COMMENTS ON "UNITS FOR DIMENSIONLESS COUNTING QUANTITIES, ENUMERATION, AND CHEMICAL CONCENTRATION" CCU/13-09.3

Introduction

The following comments on Working Document CCU/13-09.3 are intended to clarify the use of the physical quantity entity (symbol ent) as the appropriate atomic-scale unit and fundamental reference quantity for the amount of any substance. There are some similarities in the document with concepts that I have been endeavouring to introduce in a number of publications over the past several years [1–4], which, in turn, are entirely equivalent to concepts proposed earlier by Cesare Curti [5]. But there are also some inconsistencies in the document—primarily the claim that the entity or "molecule" (symbol "mcl") is dimensionless and can be replaced by the number 1, so that the unit can be inserted or extracted at will—that lead to the "problems" discussed in the document. When the entity is used consistently—in particular, since it is a physical quantity with the dimension of chemical amount, it cannot be set equal to the number one—such "problems" do not arise. On the contrary, many concepts are immediately made clearer and the well-known confusion that permeates this subject is swept away.

1. Preliminary remarks on terminology and symbols

Currently, we have six different terms and two different symbols for referring to relative entity masses: "relative atomic mass" or "atomic weight," $A_r(X)$, for atoms and subatomic particles, "relative molecular mass" or "molecular weight," $M_r(X)$, for some molecules, and "relative formula mass" or "formula weight" for other particles and groups of particles. The obvious all-inclusive name is "relative entity mass." The appropriate (single) symbol is $M_r(X)$, maintaining some continuity with current terminology—"*M*" refers to mass, "r" refers to relative.

According to IUPAC and others, the name "amount of substance" for the physical quantity represented by $n(X)$ has been a source of confusion and should be replaced by a more easily comprehended term. Consider a 2 litre beaker, 90% full of water at room temperature. To the precision indicated, the *volume* of water is $V(H_2O) = 1.8$ L; the *mass* of water is $m(H_2O) = 1.8$ kg; and the *amount* of water is $n(H_2O) = 100$ mol. The physical quantities involved are clearly *volume*, *mass* and *amount*. However, a glance at a dictionary or thesaurus shows that there are different kinds of "amounts" just as there are different kinds of "currents." There is a direct analogy with "*electric* current." An appropriate adjective is needed; the technical term should be "*chemical* amount." Although the term "chemical" may seem inappropriate for some entities such as photons, for example, in the absence of a more inclusive term, this would seem to be adequate. The adjectives are needed in order to distinguish these physical quantities from other types of "amounts" and "currents," respectively. In practice, the adjectives can usually be omitted. The name "amount of substance" should therefore be abandoned and replaced by the formal term "chemical amount." [The widely abused term, "number of moles," should never be used as a substitute for chemical amount.]

The name "number of entities" refers to the number of entities in a sample, represented by $N(\mathrm{X})$, a dimensionless quantity. The dimensional quantity chemical amount, $n(\mathrm{X})$, is related to $N(\mathrm{X})$ by $n(\mathrm{X}) = N(\mathrm{X})$ ent, an aggregate of $N(\mathrm{X})$ entities, where "ent" is the symbol for a single entity, the ("natural") atomic-scale unit for chemical amount. Note that ent has the dimension of chemical amount—which should be changed to **C** rather than **N**, which confusingly suggests a number. The entity needs to be formally adopted as a non-SI unit of chemical amount accepted for use with SI, just as the dalton is for mass. One entity cannot be replaced by the (dimensionless) number 1. The CIAAW, following a statement from IUPAC, has proposed that any redefinition of the mole should state explicitly that the mole is an Avogadro number of entities. Without the adoption of the entity as an atomic-scale unit for chemical amount, the mole cannot be defined as "an Avogadro number of *entities*." By using ent, the mole can be defined quite simply as mol = (g/Da) ent, where g/Da is the Avogadro number stemming from writing the substance mass in terms of grams rather than daltons, observing the mathematical identity, g ≡ (g/Da) Da. [Note that the Avogadro *constant*, defined by $N_\mathrm{A} = N(\mathrm{X})/n(\mathrm{X})$, is $N_\mathrm{A} = 1\ \mathrm{ent}^{-1}$, with the dimension of number per chemical amount: $\mathbf{1C}^{-1}$.]

