Ten reasons NOT to fix the numerical value of the Avogadro constant

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In September 2010, I circulated a draft paper to several authors who had publically proposed redefining the mole in terms of a fixed numerical value of the Avogadro constant, describing why I thought such a redefinition would be a bad idea. A revised version [1] of that paper has now been published in *Metrologia*. A second paper [2], describing a problem with the current "conventional definition" of amount of substance, has also been accepted for publication by *Metrologia*. A discussion of the didactical problems relating to amount of substance has been submitted to *Journal of Chemical Education* [3].

The Comité consultatif pour la quantité de matière – metrologie en chimie (CCQM) restated its "preference" for a redefinition of the mole based on a fixed [numerical] value of the Avogadro constant at its 15th meeting in 2009 [4]. The Interdivisional Committee on Terminology, Nomenclature and Symbols (ICTNS) of the International Union of Pure and Applied Chemistry (IUPAC) has also supported the redefinition, and this support has been ratified by the IUPAC Executive Committee on behalf of the IUPAC Bureau [5]. Opposition to the redefinition has come from the Chemistry Section of the French Academy of Sciences [6] and from Andres *et al*. of the Swiss Federal Office of Metrology (METAS) [7].

The Comité consultatif des unites (CCU) has recommended the use of "explicit constants" definitions for the seven SI base units along with the redefinition of four of those units, including the mole [8]: the wording of the CCU recommendation with respect to the mole is at best debateable. As the question of redefinition must be re-examined in preparation for the 24th Conférence générale des poids et mesures (CGPM) in autumn 2011, I have taken this opportunity to summarize the arguments against such a change in the basis for the definition of the mole.

1. **There would be no metrological benefit from fixing the numerical value of N_A.** It is widely accepted that fixing the numerical values of the Planck constant h and the elementary charge e would allow the results of many measurements to be expressed more precisely in SI units, so-called "quantum metrology". No such claim can be made for fixing the numerical value of N_A. There are two non-trivial physical constants whose uncertainties would depend on the uncertainty in N_A: the Faraday constant F and the molar gas constant R (assuming the kelvin is also to be redefined in terms of a fixed numerical value of the Boltzmann constant k_B).[1] The residual uncertainties in F and R would still be almost three orders of magnitude lower than the relative measurement uncertainties of the best direct determinations of these constants, and so of the best measurements of the corresponding physical quantities. (see also Appendix 1)

[1] See Appendix 2 for a discussion of the molar Planck constant $N_A h$.

2. **No new techniques have become available for the general measurement of amount of substance.** The metre was redefined in 1983 in part because laser interferomery had arisen as an extremely precise method of measuring length. The current push towards redefining the kilogram in terms of a fixed $\{h\}$ and the ampere in terms of a fixed $\{e\}$ comes in part because of the measurement of electrical quantities by the Josephson effect and the quantum Hall effect. No comparable development in the measurement of n has occurred that might justify a redefinition of the base unit.
3. **Amount of substance is not a count of entities**, any more than electric charge is a count of elementary charges. The unit of amount of substance wasn't introduced because chemists didn't want to deal with big numbers: it was in use (as the Mol. or mol.) even before Raoult needed to describe colligative properties, such as boiling-point elevation and melting-point depression, in 1882, and before the Avogadro constant had been estimated.
   Despite the title of their most recent paper [9], the International Avogadro Coordination (IAC) do not "count atoms of silicon": they compare a measurement of a microscopic quantity (the {220} lattice distance of silicon) with a measurement of a macroscopic quantity (the volume of a one-kilogram silicon sphere), as is the basis for almost all practical measurements of amount of substance.
4. **Amount of substance is a useful quantity dimension at the macroscopic scale,** and should not be confused with the dimension **1**: any unit of amount of substance based on a fixed $\{N_A\}$ would risk being confused with a unit of dimension **1**, as already happens despite the current definition.
   A statement such as "the standard molar entropy of chlorine gas is 223.081(10) $JK^{-1}mol^{-1}$" obviously refers to an ensemble of chlorine molecules, and cannot be reduced to the scale of an individual molecule. While convenient in contexts such as industrial chemistry and chemical engineering, the use of specific quantities (per unit mass) represents a loss of information, as can be illustrated by Clausius' failure to realize that all ideal gases share the same molar gas constant.
5. **The Avogadro constant is irrelevant for the measurement of amount of substance.** Chemists were measuring stoichiometric quantities for more than a hundred years before Perrin determined N_A. The vast majority of modern measurements of n would be recognizable to Dalton and Gay-Lussac.
6. **The mole is not "thought of by chemists as an Avogadro number of entities"** as the IUPAC ICTNS would have us believe. I contend that never in the field of chemical science has anyone ever thought "I've got to weigh out 6.02×10^{21} molecules of benzoic acid" or "I'm going to need 1.5×10^{21} hydrogen ions to neutralize that solution."
7. **The current confusion surrounding amount of substance does not stem from the current definition of the mole.** In my experience, it stems from an undue emphasis on the numerical value of the Avogadro constant when introducing the subject. Educators have great fun telling kids that there are 6×10^{23} atoms in 12 grams of carbon 12, and that that's a *really big* number, far too large to count: is it any surprise that students are confused as to how they're supposed to measure it? The standard approach to teaching amount of substance misses the more fundamental point entirely: that one doesn't need to know the numerical value of N_A to measure n, one merely needs to know the relative masses (or other relative quantities) of the entities in question.

