COMMENTS ON MOLE WORKSHOP PRESENTATIONS

BP Leonard, The University of Akron, May 11th, 2014

I. Confusing the "Avogadro *number*" and the "Avogadro *constant*"

There are two distinct and independent quantities that are often confused with each other.

1. The gram-to-dalton mass-unit ratio, g/Da

This arises from expressing substance mass, $m(X)$, in terms of grams for macroscopic samples while (sample-average) entity masses, $m_a(X)$, are catalogued in terms of daltons: $m_a(X) = M_r(X)$ Da, where $M_r(X)$ is the relative entity mass, and X represents the kind of entity comprising the substance. We can express the substance mass in terms of daltons or grams:

$$m(X) \; = \; N(X)m_a(X) \; = \; N(X)M_r(X)\,\text{Da} \; = \; [N(X)/(\text{g}/\text{Da})]M_r(X)\,\text{g} \qquad (1)$$

noting how the "scale-factor" (for *mass*), g/Da, arises automatically, thereby normalizing the large number $N(X)$, so that, for macroscopic samples, $N(X)/(\text{g}/\text{Da}) = O(1)$. We can rewrite equation (1) in dimensionless form as:

$$N(X)/(\text{g}/\text{Da}) \; = \; m(X)/[M_r(X)\,\text{g}] \qquad (2)$$

from which we see that, when $m(X) = M_r(X)$ g—i.e., a "mass that, when expressed in grams, has a numerical value equal to the relative entity mass"—then $N(X) = $ g/Da, a fixed (although currently inexactly known) number, *independent* of the substance. [The *mass* $M_r(X)$ g was originally called a "gram-atom" ("gram-molecule") or "chemical mass unit."] This number, g/Da, is what is properly known (today) as the "Avogadro *number*." [Perrin originally called it "Avogadro's constant," but a very similar name—the

"Avogadro constant"— was confusingly later chosen as the name for the quantity described in Section 2, when the SI mole was invented. The Avogadro *number* and the Avogadro *constant* continue to be confused with each other, as a glance at almost any textbook or online tutorial will confirm.]

Importantly, note that the Avogadro *number*, g/Da, is totally independent of the SI mole (and the SI Avogadro *constant*). It arises simply from the mathematical identity, $g \equiv (g/Da) \, Da$—i.e., the gram is an Avogadro number of daltons. Also note that the Avogadro number is not some "universal constant of Nature"—it is simply the ratio of two man-made mass units. The definitions of the gram and the atomic-scale mass unit have changed (a little) over the past century or so. Currently, with the definitions $g = 0.001 m(IPK)$ and $Da = m_a(^{12}C)/12$, we have, using the CODATA 2010 value:

$$g/Da \; = \; 0.012 m(IPK)/m_a(^{12}C) \; \approx \; 6.022 \; 141 \; 29 \times 10^{23} \tag{3}$$

The Avogadro *number* is what the International Avogadro Project measures, equivalent to measuring the mass of the carbon-12 atom in terms of the IPK. It is a scale factor (for *mass*) from the atomic to the macroscopic scale.

2. The number-to-amount ratio, $N(X)/n(X)$, independent of X

The architects of the (current) SI mole made (at least) *three* fundamental mistakes, described in the next paragraph. Given the atomic-structure of matter, the concept of "number of entities" in a sample of a substance consisting of a collection of chemically equivalent entities (with possibly different isotopes) is intuitively obvious and can be considered to be a useful physical quantity. The symbol $N(X)$ is also appropriate—the "N" signifies a *number* and the argument (shown here as "X") specifies the kind of entity involved; e.g., number of carbon atoms, $N(C)$, number of water molecules, $N(H_2O)$, etc. [It is obviously essential to specify the kind of entity so as to avoid ambiguity, since, for example, $N(O) = 2N(O_2)$, etc.] Contrary to what many people have said, there is nothing confusing about the concept of "amount of substance," $n(X)$, provided it is understood to be a technical term representing "amount of [a specified substance with a bulk name]"— e.g., amount of benzene, $n(C_6H_6)$—or "amount of [a collection of specified entities]"

when there is no corresponding bulk name—e.g., amount of a collection of sodium ions, $n(Na^+)$. The physical quantity is "amount," but because there are different kinds of "amounts" (although not many), it would be better for the formal *technical* name to be "chemical amount"—the analogy with "electric current" is appropriate. In both cases, the adjectives can usually be omitted in practice. [For those who would argue that subatomic particles and photons, etc., are not "chemicals," the adjective "chemical" should be taken to mean "physiochemical."] I will use "amount of substance," "amount," and "chemical amount" interchangeably.

