]/[length]. In these cases reference to the dimension disappears because the quantities are of the same dimension, and so we end up with a pure ratio. This does not mean that the quantities of which these ratios are formed are themselves counting quantities.

[7] This holds in particular for the suggestion of treating [entities] as the dimension of amount of substance (see Leonard 2007b). If [entities] is a suitable dimension for amount of substance, it would seem at least as suitable as a dimension for number of entities.

If anything, the new definition seems to speak in favor of abolishing amount of substance altogether (McGlashan 1997). If counting quantities are really just dimensionless counts, and if amount of substance really is just a counting quantity, then why include it in the SI at all? It seems no different from counts of populations in biology, which we also do not include as separate quantities in the system of units.[8] If, by contrast, we think amount of substance has a special dimension, then we need to know just how this dimension differs from other types of counting quantities.

5. Does amount of substance have its own dimension?

If amount of substance is a mere counting quantity, then, it seems it has no place in the SI. Not because it is discrete or because counting quantities are not useful, but because counting quantities have no dimensions. So at best we might include counting quantities generically, so to speak. There is no point in including a particular counting quantity as a base quantity. This raises the question, whether we have any reason to believe that amount of substance has its own dimension in the first place. If it did, we might think it worth including it in the SI, but would have to reject the proposal that it is a mere counting quantity. Two questions need to be distinguished. One question is how many independent dimensions we need to distinguish for a consistent, workable system of units. The answer to this question is difficult, and unlikely to be answerable purely a priori. The SI makes the explicitly conventional assumption that "physical quantities are organized into a system of dimensions" (Bureau International des Poids et Mesures 2006, 105) and treats the base quantities as conventionally independent of each other (104), but makes no attempt to justify these conventions. The question regarding the dimensionality of amount of substance is of a different sort. The question is whether amount of substance even has a dimension, whether independent of the others or derived from them. If amount of substance were indeed a counting quantity, it would seem to be clear a priori that it does not have its own dimension. Here I shall argue that we should treat amount of substance as having its own dimension, even though this dimension is not independent of other dimensions in the SI.

Wheatley (2011a) provides two reasons for treating amount of substance as a dimension in its own right. One reason is that microscopic measurements, i.e., counts of entities, are impractical in chemistry (74). That means there are good pragmatic reasons for accepting amount of substance in addition to, or instead of, number of entities. But the usefulness of amount of substance is not really what's in doubt; the question is whether it is a legitimate candidate for having its own dimension. Wheatley's other reason speaks more directly to this point: amount of substance is used to define intensive quantities, like molar mass. Mass, volume, and amount of substance are all bulk measures of the size of a sample, and they are all extensive quantities: they vary as the sample in question is divided or as samples are combined. Molar quantities, like molar mass and molar volume, are intensive quantities, which means they do not change with sample size. Amount of substance plays the role of a second extensive quantity for defining these molar quantities. Molar mass, for example, is defined as the ratio of mass to amount of substance: $M(B) = m/n_B$, where the index B indicates a particular substance, e.g., sodium or methane. It is instructive to compare this case with a very familiar relationship between two extensive quantities and an intensive quantity: mass-density as mass per volume, $\rho=m/V$. While different materials have different characteristic mass-densities, the relation between density, mass, and volume can be stated independently of any particular material. The molar mass of different

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[8] Emerson (2004) argues for the recognition of counting quantities in the SI, not by listing particular ones explicitly, but by including something like a generic concept of a counting quantity.

chemical substances is also characteristically different for different substances. But whereas density in general relates to two extensive quantities each of which can be specified independently of the materials involved, molar quantities cannot be so specified. Instead molar quantities are defined in terms of an unspecified extensive quantity (e.g., mass or volume), and a specified quantity: amount of substance, n_B. The specification provides the kind of substance, If amount of substance had no dimension, the molar mass would be given in units of mass instead of mass/mol, which would mean that molar mass would not be an intensive quantity and would be expected to vary with sample size.