8. **A definition of the mole in terms of a fixed numerical value of N_A would not be "conceptually simpler" than the current definition.** It is only conceptually simpler in terms of a misconception of amount of substance as a count of entities. The present definition allows the theory behind the calculation of molar mass to be explained to elementary students: the proposed redefinition would incorporate all the high-level theory of the Rydberg constant into the justification of everyday molar-mass calculations.
9. **The current measurement uncertainty in N_A is conceptually meaningful.** The Avogadro constant relates quantities measured at the macroscopic scale with similar quantities measured at the atomic scale. The uncertainty in the measured value of N_A is a simple statement of the uncertainty in our ability to compare the two scales of measurement. This uncertainty would still be present in any redefined system of units, it would merely be transferred to the molar mass constant M_u and so retained in the atomic mass constant m_u. There is no benefit to be gained from simply transferring the measurement uncertainty from a well-known physical constant onto an (unduly) obscure one.
10. **There is no reason to remove the implicit link to the kilogram from the definition of the mole**, especially as amount of substance is most commonly measured through measurements of mass. The ampere is currently defined in terms of the newton because, for nearly 100 years, the most accurate way of measuring electric current was through the Biot–Savart law. The metre is defined in terms of the second because the most accurate way of measuring length (at the laboratory scale) is by laser interferometry. Under the "explicit-constant" definitions proposed by the CCU [8], not one of the SI base units would be defined by a constant of the same kind as the unit!
    Leonard's contention that the uncertainty in the realization of the kilogram is transmitted to the mole [10] is incorrect: the current definitions of the mole and the kilogram are exact, although any practical realization of the mole will, of course, have a measurement uncertainty. The contention of May *et al*. [11] that users consider the mole to be a unit of mass because of the present definition is simply illogical: users do not consider the ampere to be a unit of force, after all!

The conditions for redefinition of the kilogram [12,13] have not been met [9] in time for the 2010 CODATA adjustment of the fundamental physical constants. Nevertheless, the CIPM has included a draft resolution on the possible revision of the SI [14] with the convocation to the 24th CGPM to be held in October 2011: the draft resolution includes the redefinition of the mole in terms of a fixed numerical value of N_A at some future date "as soon as the recommendations of Resolution 12 of the 23rd meeting of the General Conference are fulfilled".

The most relevant recommendation of the 23rd CGPM is:

> *National Metrology Institutes and the BIPM should, together with the International Committee, its Consultative Committees, and appropriate working groups, work on practical ways of realizing any new definitions based on fixed values of the fundamental constants [and] prepare a* mise en pratique *for each of them* [15]

I look forward to the proposed *Mise en pratique* for the redefined mole, upon which the chemical metrology community has yet to have a chance to debate. If it suggests that chemists should undertake precision dimensional and density measurements on single crystals in order to measure *n* at the highest level, it would be a very eloquent argument against the proposed redefinition; if it merely repeats the principles of the current *Mise en pratique* [16], it would be an admission that the proposed redefinition is, in fact, impractical and unnecessary.