Now to the three above-mentioned mistakes. When the SI mole was introduced in 1971, "amount of substance" was defined as being proportional to the corresponding number of entities: $n(X) = \text{const } N(X)$. This in itself is OK, noting that "const" must have the dimension of amount of substance, since $N(X)$ is dimensionless. When $N(X) = 1$, $n(X)$ is the amount of a single entity; call this n_1. This is clearly independent of any substance. The quantity n_1 is a "reference constant" for linking $n(X)$ and $N(X)$, and has the dimension of chemical amount. Since this is the smallest (non-trivial) amount, it is an appropriate atomic-scale *unit* of chemical amount. Let this have (for example) the symbol: en1 ("en-one"). Then we would have $n(X) = N(X)$ en1—i.e., amount (of a specified substance) is the corresponding number of entities times the amount of a single entity. Unfortunately (for, literally, millions of chemistry students and others), the architects of the SI mole:

(i)　　placed the proportionality constant in the denominator on the right, with the dimension of "*reciprocal* amount of substance"

(ii)　　called it the "Avogadro *constant*," thereby potentially confusing it with the Avogadro *number*, independently defined as g/Da, stemming from expressing substance mass in terms of grams rather than daltons.

(iii)　　and gave it the symbol "N_A"—which strongly suggests that the Avogadro *constant* is a (dimensionless) number, reinforcing the confusion with the Avogadro *number*.

So, instead of the simple relationship linking $n(X)$ and $N(X)$:

$$n(X) \;=\; N(X) \text{ en1} \tag{4}$$

—an aggregate of $N(X)$ atomic-scale amount units, which is easy to understand, we were given the incredibly mysterious "definition" of amount of substance as:

$$n(X) \;=\; N(X)(1/N_A) \tag{5}$$

—an aggregate of $N(X)$ "reciprocal Avogadro constants," guaranteed to cause widespread confusion. It is virtually impossible to conceptualize "amount of substance" and the "Avogadro constant" from equation (5) without getting stuck in a circular-logic loop! These three mistakes—all involving the "Avogadro constant"—are at the core of the well-known and well-documented confusion that permeates this subject. The Avogadro constant is certainly a "reference constant"—but for the physical quantity "*reciprocal* amount of substance"! [It can hardly be called a "fundamental constant of Nature."] Even if conceptualized as a reference constant for "number per amount of substance," this does not help us understand what "amount of substance" means.

3. Correct interpretation

By contrast, we can take the easily understood relationship, $n(X) = N(X)$ en1, one step further by identifying the amount of one entity (of any kind) as (the existence of) a single entity, replacing en1 by a symbol representing one entity, for example: ent. Thus the fundamental relationship linking amount (of a specified substance), $n(X)$, and the corresponding number of entities, $N(X)$, is:

$$n(X) \;=\; N(X) \text{ ent} \tag{6}$$

—amount (of a specified substance) is an aggregate of $N(X)$ entities, where 1 ent is the atomic-scale unit of chemical amount. The concept of "amount" (of a specified substance) is now "intuitively obvious" and therefore suitable as a base physical quantity.

We note that 1 ent, the appropriate reference constant linking $n(X)$ and $N(X)$, has the dimension of chemical amount—it is *not* the number 1. [There is no need to introduce the poorly understood "Avogadro *constant*" at all. However, for historical reference, it should be noted that N_A is *defined* as $N(X)/n(X)$—the *number* of entities per chemical amount—and, from (6), is (always) 1 ent^{-1}, one per entity.]

II.   The entity-based definition of the mole

We are now in a position to define the mole as the macroscopic unit for chemical amount in terms of the entity, corresponding to $m(X) = M_r(X)$ g, by setting $N(X) = $ g/Da in equation (6):

$$\text{mol} = (\text{g/Da}) \text{ ent} \tag{7}$$

—"the mole is an Avogadro number of entities"—as it is often thought of by chemists. It is absolutely imperative to emphasize that the atomic-scale unit (and reference quantity), one entity, has the dimension of chemical amount—it is *not* the atomic-scale counting unit, one (1). The latter is the appropriate atomic-scale "unit" for $N(X)$, not $n(X)$. It is also important to emphasize that the unit entity and the unit mole are both *independent of any substance*, as all proper units must be. The prescription in the current and pending CCU definition statements that the kind of entity must be *specified in the definition* confusingly implies that the mole is substance dependent. As mentioned above, the substance (kind of entity) *must* be identified in the arguments of $N(X)$ and $n(X)$, but the kind of entity is irrelevant to the definition of the mole.