Even this argument in favor of treating amount of substance as having its own dimension might seem to rest ultimately on pragmatic considerations.[9] Which dimensions a quantity has seems to depend on the system of units we choose, as illustrated by the different assignments of dimensions to electromagnetic quantities by the centimeter-gram-seconds system of units and the SI respectively. One consequence of this difference is that the constant vacuum permittivity ε_0 is dimensionless in cgs units, while it has the units $A^2 \cdot s^4 \cdot kg^{-1} \cdot m^{-3}$ in the SI. If our choice of system of units is purely conventional, and if the dimensionality of a quantity depends on the choice of systems of units, then it might seem that nothing of importance can depend on whether a quantity has dimensions or not.

One possibility is to deny that choices of systems of units are entirely arbitrary. One might suggest, for example, that some quantities are indeed fundamental and that those quantities should hence serve as base quantities in any system of units. This would still permit some choice in the units designated as base units (e.g. whether to use centimetre or metre for length), but it might seem that doing so would fix which dimensions derived quantities have by fixing which quantities, and thereby which dimensions, would count as the base quantities in any eligible system of units (see Skow 2017 for a proposal along these lines).

Even if we don't want to embrace such a strong metaphysical commitment to a preferred set of base quantities, the considerations for treating amount of substance as having its own dimensions are somewhat different from those concerning other quantities, like angles. Angles are a notorious problem case for unit assignments, because for plane and phase angles the units are m/m and for steradian the units are m^2/m^2. Since in both cases the dimension, length, cancels out, we end up with angles being apparently dimensionless. This has been another longstanding issue in the SI, with radian and steradian initially introduced as supplementary units. From 1995 onwards the CGPM has been treating them as 'dimensionless derived units'. In the draft of the new SI, this history is noted and the relationship of these units to length is specified as follows: "The units rad and sr correspond to ratios of two lengths and two squared lengths, respectively." (*Draft of the ninth SI Brochure - Dated 05 February 2018,* 34)

There are two important differences between the case of angles and that of amount of substance. First, angles are derived units, not base units, and second the relationship of angles to the dimension length is quite clear from the units, it's just that the dimension cancels out. That's a very different way of ending up as a dimensionless quantity compared to a quantity like number of entities, which is dimensionless in virtue of being a counting quantity, not in virtue of its dimensions cancelling out. We may have a choice as to whether or not we use radian and steradian as dimensionless derived units or as supplementary units, but no similar choice seems to arise in the case of number of entities or amount of substance. Whereas the units for angles can be derived from the SI base quantity length, but it so happens that these units cancel out, number of entities and similar counting quantities do not seem to have a clear connection to any of the base

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[9] I would like to thank one of the referees for inviting me to consider this point.

quantities and dimensions of the SI. If amount of substance were like number of entities, then it would be unclear how it could be derived from any of the base units. Secondly, amount of substance is meant to be a base unit, so it doesn't simply inherit dimensions from its relationship to the base quantities in the SI. The question whether it has a dimension must draw on considerations independent of the system of units under discussion.

There seems to me to be a third, related reason for thinking that amount of substance must be treated as a quantity with its own dimension. A mole of zinc atoms is well defined, as is a mole of carbon dioxide molecules, or of sodium chloride ions. However, a mole of *zinc atoms or carbon dioxide molecules* is not well defined. If a mole is just a very large number, why isn't this so? After all, nothing prevents us from describing a set of $6.022\ 140\ 76 \times 10^{23}$ entities, each of which is either a molecule of carbon dioxide or an atom of zinc. True, such a set might look somewhat gerrymandered, but it still has a well defined cardinality. What, then, is the reason for thinking that the mole is not well defined for such a set?

The definition of the mole explicitly demands that the kind of entity must be specified, but implicit in this demand is the thought that the entities "counted" should be of the same (chemical) kind. Not only do we have to decide whether we are counting atoms, ions, or molecules, but we also have to say, which chemical kind of atom, molecule, or ion is measured. This, in turn, implies that really only chemical kinds, and perhaps physical kinds (e.g., electrons, protons…) are eligible for being measured in moles. The current definition of amount of substance makes this clear: it is the quantity used to "specify the amount of *chemical elements or compounds*". Even the proposed redefinition of the mol demands that the entities must be specified, although this leaves it open what type of specification would be appropriate. In most measurement contexts, this restriction will seem too obvious to state. But as a conceptual point we should note that the set of entities such that each element is either a zinc atom or a carbon dioxide molecule is not underspecified. Cardinalities are not in general restricted to numbering only collections of entities of the same kind. Perhaps, then, the reason that amount of substance has to be treated as its own dimension lies precisely in the fact that it imposes restrictions beyond mere cardinality: not only are we interested in the number of entities, but we are only interested in numbers of entities for chemical kinds.

