Re-thinking the (confusing) mole: concerns and issues

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"Thinkshop" on the redefinition of the mole
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Disclaimer:

not talking on behalf of any Institute or Organization, only from a background of having been:

- author of primary isotopic measurement standards for U and Pu (at IRMM, 1970-1998) for the Internat'l Nuclear Material Control
- involved in various forms in all IUPAC-CIAAW meetings since 1971
- PTB-invited to participate (1981-2008) in the International Si Avogadro project to deliver a relative atomic weight of Si in Si single crystals
- (Founding) Editor-in-Chief of ACQUAL 1996 - 2011
- advising / consulting / seminaring on "Metrology in Chemistry" in about 130 cities on 5 continents (since 1995 to date)

This seminar has been composed to raise awareness amongst (other than physical) chemists about the persisting confusion about the concepts 'mole' and 'amount of substance' as well as about the lack of attention paid to it in the 2005-2014 discussions about the re-definition of the mole

Paul De Bièvre

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The perception by practicing analytical chemists of the concepts
'amount-of-substance' and 'mole' (both man-made),

is different from the perception of these concepts as intended by
the International System of Units, SI and its structuring bodies;

a story of mutual non-understanding

remedy: work from both sides towards understanding by

- clarifying and
- looking at practical examples

ref: "Second opportunity for chemists to re-think the mole" [De Bièvre 2013]

1

1. Atomic mass *m* (^{i}E) E stands for element, ^{i}E for nuclide

- *m* (^{i}E) values result from the measurement of any ^{i}E frequency in a synchrotron, relative to the ^{12}C frequency, yielding a frequency ratio which is a number-ratio (unit: 1) see entry 1.10 Note 3 in [VIM 2008/2012]

- this frequency ratio is equal to the corresponding mass ratio *m* (^{i}E) / *m*(^{12}C) which also is a number-ratio (unit: 1)

- these number-ratios are converted to "atomic mass" values by making use of the dalton (Da) where Da = *m*(12C)/12 [IUPAC 1993] [IUPAC 2007] [Baranski 2013] "the name dalton, with symbol Da, is used as an alternative name for the unified atomic mass unit";

see pp 20 and 41 in [IUPAC 1993] and pp 22 and 92 in [IUPAC 2007]

present concepts in the SI for amount of substance as well as for the 1971 and CCQM-envisaged "2015" definition of the mole not needed

2

2. relative atomic weights A_r (IUPAC-CIAAW) are derived from m (E):

$m(\text{E}) = \Sigma f(^i\text{E}) \cdot m(^i\text{E})$

$m(^i\text{E})$: atomic mass of nuclide ^{i}E

$f(^i\text{E})$: fractional abundance of ^{i}E

$= \Sigma R_{i/j} \cdot m(^i\text{E}) / \Sigma R_{i/j}$

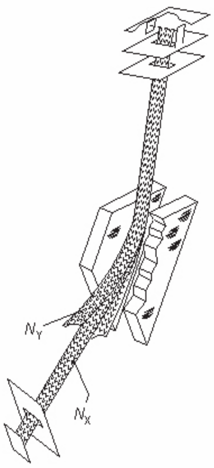
- f and R are number-ratios (unit: 1) measured by isotope ratio mass spectrometry (De Bièvre 2011/1) (see picture in next slide)

- values for A_r can be converted to m (E) by expressing them in Da, similar to atomic mass values under point 1

(➔ CIAAW to decide)

present concepts in the SI for amount of substance as well as for the 1971 and CCQM-envisaged “2015” definition of the mole not needed

THE MASS SPECTROMETER (MS)
turned into AN AMOUNT COMPARATOR (AmCo)
THE MODERN CHEMIST’S BALANCE



What chemists need is given by the AmCo!

it directly compares numbers of atoms

(or sometimes of molecules): $R_B = \frac{N_X}{N_Y}$

in the international SI unit:

the mole

1 mole contains $\{N_A\}$ atoms (molecules, entities), of the substance specified.

the AmCo sorts - then counts and compares an unknown number N_X of entities to a known number of entities (e.g. added) through a ratio - R_B - measurement of numbers of entities.

Source: P De Bièvre, Fresenius J Anal Chem 337 (1990) 766 - 771 (amended)

© P. De Bièvre Ispra Nov 1998
Jan 2004

irmm

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The balance, used in early chemistry, compares masses or "weights"

From early times, mass (or weights) were compared by a single instrument:
the balance

Recognising its status, science gave this measuring process a base (SI) unit:
the kg

But science and technology discovered the fact that atoms combine in simple numbers, so chemists cannot use the balance directly to compare numbers of entities.
They must divide mass values by "atomic weights" to get what they need.
The balance does not take into account the particulate nature of matter.