According to the Green Book, the name or symbol for a physical quantity should not involve the name of a unit. The term "molar" is a well-known violation of this rule. It should be abandoned and replaced by the self-evident generic term "amount-specific," referring to any quantity of the form: (extensive quantity)/$n(\mathrm{X})$. In particular, if $m(\mathrm{X})$ is the total mass of a substance (identified by X) in a sample and $n(\mathrm{X})$ is the corresponding chemical amount, the amount-specific mass is $M(\mathrm{X}) = m(\mathrm{X})/n(\mathrm{X})$.

2. Origin of the Avogadro number

By definition of the sample-average entity mass, $m_\mathrm{av}(\mathrm{X})$, allowing for the presence of various isotopes, the total mass of a sample, $m(\mathrm{X})$, is related to the corresponding number of entities, $N(\mathrm{X})$, by:

$$m(\mathrm{X}) = N(\mathrm{X}) m_\mathrm{av}(\mathrm{X}) \tag{1}$$

The sample-average entity mass is expressed in terms of the atomic-scale mass unit, the dalton, $\mathrm{Da} = m_\mathrm{a}(^{12}\mathrm{C})/12$, and catalogued in terms of the relative entity mass, $M_\mathrm{r}(\mathrm{X})$:

$$m_\mathrm{av}(\mathrm{X}) = M_\mathrm{r}(\mathrm{X})\ \mathrm{Da} \tag{2}$$

Then the total substance mass can be written in terms of the dalton as:

$$m(\mathrm{X}) = N(\mathrm{X}) M_\mathrm{r}(\mathrm{X})\ \mathrm{Da} \tag{3}$$

For a macroscopic mass unit, chemists have traditionally preferred the gram (rather than the kilogram):

$$m(\mathrm{X}) = [N(\mathrm{X})/(\mathrm{g/Da})] M_\mathrm{r}(\mathrm{X})\ \mathrm{g} \tag{4}$$

where we see the appearance of the factor g/Da. This is the Avogadro number:

$$\mathcal{N}_{\mathrm{Avo}} = \mathrm{g/Da} \tag{5}$$

—the gram-to-dalton mass-unit ratio, stemming from the mathematical identity:

$$\mathrm{g} \equiv (\mathrm{g/Da})\ \mathrm{Da} \tag{6}$$

The Avogadro number arises simply from writing the substance-mass in terms of grams rather than daltons. It is independent of other quantities and units (in particular, chemical amount or the mole).

Equation (4) can be written in dimensionless form as:

$$Z(\mathrm{X}) = N(\mathrm{X})/\mathcal{N}_{\mathrm{Avo}} = m(\mathrm{X})/[M_{\mathrm{r}}(\mathrm{X})\ \mathrm{g}] \tag{7}$$

where Z(X) is the relative number of entities. In the past, the quantity M_{r}(X) g has been known as the "gram-atom," the "gram-molecule" or the "chemical mass unit"—these are substance-dependent *mass* "units," different for each substance. We note that when Z(X) = 1, i.e., $N(\mathrm{X}) = \mathcal{N}_{\mathrm{Avo}}$, then $m(\mathrm{X}) = M_{\mathrm{r}}(\mathrm{X})$ g—the "mass in grams numerically equal to the relative entity mass."

3. The chemical amount equation

The name "entity" is an *inclusive* term for (the existence of an) atom, molecule, subatomic particle, ion, radical, formula unit, photon, . . . , any other specified particle or group of such particles. The entity (symbol ent) is a physical quantity (with the dimension of chemical amount **C**); it is not dimensionless (dimension **1**); in particular, it is not the number 1, nor can it be replaced by 1. One atom of carbon is an amount of carbon (the smallest amount retaining the *chemical* properties of carbon) equal to one entity, $n(\mathrm{C}) = 1$ ent (not 1). One molecule of water is an amount of water (the smallest amount) equal to one entity, $n(\mathrm{H_2O}) = 1$ ent (not 1). Being independent of the substance, the entity is an appropriate atomic-scale unit for chemical amount—a non-SI unit of chemical amount (that should be) accepted for use with SI, just as the dalton is a non-SI unit of mass accepted for use with SI. And, being the smallest possible amount of any substance, the entity is a "natural" fundamental reference constant for chemical amount.

Just as one entity of any specified substance is an amount of that substance, an aggregate of any number of entities of a substance is also an amount of that substance. If N(X) is the total number of entities in a sample of a substance identified by X, the corresponding amount of that substance, n(X), is an aggregate of N(X) entities:

$$n(\mathrm{X}) = N(\mathrm{X})\ \mathrm{ent} \tag{8}$$

This is the defining chemical amount equation, relating $n(\mathrm{X})$ and $N(\mathrm{X})$ and the fundamental reference constant ent. Note that $n(\mathrm{X})$ has the dimension **C**; $N(\mathrm{X})$ has the dimension **1**; and ent has the dimension **C**. [This should be compared with the traditional relationship involving the Avogadro constant, N_A, which has the incomprehensible dimension "reciprocal chemical amount" $\mathbf{C}^{-1}$.] Equation (8) says in a straightforward and easily understood way that the amount of any specified substance is an aggregate of $N(\mathrm{X})$ entities of that substance.