Summarizing, we now have, with an obvious similarity in structure:

Number of entities:
$$N(X) = N(X)1 = [N(X)/(\text{g/Da})](\text{g/Da}) = Z(X)(\text{g/Da}) \tag{8}$$

Substance mass:
$$m(X)/M_r(X) = N(X) \text{ Da} = [N(X)/(\text{g/Da})] \text{ g} = Z(X) \text{ g} \tag{9}$$

Chemical amount:
$$n(X) = N(X) \text{ ent} = [N(X)/(\text{g/Da})] \text{ mol} = Z(X) \text{ mol} \tag{10}$$

—in terms of both atomic-scale units, [1, Da, ent], and macroscopic units, [(g/Da), g, mol]. The stoichiometric equations can be written in dimensionless form as:

(a) using atomic-scale units:

$$N(X)/1 \ = \ m(X)/[M_r(X) \ Da] \ = \ n(X)/ent \qquad\qquad (11)$$

(b) using macroscopic units:

$$Z(X) \ = \ N(X)/(g/Da) \ = \ m(X)/[M_r(X) \ g] \ = \ n(X)/mol \qquad\qquad (12)$$

The quantity $Z(X)$ is the "relative number of entities," $N(X)/(g/Da)$. It is also *correctly* called the "number of moles," $n(X)/mol$. The common use of the term "number of moles"—as a substitute for "amount of substance," $n(X)$—is simply wrong. If $n(X)$ is the amount of the substance, the "number of moles" is $n(X)/mol$. To say that "the number of moles of H_2O is 1.234 mol H_2O" is nonsense—and suggests that the mole is substance dependent. The correct statement is "the amount of water is 1.234 moles"—in symbols: $n(H_2O) = 1.234$ mol. [The number of moles, in this case is (the *number*) $Z(H_2O) = 1.234$.] There is absolutely no reason why beginning science students (or their teachers) should have any trouble understanding any of this, if the terminology and symbols are handled correctly.

III. The "atomic-scale unit of chemical amount equals one" fallacy

Many chemists seem to agree that the mole should be defined as an Avogadro number of entities. This is correctly represented symbolically by mol = (g/Da) ent. [In fact, this conforms to the current definition, mol = $0.012m(IPK)/M(^{12}C)$—but *not* the pending CCU definition, mol = $N*/N_A$, where $N*$ is a fixed exact number, not equal to the Avogadro *number*, g/Da, that would (still!) appear in the substance mass relationship, equation (9), simply because g $\equiv$ (g/Da) Da.] Note that mol = (g/Da) ent implies that:

$$Da \ ent^{-1} \ = \ g \ mol^{-1} \ = \ kg \ kmol^{-1}, \ exactly \qquad\qquad (13)$$

—i.e., dalton per entity, the atomic-scale unit for amount-specific mass (unfortunately known as "molar" mass, in violation of the commonsense Green-Book rule eschewing

unit names in the names of physical quantities) is exactly the same as the usual macroscopic units for amount-specific mass. [This equivalence is violated by the pending CCU proposal; instead, we would have: $N_A\mathrm{Da} \equiv \mathrm{Da}\ \mathrm{ent}^{-1} = (1+\kappa)\ \mathrm{g}\ \mathrm{mol}^{-1}$.]

For some reason, having agreed that a mole is an Avogadro number of entities, some experts argue that the corresponding atomic-scale unit is one (1), rather than one entity (1 ent). In symbols, this would mean mol = (g/Da)1—"an Avogadro number of ones" or simply "the Avogadro number." [This is certainly a plausible alternative, but it is *not* an Avogadro number of entities.] One entity, the smallest (non-trivial) amount of any substance, is certainly not the number 1. A substance is a collection of entities such as atoms, molecules, ions, etc., not a "collection of ones."

To see the fallacy clearly, consider g = (g/Da) Da—"the gram is an Avogadro number of daltons." The dalton, Da, is the atomic-scale unit of *mass*. Nobody would recommend replacing Da by (the dimensionless number) 1. Now consider mol = (g/Da) ent—"the mole is an Avogadro number of entities." The entity, ent, is the atomic-scale unit of *chemical amount*. Why would anyone recommend replacing ent by the (dimensionless number) 1? This is a serious misconception, delaying progress in reducing confusion. It should be obvious that "the mole is an Avogadro number of entities" (an *amount*) is not the same as "the mole is the Avogadro number" (a *number*).