For these reasons, I urge the CCQM to reconsider its stated "preference" for a redefinition of the mole in terms of a fixed value of the Avogadro constant. Users are served perfectly well by a definition based on the molar mass of carbon 12, and the admitted shortcomings in the present wording of the definition could easily be resolved by an "explicit-constant" definition of the type:

> **The mole, mol, is the unit of amount of substance; its magnitude is set by fixing the numerical value of the molar mass of unbound carbon 12 atoms, at rest and in the ground state, to be equal to exactly 0.012 when it is expressed in the unit kg mol^{-1}.**

In this International Year of Chemistry, our time and energy would be better spent explaining why we ***don't*** measure amount of substance by counting elementary entities, rather than by pretending that somehow we do.

Appendix 1: Effect of redefinition on the fundamental physical constants

Table. Relative measurement uncertainties ($10^9 u_r$) in various physical constants under the current definitions of the SI base units and under three possible redefined systems: redefinition of the kilogram and the ampere, with additional redefinition of the kelvin or of the kelvin and the mole. $m(\mathcal{K})$ = mass of the International Prototype Kilogram; μ_0 = magnetic constant; $T_{tp}(H_2O)$ = triple point of Vienna Standard Mean Ocean Water (VSMOW).

	current	kg-A	kg-A-K	kg-A-K-mol
N_A	50	1.4	1.4	0
h	50	0	0	0
e	25	0	0	0
F	25	1.4	1.4	0
m_u	50	1.4	1.4	1.4
R	1700	1700	1.4	0
k	1700	1700	0	0
V_m	1700	1700	1.4	0
$N_A h$	1.4	1.4	1.4	0 (*a*)
m_e	50	1.4	1.4	1.4
α^2	1.4	1.4	1.4	1.4
$A_r(e)$	0.42	0.42	0.42	0.42
M_u	0	0	0	1.4
constants with fixed numerical values	$m(\mathcal{K})$ μ_0 $T_{tp}(H_2O)$ M_u	h e $T_{tp}(H_2O)$ M_u	h e k M_u	h e k N_A

Adapted from [1]: values calculated on the basis of the 2006 CODATA adjustment [17].
(*a*) See, however, Appendix 2.

Appendix 2: Molar Planck constant

An oversight in the preparation of manuscript [1] led to the omission of a discussion of the molar Planck constant $N_A h$. The discussion is important in this context, as May *et al.* [11] include the molar Planck constant in their list of physical constants whose value would be fixed by fixing the numerical value of the Avogadro constant.

Under the current CODATA adjustment [17], the molar Planck constant is not dependent on the values of either N_A or h: instead it is given by (1)

$$N_A h = \frac{c\alpha^2 A_r(e) M_u}{2R_\infty} \quad (1)$$

where α, $A_r(e)$ and R_∞ are independently refined constants while c and M_u have defined values. As such, the uncertainty in the value of $N_A h$ ($u_r = 1.4 \times 10^{-9}$) is much lower than the uncertainties in the values of N_A or h on their own, and is essentially due to the uncertainty in α^2.

Under proposals to redefine the kilogram and the mole in terms of fixed numerical values of h and N_A respectively, (1) would have to be reinterpreted as a definition of M_u (2), which would have the same measurement uncertainty as $N_A h$ at present.

$$M_u = \frac{2R_\infty N_A h}{c\alpha^2 A_r(e)} \quad (2)$$

There has been some interest in the utility of the molar Planck constant as a stringent test of Einstein's mass–energy equivalence [18,19]. The principle behind such tests is the examination of a neutron-capture reaction $^{A}X(n,\gamma)^{A+1}X$ (more than one γ photon is usually emitted), where (3) must hold for mass–energy equivalence.

$$\Delta E = c^2 \Delta m \quad (3)$$

The importance of the molar Planck constant in this method is that Δm can only be measured in daltons, but must be compared to γ wavelengths measured in metres. The conversion factor (CODATA 2006 values) is

$$(1\ \text{m}^{-1})h/c = 1.331\ 025\ 0394(19) \times 10^{-15}\ \text{Da} \quad (4)$$

with $u_r = 1.4 \times 10^{-9}$, more than an order of magnitude better than the $u_r = 5.0 \times 10^{-8}$ in the value of the atomic mass constant [17].