4. Relating mass and chemical amount: origin of the mole

Equations (7) and (8) can be combined to give:

$$Z(\mathrm{X}) = N(\mathrm{X})/\mathcal{N}_\mathrm{Avo} = m(\mathrm{X})/[M_\mathrm{r}(\mathrm{X})\ \mathrm{g}] = n(\mathrm{X})/[\mathcal{N}_\mathrm{Avo}\ \mathrm{ent}] \qquad (9)$$

Now, when $Z(\mathrm{X}) = 1$, representing a reference macroscopic sample, we have $N(\mathrm{X}) = \mathcal{N}_\mathrm{Avo}$, and $m(\mathrm{X}) = M_\mathrm{r}(\mathrm{X})$ g, and $n(\mathrm{X}) = \mathcal{N}_\mathrm{Avo}$ ent. Since, for this macroscopic sample, the quantity $\mathcal{N}_\mathrm{Avo}$ ent has the dimension **C** and is independent of any substance, it is the appropriate macroscopic unit for chemical amount—the mole:

$$\mathrm{mol} = \mathcal{N}_\mathrm{Avo}\ \mathrm{ent} = (\mathrm{g/Da})\ \mathrm{ent} \qquad (10)$$

—i.e., "one mole is an Avogadro number of entities," where the Avogadro number is the gram-to-dalton mass-unit ratio, conforming to the CIAAW proposal. The current mole definition is (implicitly) of this form. We then have the important identities:

$$\mathrm{Da\ ent^{-1}} = \mathrm{g\ mol^{-1}} = \mathrm{kg\ kmol^{-1}},\ \text{exactly} \qquad (11)$$

relating the atomic-scale unit for amount-specific mass, dalton per entity, to the corresponding macroscopic units, gram per mole and kilogram per kilomole.

Now (9) can be written:

$$Z(\mathrm{X}) = N(\mathrm{X})/\mathcal{N}_\mathrm{Avo} = m(\mathrm{X})/[M_\mathrm{r}(\mathrm{X})\ \mathrm{g}] = n(\mathrm{X})/\mathrm{mol} \qquad (12)$$

—fundamental relationships of stoichometry. Given *any two* of $N(\mathrm{X})$, $m(\mathrm{X})$, $M_\mathrm{r}(\mathrm{X})$ and $n(\mathrm{X})$, the *other two* can be found from these equations. These relationships are easily comprehended even by beginning science students. They are the equations that should be used—rather than the use of the mysterious and confusing so-called "conversion factors"—equivalent to (erroneously) equating the *denominators* in (12) —and the "factor-label" method that seems to be ubiquitous. We note in particular from (12) that $n(\mathrm{X}) = [N(\mathrm{X})/\mathcal{N}_\mathrm{Avo}]\ \mathrm{mol} = [N(\mathrm{X})/(\mathrm{g/Da})]\ \mathrm{mol}$.

5. Amount-specific mass

One of the important aspects of using the entity as an atomic-scale unit for chemical amount is the insight it gives into understanding amount-specific quantities—in particular, amount-specific mass, $M(\mathrm{X}) = m(\mathrm{X})/n(\mathrm{X})$. From equations (1) and (8), we have:

$$M(\mathrm{X}) \;=\; m(\mathrm{X})/n(\mathrm{X}) \;=\; [N(\mathrm{X})m_{\mathrm{av}}(\mathrm{X})]/[N(\mathrm{X})\ \mathrm{ent}] \;=\; m_{\mathrm{av}}(\mathrm{X})\ \mathrm{ent}^{-1} \qquad (13)$$

the (sample-average) entity mass per entity, which is self evident. [This is much easier to comprehend than the conventional formula involving the Avogadro constant, $M(\mathrm{X}) = N_{\mathrm{A}}m_{\mathrm{av}}(\mathrm{X})$.] Note that the dimension of $M(\mathrm{X})$ is mass per chemical amount, $\mathbf{MC}^{-1}$. This can be written in terms of the catalogued relative entity mass by substituting $m_{\mathrm{av}}(\mathrm{X}) = M_{\mathrm{r}}(\mathrm{X})$ Da into (13):