IV. The "continuous versus discrete" fallacy

Many experts claim that the SI mole and the quantity amount of substance, $n(X)$, are *continuous* concepts that are inappropriate for substances that, according to atomic theory, are clearly made up of a collection of *discrete* entities. This is reinforced by the fact that the SI treats number of entities, $N(X)$—clearly an integer-valued quantity (it cannot vary by less than 1)—as a continuous differentiable real-number-valued variable. By contrast, nobody (as far as I know) seems to "worry" about substance mass being treated as a continuous differentiable real-number-valued variable—presumably because "mass" is considered to be a "continuous" quantity (at least at the length scales of interest to chemistry). But "substance mass" differs from "mass" in general. Substance mass, $m(X)$, is a *discrete-valued* quantity, no different, in this regard, from number of entities, $N(X)$. Substance mass cannot vary by less that the mass of a single entity—*it is not*

continuous. So any criticism of the SI's treatment of amount of substance and number of entities as "continuous" variables should apply equally to substance mass. The fact is that all three of $N(X)$, $m(X)$, and $n(X)$ are (in principle) discrete-valued quantities. $N(X)$ cannot vary by less than 1; $m(X)$ cannot vary by less that one entity mass, $m_a(X)$; and $n(X)$ cannot vary by less than one entity, 1 ent. If we have a sample with a "relatively small" number of entities, $N(X)$ can indeed be treated as an integer; $m(X)$ can be treated as an integer number of (sample-average) entity masses, $m(X) = N(X)m_a(X)$; and $n(X)$ can be treated as an integer number of entities, $n(X) = N(X)$ ent. These are not "continuous" variables; and discrete mathematics and statistics must be used instead of the "continuous" techniques familiar to thermodynamics. Masses would be expressed in daltons, Da, or SI multiples of the dalton (kDa, MDa, etc.). Amounts would be expressed in entities, ent, or SI multiples of the entity (kent, Ment, etc.). [Note that ent does not take SI submultiples.]

However, if the number of entities involved is "relatively large," each of $N(X)$, $m(X)$, and $n(X)$ may be treated as continuous differentiable real-number-valued variables. This is one of the *fundamental principles of continuum mechanics*. [Just what constitutes "relatively small" and "relatively large" is a matter of the precision used in the analysis. The general commonsense rule of continuum mechanics is: if addition (or subtraction) of *one* entity makes *no measurable difference* (within the desired precision), then all variables may be treated as continuous.] The point is that the equations:

Number of entities:

$$N(X) \ = \ N(X)1 \ = \ [N(X)/(\text{g/Da})](\text{g/Da}) \ = \ Z(X)(\text{g/Da}) \qquad (14)$$

Substance mass:

$$m(X)/M_r(X) \ = \ N(X) \, \text{Da} \ = \ [N(X)/(\text{g/Da})] \, \text{g} \ = Z(X) \, \text{g} \qquad (15)$$

Chemical amount:

$$n(X) \ = \ N(X) \, \text{ent} \ = \ [N(X)/(\text{g/Da})] \, \text{mol} \ = \ Z(X) \, \text{mol} \qquad (16)$$

are valid at any scale, large, medium or small.

The widespread claim (by experts) that the SI mole and amount of substance, $n(X)$, together with the treatment of $N(X)$, are only valid for "continuous" quantities (as

used in thermodynamics, for example)—and not valid for "small" numbers of entities—is simply based on a fallacy. This is a "Red Herring" that only increases the confusion permeating this subject. This appears to be a motivating factor for the CIAAW proposal to change the name "amount of substance" (somehow perceived as implying a "continuous" quantity) to "number of entities" (supposedly implying a discrete-valued quantity). If this is the case, this proposal is based on a fallacy. Also, "number of entities" is already the name of $N(X)$. Does the CIAAW proposal imply eliminating $n(X)$ as a distinct quantity? If so, then the mole is simply the "Avogadro number"—not an "Avogadro number of entities." And we would have $N(X) = N(X)/(g/Da)$ mol $= Z(X)$ mol—and we would work with the relative number of entities, $Z(X) = N(X)/(g/Da)$, which is equal to the "number of moles"!