PDB03049

Source: P De Bièvre, Fresenius J Anal Chem 337 (1990) 766 – 771 (amended)

3

3. stoichiometric studies are about number-ratios of small integer numbers of atoms (unit: 1)

- in a molecule [Meinrath 2011] [Brand 2014]
  - e.g. in the synthesis of NH_3: $N_2 + 3\,H_2 \rightarrow 2\,NH_3$
    - the number-ratios 1/3, 1/2, 3/2, 3/1, 2/1 and 1/3 are important; they are accessed through measured mass ratios or measured volume ratios (again in the unit 1) [Furio 2000]
- between molecules
  - e.g. one protein molecule docking into one bacteria leading to mutual destruction
- in synthesizing new molecules with new properties
  - (i.e. new materials)

present concepts in the SI for amount of substance as well as for the 1971 and CCQM-envisaged "2015" definition of the mole not needed

3.2

stoichiometric studies and analytical measurements

are based on reactions of integer numbers of (identified) atoms and molecules (incl very big protein molecules) (unit 1), reacting with each other

they are served well by
a unit for small but integer numbers, (unit 1)

not by a unit for large non-integer numbers
as is the present SI unit mole

present concepts in the SI for amount of substance as well as for the 1971 and CCQM-envisaged “2015” definition of the mole not needed

3.3

The stoichiometric problem in other words:

when talking metrological language in stoichiometric and analytical measurements, we are confronted with a choice between

a) building down from a macroscopic level concept (the present “mole”, or the “physical” mole) which is a large number of entities (incl non-integer numbers) and related base quantity ‘amount of substance’;

the latter is based on a perception of matter as being “continuous”, and having the property of “inertia” with associated quantity of ‘mass’

3.4

b) building up from an atomic level concept ("one entity" – atom, molecule-) and its integer multiples), consistent with a "discrete" or "granular" perception of matter based on its property of "numerosity" and associated quantity 'number-of-entities'

or

- 'metrological amount' or
- 'chemical amount' ? or
- 'chemical mole' ?

applicable to entities, events or phenomena, on the macroscopic level

for more on "numerosity" and "mass": see
[Rocha 1990] [Rocha 2011] [De Bièvre 2011/1] [De Bièvre 2011/2]

3.5

Hence: choose (= a matter of convenience) a unit for a
discrete elementary quantity as a unit on the atomic level ("1"),
and an integer multiple of that elementary entity
(an aggregate) as a unit for a
continuous quantity on the macroscopic level

because:

stoichiometric (as well as ultra-low level analytical) measurement
is about the chemical world on the atomic level (atoms, molecules),
based on the discrete, discontinuous, granular structure of matter;

that is very different in principle from the SI perception of the need for a unit for "aggregates" of very large numbers, the 1971 SI philosophy

4

4. analytical science at low levels (trace and "ultra-"trace level), is about measuring very small numbers of atoms or molecules

- e.g. 60 000 atoms of an identified isotope in one g of a river sediment in Iraq downstream a suspected nuclear reprocessing plant (unit: 1)

- e.g. 10^6 molecules of an identified "drug" or sperm in a forensic sample as proof of presence (vs absence) at a particular place (unit: 1)

number-of-entities (atoms, molecules) measured by counting: the unit 1 does not need to be defined because it is simply the unit of a count [Mills 2011]; see entry 1.10 Note 3 in [VIM 2008/2012]

present concepts in the SI for amount of substance as well as for the 1971 and CCQM-envisaged "2015" definition of the mole not needed

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5. measurements of radioactivity

number-of-entities (events, atoms) N are counted:

$$A = \lambda N$$

choose the unit 1 because the unit for 'number of entities' is 1, see entry 1.10 Note 3 in [VIM 2008/2012]

it is not one entity (i.e. 1 entity), since

- the description of a quantity (i.e. number of entities) may not be used in the name of a unit [IUPAC 2007]

- a huge number of entities (each corresponding to a different molecule) would have to be conceived

present concepts in the SI for amount of substance as well as for the 1971 and CCQM-envisaged "2015" definition of the mole not needed

6

6. Measurement of mass fractions, volume fractions, number-ratios:
- " … any quantity that is defined as the ratio of two quantities of the same kind such as mass fractions … is a number (unit: 1)

- "1" can serve -as any unit- as 'reference' for metrological traceability of measurement results: entry 2.41 Note 1 in [VIM 2008/2012], a compulsory prerequisite for comparability of these results: see entries 2.46 in [VIM 2008/2012] & section 1.3 in [SI 9 2013]