$$M(\mathrm{X}) \;=\; m(\mathrm{X})/n(\mathrm{X}) \;=\; M_{\mathrm{r}}(\mathrm{X})\ \mathrm{Da}\ \mathrm{ent}^{-1} \qquad (14)$$

then, from (11):

$$M(\mathrm{X}) \;=\; m(\mathrm{X})/n(\mathrm{X}) \;=\; M_{\mathrm{r}}(\mathrm{X})\ \mathrm{g\ mol}^{-1} \;=\; M_{\mathrm{r}}(\mathrm{X})\ \mathrm{kg\ kmol}^{-1} \qquad (15)$$

We see that this is consistent with (12).

6. Examples of the use of the entity

The Avogadro constant

The Avogadro constant has not appeared in any of the above analysis (except parenthetically). It is defined as the amount-specific number of entities:

$$N_{\mathrm{A}} \;=\; N(\mathrm{X})/n(\mathrm{X}) \qquad (\text{dimension: } \mathbf{1C}^{-1}) \qquad (16)$$

independent of the substance. From (8) we see that:

$$N_{\mathrm{A}} \;=\; 1\ \mathrm{ent}^{-1} \qquad (17)$$

—the Avogadro constant is the *number* one per entity. Using (10), this can be written:

$$N_{\mathrm{A}} \;=\; \mathcal{N}_{\mathrm{Avo}}\ \mathrm{mol}^{-1} \;=\; (\mathrm{g/Da})\ \mathrm{mol}^{-1} \;\approx\; 6.022\ 141\ 79 \times 10^{23}\ \mathrm{mol}^{-1} \qquad (18)$$

—the Avogadro constant is an Avogadro *number* per mole. It is *not* an "Avogadro number of *entities* per mole." The latter is a conversion factor (which, like all true conversion factors, is dimensionless and identically equal to one). From (10):

$$(\mathcal{N}_{\mathrm{Avo}}\ \mathrm{ent})/\mathrm{mol} \;=\; [(\mathrm{g/Da})\ \mathrm{ent}]/\mathrm{mol} \;\equiv\; 1 \qquad (\text{dimension: } \mathbf{1}) \qquad (19)$$

Number concentration and amount concentration

The *number concentration* is the number of entities of a given substance per volume, $c_N(\mathrm{X}) = N(\mathrm{X})/V$, with dimension: $\mathbf{1L}^{-3}$. The *amount concentration* is the amount of a given substance per volume, $c_n(\mathrm{X}) = n(\mathrm{X})/V$, with dimension: $\mathbf{CL}^{-3}$. They are clearly different quantities. They are related by:

$$c_n(\mathrm{X}) \;=\; [N(\mathrm{X})\ \mathrm{ent}]/V \;=\; c_N(\mathrm{X})\ \mathrm{ent} \tag{20}$$

—an aggregate of $N(\mathrm{X})$ *entities* per volume.

For example, if $c_N(\mathrm{X}) = 5000\ \mathrm{mL}^{-1}$, then $c_n(\mathrm{X}) = 5\ \mathrm{kent\ mL}^{-1} = 5\ \mathrm{Ment\ L}^{-1} = (5\times10^6)/\mathcal{N}_{\mathrm{Avo}}\ \mathrm{mol\ L}^{-1} \approx 8.303 \times 10^{-18}\ \mathrm{mol\ L}^{-1}$.

Rate constants

If $c_n(\mathrm{X})$ is the *amount* concentration of a reactant, the rate equation for a second-order reaction is:

$$\mathrm{d}c_n(\mathrm{X})/\mathrm{d}t \;=\; -k\,c_n(\mathrm{X})^2 \tag{21}$$

The dimension of k is $\mathbf{C}^{-1}\mathbf{L}^3\mathbf{T}^{-1}$. If we know that $k = 10^{8.2}\ \mathrm{mol}^{-1}\ \mathrm{L\ s}^{-1}$, since mol = $\mathcal{N}_{\mathrm{Avo}}$ ent, we can write k as:

$$k \;=\; (10^{8.2}/\mathcal{N}_{\mathrm{Avo}})(1000\ \mathrm{mL})\ \mathrm{ent}^{-1}\ \mathrm{s}^{-1} \;=\; 10^{-12.6}\ \mathrm{ent}^{-1}\ \mathrm{mL\ s}^{-1} \tag{22}$$

[In terms of the Avogadro constant, $k = 10^{-12.6} N_{\mathrm{A}}\ \mathrm{mL\ s}^{-1}$, consistent with $N_{\mathrm{A}} = \mathrm{ent}^{-1}$.]