The current definition of the mole builds in this restriction by linking amount of substance to mass. It does so in part for historical reasons—mass was a quantity easily measurable for substances in bulk, and the first quantitative laws in chemistry, such as the law of definite proportion, were formulated in terms of mass.[10] But the link between mass and amount of substance is not just a historical coincidence. The reason it worked in the first place is that what we now think of as different chemical elements do in fact differ systematically by mass: atoms of the same element are very close in mass. Mass, or more specifically molar mass, could therefore serve as a useful *proxy for sameness of chemical elements*, even though we now of course take atomic number to be the determining feature for belonging to a particular chemical kind.[11] This proxy status of mass is reflected in the current definition of the mole. By defining the mole as "as many elementary entities as there are atoms in 0.012kg of carbon-12", the current definition makes use of the assumption that any sample of 0.012kg of carbon-12 contains the same number of atoms,

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[10] For a historical overview emphasizing the role of mass in the development of modern chemistry, see (Sutcliffe and Woolley 2012).

[11] Membership conditions for chemical kinds are contested (Needham 2000; LaPorte 2004). For elements, the main difficulty would seem to arise from the presence of isotopes, whereas for compounds the difficulties stem from isomers. See Hendry (2006) for a defense of a realist conception of chemical kinds for elements, but with some hesitations regarding the status of compounds as kinds.

and more generally of the idea that equal mass samples of the same substance[12] contain the same number of elementary entities.[13]

In the new definition of the mole this connection to mass is missing. Instead the mole is defined as a pure number of elementary entities, and the definition gives no particular indication of where that number comes from. The new definition assumes that the function of "as many elementary entities as there are atoms in 0.012kg of carbon-12" in the current definition merely serves as a way of denoting $6.022\ 140\ 76 \times 10^{23}$, just as "as many entities as there are planets in the solar system" might be used to refer to 8. But as we've seen, this strange seeming way of defining the mole served an important function: through fixing the molar mass of carbon-12, $M(^{12}C)$, and thereby indirectly the molar mass constant M_u, the old definition provides a reason for thinking that amount of substance is more than just a cardinality. It is a cardinality related to the way in which mass is partitioned for the kind of entity in question: a requirement on the cardinality is that the total mass is distributed equally over the entities counted (once again with allowances for isotopes). That is not the case for entities of different chemical kinds, which explains why we cannot use the mole as a unit for just any gerrymandered set of entities. Empirically this will of course remain true even on the new definition, but it is no longer a definitional requirement, which is why amount of substance now starts to look like a counting quantity, and Avogadro's constant like a conversion device for getting rid of large numbers. On the old definition, by contrast, it is clear what amount of substance adds, conceptually, over number of entities. Number of entities, as a mere cardinality, places no constraints on how mass is distributed over the entities in question, and even though in practice number of entities will be applied only to samples of the same substance, there is nothing in the definition of the quantity to prevent it from being applied to gerrymandered sets. You could ask how many atoms are in a sample containing gold and copper and get a well-defined cardinality, but you cannot ask what the amount of substance in the sample is without specifying the proportion of gold and copper respectively (in which case you are really asking for the amount of gold and the amount of copper).

Amount of substance, then, is more than a mere counting quantity, because it can only be applied to samples of the same chemical substance, which is a constraint not placed on counts of entities in general. Historically[14] this connection between sameness of chemical kind and amount of substance has been reflected in the definitional connection between amount of substance and mass. The current draft of the 9th SI brochure points in a different direction. While the mole is still the unit for amount of substance, the recommendation is that in any particular case, "of substance" is to be dropped in favor of a specification of the entity: "In the name "amount of substance", the word "substance" will typically be replaced by words to specify the substance concerned in any particular application, for example "amount of hydrogen chloride, HCl", or "amount of benzene, C_6H_6". It is important to give a precise definition of the entity involved (as emphasized in

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[12] For mass this will only hold strictly for samples drawn from the same source, due to different proportions of different isotopes for different samples. Hence the specification carbon-12 in the definition, which is one of the two stable isotopes of carbon.