- example: a primary measurement standard (entry 5.4 in [VIM 2008/2012] for glucose mass fraction measurements can be prepared through a measured mass ratio of near-pure glucose and near-pure water ("pure" does not exist;
in this procedure of preparing a value of a ratio, uncertainties of measurements of small mass fractions of impurities are negligible contributions to the uncertainty of the prepared ratio value, not influencing the mass ratio itself)

present concepts in the SI for amount of substance as well as for the 1971 and CCQM-envisaged "2015" definition of the mole not needed

7

7. Do analytical chemists think in terms of an "Avogadro constant" i.e. a fundamental constant ?
or an "Avogadro number" i.e. a "scale multiplier" [Foster 2010], also called a "scaling factor", to bridge the atomic to the macroscopic level ?

IS A BASIC QUESTION BY MANY ANALYSTS

To answer that question, we go Back to Basics (BtB):
what is measured in the International Avogadro project (the "Si route") ?

the measurement function (quantity equation) involved is

$$N_{A(vo)} = M(\text{Si}) / (\rho \cdot a_0^3 / 8)$$

$N_{A(vo)}$ = Avogadro constant N_A or Avogadro number N_{Avo} ?
M(Si) = mass of a mole of Si
ρ = density of Si in Si single crystal
a_o = interatomic distance of Si atoms in a cubic lattice

7.2

A volume ratio is measured:

a number ratio (unit:1)

$N_{A(vo)} = M(Si)/\rho\ /\ (a_0^3\ /\ 8)$

$= V_m\ /\ V_a = M\ /\ m(Si)$

$= g\ /\ Da$

V_m implies *mass of one mole, M*
that implies mass per mole,
hence of an a priori definition
of the mole, corresponding to
amount of substance

V_m = volume of one mole

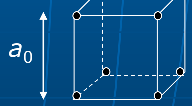
V_a = volume of one atom

$= a_0^3\ /\ 8$

M = mass of one mole

$m(Si)$ = mass of one atom

a_0 = lattice parameter



$M(Si)$ = mass of a mole, or molar mass, a term not recommended by IUPAC

Observations: 7.3

a) the present SI quantities on the right side of the quantity equation in the project lead to an Avogadro number because
the ratio of the volume of a mole to the volume of an atom
is a volume ratio i.e. a number-ratio with unit: 1
(a "scaling factor") [Foster 2010] [Romeu 2011]
there is no need to convert this into an "Avogadro constant"
with a unit "reciprocal mol", unit mol^{-1}, via the relation

$$N_A = N\ /\ n$$

used in the "mise-en-pratique" of the SI unit definition [SI 8 2006] [SI 9 2013];
besides, this relation is only applicable for a pure chemical sample [Mills 2011], not a frequent case in practical analytical chemistry;
also see [Nelson 2013]

b) thus a value for this scaling factor [Foster 2010] [Romeu 2011] is obtained in total independence from any other reference (or fundamental) constant;
"the mole [is dependent] on nothing" and is "independent of other definitions" [SI 9 2013] [Brand 2014]

Further Back to Basics: 7.4

Any measurement is the evaluation, on a measurement scale, of the ratio of
- an unknown number *Q* (↓) to
- a given number, defining the agreed unit [*Q*]: *Q* = {*Q*} • [*Q*] section 1.1 in [SI 8]

↓[Q] ↓ section 1.1 in [SI 9]

A unit is simply a part of the quantity concerned [SI8 2006] and "[a] number [of a variable] is the ratio of the value of a quantity to the value of the unit", i.e. *Q* / [*Q*] [SI 8 2006, sect 1.1] [SI 9 2014, sect 1.1] [Johansson 2014] or "the unit is simply a particular example of the quantity concerned"; see sect 1.1 in [SI 8 (2006]

evident units for <u>numerosity</u> are

on the atomic scale: one natural unit = the existence of one entity (one identified/specified atom / molecule)

on the macroscopic scale: one mol, a defined multiple of one entity: hence a large integer number of entities (atoms/molecules): 6.022 14X YZ • 10^{23} entities

---

8

8. in the new SI proposal for the mole, its definition is being connected to an interlinked network of seven reference (fundamental) constants, the numerical values of which are fixed by a (necessarily) conventional decision, and "which must be taken together to define the system [Mills 2011]"

That makes the mole dependent from a "reference set" of seven -and dependent- reference constants rather than stand alone, whereas independent measurement of said constants, is a very important metrological characteristic

this dependence carries risks [Pavese 2010] because any, however small, systematic error somewhere in the network can creep in and start to make its way through the "interrelationship" i.e. propagates itself in the network:
" a significant shift in the numerical value of one [fundamental constant] will generally cause significant shifts in others" [Pavese 2010], thus causing "… differences from numerical values … directly evaluated from … experimental data" [Pavese 2010]

present concepts in the SI for amount of substance as well as for the 1971 and CCQM-envisaged "2015" definition of the mole not needed