V. The "mole should not depend on the kilogram" fallacy

The architects of the New SI have often criticized the current mole definition, mol $= 0.012m(\text{IPK})/M(^{12}\text{C})$, because it "depends on the kilogram"—i.e., currently the IPK, a man-made artifact, the mass of which may be drifting. This argument would appear to fall flat with a "more stable" redefined kilogram—especially given the fact that the fixed-Planck-constant kilogram and fixed-Boltzmann-constant kelvin depend on both the second and the metre, etc. It is perhaps worth emphasizing that the Avogadro *number* remains as g/Da, regardless of how any of the units are redefined. If, as many chemists seem to prefer, the mole is to be redefined explicitly as an "Avogadro number of entities," the kilogram *must* be involved in the definition, since, assuming the carbon-12-based dalton is retained, the Avogadro number is: g/Da $= (0.012 \text{ kg})/m_a(^{12}\text{C})$. The only way the kilogram can be explicitly eliminated from the mole definition—without involving the "$(1+\kappa)$" correction factor—is to set g/Da equal to an exact constant. This can be done in one of (only) two ways:

(i)   Keep the carbon-12-based dalton and redefine the kilogram as an exact multiple of the carbon-12 atomic mass. This option is preferred by many chemists (and others concerned about explaining the new definitions to non-experts)—but it seems unlikely to be adopted by the CGPM.

(ii)   Adopt a "non-carbon-12-based" kilogram (such as the fixed-h definition) and redefine the dalton exactly in terms of this kilogram. This would involve decoupling the dalton from the carbon-12-based mass used for cataloguing directly measured nuclidic mass ratios, $12\{m_a(X)/m_a(^{12}C)\}$, which, being dimensionless, do not require a unit.

Defining the mole as mol $= N^*/N_A$, where N^* is an exact constant, and retaining the carbon-12-based dalton, and adopting the fixed-h kilogram—while the (inexactly known) Avogadro *number*, g/Da, still appears in the substance mass equation, as it must—results in a fundamental incompatibility between the mole, kilogram and dalton, requiring the introduction of an inexactly known *correction factor*, $N^*/(g/Da)$, sometimes known as "$(1+\kappa)$." The Avogadro *constant*, N_A, would have an exact numerical value, *when expressed in reciprocal moles*, $N_A/(mol^{-1}) = N^*$. But, given the fact that the Avogadro *constant* is widely misunderstood, redefining the mole simply to guarantee an exact numerical value of N_A (when expressed in reciprocal moles) would seem to be of little positive value—certainly not enough to offset the widespread further layers of confusion that this would create.

VI. Comments on specific presentations

1. Brand

This presentation seems to show the classical confusion between the Avogadro number and the Avogadro constant. One the one hand, Brand says that "1 mol = an agreed upon number of entities" but follows this with "(counts)," which is not at all clear. Then, later, "mol $= 6.022\ 141\ 29 \times 10^{23}/N_A$" followed by "'mol' is a dimensionless unit"—which would seem to be contradictory, unless the Avogado *constant* is dimensionless. On the other hand, if N_A represents the Avogadro *number* (which seems to be a consistent concept throughout the presentation), then mol $= 6.022\ 141\ 29 \times 10^{23}/N_A = 1$. As mentioned earlier, the CIAAW proposal to change "amount of substance" to "number of entities" appears to be motivated by the "continuous versus discrete" fallacy.

2. De Bièvre

In this presentation, De Bièvre is clearly concerned about distinguishing between the Avogadro number and the Avogadro constant, as shown by the notation "$N_{A(vo)}$," rightly concluding that the International Avogadro Project measures the Avogdro *number* (independent of any mole definition) and that the Avogadro constant is defined by $N_A = N/n$. However, he appears to be a victim of the "continuous versus discrete" fallacy, and of conceptualizing the atomic-scale unit for "amount of substance" (however renamed, if at all) as the number one (1) instead of one entity (1 ent). The statement in words that "one mole is an Avogadro number of entities" does not agree with the implied statement in symbols, "mol = [Avogadro number] × 1"—indeed, one entity is *not* the number one. The correct symbolic statement is "mol = (g/Da) ent." If the mole is to be redefined as "an Avogadro number of entities," which makes perfectly good sense, then one entity, 1 ent, must be introduced as the "defining constant"—for chemical amount; and 1 ent is then the appropriate atomic-scale unit for chemical amount, paralleling 1 Da for mass.

3. Hibbert

This presentation outlines the IUPAC-ACD support of the CIAAW proposals. However, the proposed definition of the mole: "The mole, symbol 'mol', is a number of entities equal to 6.022 14XYZ × 10^{23} entities exactly,"—is contradicted by the note "The proposed definition does not require an associated quantity other than '1'." If the mole is to be an exact number of "entities," then we need a representation of one entity. On the other hand, if the base quantity is "number of entities," as proposed by the CIAAW, then the mole would be the *number* 6.022 14XYZ × 10^{23}, not 6.022 14XYZ × 10^{23} entities. The presentation lists a number of statistics showing that teaching and learning of the mole concept remains in a high state of confusion.