[13] This is not to be confused with Avogadro's law, which states that equal volumes of gases, at the same pressure and temperature, always contain the same number of molecules. Whereas Avogadro's law shows that the number of molecules is the same, regardless of the kind of gas in question, the assumption behind the definition of the mole is precisely that differences in mass are useful for distinguishing different kinds of chemical substances.

[14] Arguably the same is true of number of entities as it is in fact used in chemistry. This prompts the choice of either not treating number of entities as a counting quantity (contrary to the SI), or of acknowledging that number of entities could in principle be used to measure the size of any sample, regardless of whether it is of a single chemical kind.

the definition of the mole); this should preferably be done by specifying the molecular chemical formula of the material involved." (*Draft of the ninth SI Brochure, 5 February 2018, 17*). This clarification of what it takes to give a precise definition of the substance only occurs a few paragraphs below the actual definition of the mole and it illustrates several of the concerns just discussed. On the one hand, the SI does recommend that the substance be specified and its recommendation seems to presuppose that a molecular chemical formula will in fact be available. At the same time, however, this recommendation of how to specify the substance in question is not part of the definition and is not motivated by the definition, whereas in the old definition, the connection to chemical substances was established indirectly through the connection with molar mass. Moreover, it has the character of a recommendation (it's 'preferable' to specify the molecular chemical formula), which leaves open the possibility that the mole is defined for entities other than chemical kinds.

Where does this leave us with respect to the question whether amount of substance has a dimension in its own right? Since amount of substance is restricted only to counts of entities of the same chemical kind, it is not a mere cardinality, and should hence not be treated as a counting quantity. As we have seen, this does not preclude it being discrete, just as charge is not a counting quantity, despite being discrete. Instead it suggests that we should treat amount of substance as having its own dimension. Its dimension arises from its connection to molar quantities, specifically molar mass. But what *is* amount of substance, or perhaps, what *is* this dimension? It's not clear that we need to give a definition beyond describing ways it might be measured or places where it occurs in laws of nature. After all, no such definitions are offered for any of the other base quantities and their dimensions.

The real difference between amount of substance and these other quantities is that amount of substance is different *for different substances*, whereas the other quantities are the same, regardless of what substances are measured. A kilogram of gold and a kilogram of helium have equal amounts of mass, but are different amounts of substance (around 5 moles for gold, and almost 250 for helium). This *is* surprising and worth noting, but it shouldn't be taken as a sign that amount of substance is not a legitimate base quantity with its own dimension, provided we understand it as linked to mass, and not as a counting quantity.

6. Conclusion

We started out with the question why amount of substance is often regarded as the odd one out among the base quantities of the SI. After reviewing some of the concerns with both the current and the proposed new definition of the mole, I have offered a cautious defense of amount of substance as a legitimate base quantity with its own dimension. This defense required rejecting the claim that amount of substance is a counting quantity, despite the fact that amount of substance is a discrete quantity. The analogy with electric current helped to show that not every discrete quantity is a counting quantity. Amount of substance is nonetheless different from charge, because there isn't a single attribute common to all samples for which we can measure amount of substance. What is common to all samples of single chemical substances is that mass is characteristically and equally distributed over entities in these samples, once again with the caveat that the distribution will only be exactly equally if the sample is composed only of one type of isotope of the chemical element. This allows mass to stand in as a proxy for different chemical substances, as demonstrated by molar mass, which is the ratio of mass to amount of substance. The question is whether this relationship should be part of the definition of amount of substance (or its unit), or whether it should merely be part of the prescriptions for its usage. Since molar mass is only a proxy, and not itself definitionally linked to different chemical substances, tying amount of substance definitionally to mass can indeed seem problematic. Without a definitional connection between amount of substance and mass, however, amount of substance starts to look like a mere cardinality, which does not do justice to the role played by amount of substance in chemistry, not just practically, but also conceptually. On balance it seems therefore that we should treat amount of substance as having its own dimension.

Ultimately the reason for the difficulties with amount of substance stem from its role as a mediator between microscopic and macroscopic measurements. If we understand continuous macroscopic measurements as resulting from discrete microscopic ones, we need quantities that connect these two different regimes. We will have to learn to live with the resulting tensions. Amount of substance is one such quantity.

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