If, instead, we were interested in the rate equation for the *number* concentration, we would have:

$$\mathrm{d}[c_N(\mathrm{X})\ \mathrm{ent}]/\mathrm{d}t \;=\; -k\,[c_N(\mathrm{X})\ \mathrm{ent}]^2 \tag{23}$$

or

$$\mathrm{d}c_N(\mathrm{X})/\mathrm{d}t \;=\; -k'\,c_N(\mathrm{X})^2 \tag{24}$$

where $k' = k\ \mathrm{ent} = 10^{-12.6}\ \mathrm{mL\ s}^{-1}$, with dimension: $\mathbf{L}^3\ \mathbf{T}^{-1}$.

Mass of the proton

The *mass* of the proton expressed in kilograms is, to the precision indicated:

$$m_{\mathrm{p}} \;=\; 1.672\ 621\ 637 \times 10^{-27}\ \mathrm{kg} \qquad (\text{dimension: } \mathbf{M}) \tag{25}$$

In terms of the dalton, the *mass* is:

$$m_{\mathrm{p}} \;=\; 1.007\ 276\ 467\ \mathrm{Da} \qquad (\text{dimension: } \mathbf{M}) \tag{26}$$

The *amount-specific mass* of the proton is the *mass* of one proton divided by the *amount* of one proton, the latter being one entity. Thus, using (11):

$$\begin{aligned} M(\mathrm{p}) &= m_\mathrm{p}/(1\ \mathrm{ent}) = 1.007\ 276\ 467\ \mathrm{Da\ ent^{-1}} \\ &= 1.007\ 276\ 467\ \mathrm{g\ mol^{-1}} \qquad (\text{dimension: } \mathbf{MC}^{-1}) \end{aligned} \tag{27}$$

This is also the *amount-specific mass* of an aggregate of any number of protons.

Ideal gas equation

If $N(\mathrm{X})$ represents the number of entities of kind X in a volume V with a pressure p and a temperature T, the ideal gas equation can be written:

$$p\,V = N(\mathrm{X})\,k_\mathrm{B}\,T \tag{28}$$

where k_B is the Boltzmann constant, $k_\mathrm{B} \approx 1.380\ 6488 \times 10^{-23}\ \mathrm{J\ K^{-1}}$. In terms of $n(\mathrm{X})$:

$$p\,V = [N(\mathrm{X})\ \mathrm{ent}][k_\mathrm{B}/\mathrm{ent}]\,T = n(\mathrm{X})\,\mathcal{R}\,T \tag{29}$$

where the universal gas constant is:

$$\begin{aligned} \mathcal{R} &= k_\mathrm{B}/\mathrm{ent} \approx 1.380\ 6488 \times 10^{-23}\ \mathrm{J\ K^{-1}\ ent^{-1}} \\ &= (\mathcal{N}_\mathrm{Avo}\,k_\mathrm{B})\ \mathrm{mol^{-1}} \approx 8.314\ 463\ \mathrm{J\ K^{-1}\ mol^{-1}} \end{aligned} \tag{30}$$

Using (12) and (15), the ideal gas equation in terms of the substance mass is:

$$p\,V = m(\mathrm{X})R(\mathrm{X})T \tag{31}$$

where the individual gas constant for the particular substance is given by $R(\mathrm{X}) = \mathcal{R}/M(\mathrm{X}) = \mathcal{R}/[M_\mathrm{r}(\mathrm{X})\ \mathrm{g\ mol^{-1}}] \approx 8.314\ 463/M_\mathrm{r}(\mathrm{X})\ \mathrm{J\ K^{-1}\ g^{-1}}$.

7. Summary

Currently there is no accepted unit for chemical amount at the atomic scale, analogous to the dalton for mass. This has led to a conceptual gap and created a lot of confusion. The accepted reference constant relating chemical amount and number of entities is the widely misunderstood Avogadro constant, with the dimension of "reciprocal chemical amount." The *reciprocal* of the Avogadro constant is one entity (with the dimension of chemical amount), which is much more easily comprehended. It therefore makes much more sense to work directly with the entity itself as both an atomic-scale unit and a reference quantity for chemical amount. But this must be done in a *consistent* manner—in particular, the physical quantity entity (with dimension **C**) cannot be replaced by the (dimensionless) number 1. Doing so leads to the "problems" raised in the Working Document. With the consistent use of the entity, these "problems" do not arise.

References

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