As is discussed in [1], the uncertainty in the value of m_u would be much reduced (effectively to the uncertainty in α^2) by redefining the kilogram in terms of a fixed $\{h\}$, but *no further reduction in the uncertainty* would be achieved by redefining the mole in terms of a fixed $\{N_A\}$ (because of the consequential uncertainty in M_u). For the same reason, the conversion factor in (4) would still have the same measurement uncertainty with fixed $\{N_A\}$. Hence a redefinition of the mole in terms of fixed $\{N_A\}$ would not allow an improvement in tests of $E = mc^2$ by this method. It is noted in passing that the current best measurements of nuclear binding energies (expressed in terms of measured wavelengths) have uncertainties more than two orders of magnitude higher than $u_r(\alpha^2)$ [19,20], so this is not currently the limiting factor in our ability to test mass–energy equivalence: the Avogadro constant remains as irrelevant to practical quantum metrology as it is to practical amount-of-substance measurements.

Appendix 3: Possible recommendation to the CIPM

RECOMMENDATION on the definition of the mole

The Consultative Committee for Amount of Substance – Metrology in Chemistry (CCQM),

considering

- its previous recommendations to the CIPM on the possible redefinition of the mole and the kilogram Q1 (2007) and Q1 (2009),
- the recommendation of the CCU to the CIPM on the future revision of the International System of Units U1 (2010),

noting

- the qualified support of the International Union of Pure and Applied Chemistry (IUPAC) for the proposed redefinition of the mole in terms of a fixed numerical value of the Avogadro constant,
- the opposition of several authors and scientific bodies to such a redefinition of the mole,
- the relative lack of awareness and discussion of this proposal, as also noted in the previous recommendations of the CCQM and by IUPAC,

further noting

- the historical link between measurements of amount of substance and the scale of atomic weights (later, relative atomic masses),
- that this link would become inexact under the proposed redefinition,
- that the mole would continue to be realized by mass or volume measurements under the proposed redefinition,
- the reduction of more than one order of magnitude in the uncertainty of the value of the Avogadro constant, and hence of related constants such as the atomic mass constant, that would be obtained by fixing the numerical value of the Planck constant in SI units,

recommends that

- any decision on redefining the mole in terms of a fixed numerical value of the Avogadro constant in SI units be deferred until such time as the benefits of such a redefinition to the chemical metrology community are clearly demonstrated and widely recognized,
- any revision of the SI to explicit-constant definitions of the base units be based on the molar mass of unbound carbon 12 atoms at rest and in the ground state being exactly 0.012 kilograms per mole.

RECOMMANDATION sur la définition de la mole

Le Comité consultatif pour la quantité de matière – métrologie en chimie (CCQM),

considérant

- ses précédentes recommandations au CIPM sur les éventuelles redéfinitions de la mole et du kilogramme Q1 (2007) et Q1 (2009),
- la recommandation du CCU au CIPM sur la révision à venir du Système International d’unités U1 (2010),

prenant acte

- du soutien qualifié de l’Union internationale de la chimie pure et appliquée (IUPAC) à l’éventuelle redéfinition de la mole fondée sur une valeur numérique fixée de la constante d’Avogadro,
- de l’opposition de la part de plusieurs auteurs et organisations scientifiques à une telle redéfinition de la mole,

- que la proposition de redéfinir la mole reste relativement inconnue et peu discutée, ce qui a été déjà remarqué par le CCQM et par la IUPAC,

notant également

- le lien historique entre les mesure de quantité de matière et l'échelle des poids atomiques (ultérieurement, des masses atomiques relatives),
- que ce lien deviendrait inexacte avec la redéfinition de la mole,
- que la mole serait toujours réalisée par des mesures de masse ou de volume, même après la redéfinition,
- la réduction de plus d'un ordre de grandeur dans l'incertitude de la valeur de la constante d'Avogadro, et donc dans les incertitudes des constantes telles que la constante de masse atomique, qui serait obtenue en fixant la valeur numérique de la constante de Planck en unités SI,

recommande que

- la décision de redéfinir la mole soit différée jusqu'à ce que les avantages d'une telle redéfinition pour la communauté de la métrologie en chimie soient clairement démontrés et largement reconnus,
- la révision du SI introduisant des définitions « à constante explicite » pour les unités de base soit fondée sur la masse molaire d'atomes non liés de carbone 12 au repos et dans l'état fondamental étant égale à exactement 0.012 kilogrammes par mole.

Appendix 4: Consequential amendments to Draft Resolution A

Section "considering"

- Delete tenth point "that it is also possible to redefine the mole so that it is linked to an exact numerical value of the Avogadro constant N_A, and is thus no longer dependent on the definition of the kilogram even when the kilogram is defined so that it is linked to an exact numerical value of h, thereby emphasizing the distinction between amount of substance and mass,"
- In eleventh point: delete "and N_A"; insert "and" before "k"[2]
- In twelfth point: delete "and mole"; insert "and" before "kelvin"

Section "takes note"

- Replace sixth point "the Avogadro constant N_A is exactly 6.022 14X × 10^{23} reciprocal mole," with "the molar mass of unbound carbon 12 atoms at rest and in the ground state $M(^{12}C)$ is exactly 0.012 kilogram per mole,"
- In paragraph (ii): delete "and N_A"; insert "and" before "k"

Section "from which it follows"

- Delete fourth point "the mole will continue to be the unit of amount of substance of a specified elementary entity, which may be an atom, molecule, ion, electron or a specified group of such particles, but its magnitude will be set by fixing the numerical value of the Avogadro constant to be exactly 6.022 14X × 10^{23} when it is expressed in the unit mol^{-1}."[3]

Section "further notes that since"

- In first point: delete "and mole"; insert "and" before "kelvin"

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[2] This point, as originally agreed by the CCU, is misleading in that it implies that there are significant reductions in the uncertainties of physical constants that are dependent on fixing the numerical value of N_A, which is not the case. It also fails to mention the new uncertainty in the value of M_u that would be introduced by fixing the numerical value of N_A.

[3] It is arguable that a mole defined by a fixed numerical value of N_A would no longer be a unit of amount of substance as that term is usually understood; it would certainly be a drastic departure from the 200-year history of amount of substance measurements.

- Replace point four: "although the existing definition of the candela is not linked to a fundamental constant, it may be viewed as being linked to an exact value of an invariant of nature," with "although the existing definitions of the mole and the candela are not linked to fundamental constants, they may be viewed as being linked to exact values of invariants of nature,"

Section "the International Committee will also propose"

- In the introductory paragraph, insert ", mole" after "metre"
- Insert new point after second point: "the mole, mol, is the unit of amount of substance; its magnitude is set by fixing the numerical value of the molar mass of unbound carbon 12 atoms, at rest and in the ground state, to be equal to exactly 0.012 when it is expressed in the unit kg mol^{-1},"

Section "In consequence"

- Delete fifth point "the definition of the mole in force since 1971 (14th CGPM, 1971, Resolution 3) based on a definition whereby the molar mass of carbon 12 had the exact value of 0.012 kg mol^{-1} will be abrogated,"
- In sixth point: insert ", mole" after "second"; insert ", the 14th CGPM (1971, Resolution 3)" after "the 13th CGPM (1967/68, Resolution 1)"

Section "further notes that on the same date"

- Delete fourth point "that the molar mass of carbon 12 $M(^{12}C)$ will be exactly 0.012 kg mol^{-1} but with a relative uncertainty equal to that of the recommended value of N_A just before the redefinition and that subsequently its value will be determined experimentally."

Section "encourages"

- Delete "and N_A,"; insert "and" before "k"

Section "invites"

- In second point: delete "and mole,"; insert "and" before "kelvin"

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