9

9. in physico-chemical measurements, chemical study work often starts from a perception of matter on the macroscopic level as being “continuous” and to be studied by means of big “aggregates” of things having a continuous structure;
they are called “aggregates” or “collections” or “ensembles”
(appropriate to be used in differential calculus and in thermodynamics)
they have been attributed to a quantity called ‘amount of substance’ “by lack of a better term”:

the 2009 IUPAC-ICTNS request to CCQM and CCU [IUPAC 2009] [Lorimer 2010] for a better term, is unanswered to this very day [Karol 2014/1]

the chosen unit called mole (symbol mol) is constituted by a large number of things “per mole”, implying a unit with the dimension reciprocal mol i.e. mol^{-1}

but, if that is the description of the quantity ‘amount of substance’, we may have a circular reasoning at hand (“number per mole”) [Johansson 2014/1] [Price 2011/1], requiring a definition of a “mole” to define the mole

9.2

the unit for amount of substance was coined to be a reciprocal number (mol^{-1}) in search of a quantity; that quantity was to become ‘amount of substance’ in 1971, a man-made concept not based on a property of matter;

it forced analytical chemists to think in reciprocal mole and reciprocal amount of substance) which many of them simply did not (want to) do …

In other words:

a) chemists were used to think in ‘number of entities’
b) they were required to express that as amount of substance (aos)
c) the definition of the mole is in essence “aos / number”;
therefore chemists had to express in “ $number^{-1}$ ”
d) they refused to do that and have stuck to a)

Note: any “aggregate” of entities can be expressed as an integer multiple of “1” rather than “mol^{-1}”

9.3

so here was an ill-understood unit (mole) “in search of a quantity” leading to remarkable statements such as “a unit in search of a quantity of which the mole is the unit” [Furio 2000] [Furio 2002] [Mills 2009] [Rocha-Filho 2011] [Baranski 2012]

in addition the quantity itself was -and still is- unclear: “the name amount of substance is not well chosen” [Mills 2009] [De Bièvre 2014] and “is practically unknown to most teachers” [Furio 2000]; however, logically, it is a number [Emerson 2014]

there are claims that “amount of substance is not a quantity in accordance with the term’s definition of quantities and units” [Johansson 2014/2] and even that amounts of substance are not quantities and therefore not base quantities [Emerson 2014]

9.4

Diagnosis: present status is one of two divergent concepts in thinking:

1. the quantity of which the mole is supposed to be the unit, is still not well understood
    - a) (metro-)logically and
    - b) in practice

2. there are two “incompatible” concepts clashing in the minds:
    - one -the present SI- largely ignored by practicing chemists (analytical and synthesizing, and those involved in teaching), and
    - one by the analyst in a laboratory as well as in (most) teaching

3. the macroscopic view is (still) clearly preferred in the “new SI” [Milton 2009]

see for more on this in [Price 2011/1] [Wang 2014];
they are put next to each other in the next slide:

left column right column

9.5

1. in present SI	2. chemists' practice
measurement (no counting)	enumeration (counting)
continuous nature of matter in both [SI 8 2006] and [SI 9 2013]	discrete, quantized nature of matter [Cooper 2010]
"inertia" based on the property of matter: "mass"	"numerosity" based on the phenomenon: existence of "entities" [De Bièvre 2007/1] [Rocha 1990] [Rocha 2011] [De Bièvre 2011/2]

NOTE: a quantity is a property of a body (e.g. mass), phenomenon (e.g. existence of entities) or substance [see entry 1.1 in [VIM 2008/2012]

unit: kilogram (symbol kg) [SI 8 2006], a macro unit no identification of entities needed	unit: 1, a micro unit entry 1.10 Note 3 in [VIM 2008/2012] identification of entities required
(any "real number" e.g. 7,54) enabling differential calculus	(only natural number 1, 2, 3, …) not needing differential calculus [Pavese 2010]

9.6

there are two "incommensurable" (incompatible) views of the nature of matter:
continuous and atomistic (Fang 2014);

attempting to converge these two paradigms is compounded by the lack of knowledge of the history of chemistry, is at the origin of the problems with the mole ever since 1971;

in the present state of affairs in the redefinition of the SI mole, it is likely to stay on, rather than be tackled and cured

more extensive thinking about this perception in [Price 2011] [Emerson 2012] [Johansson I 2014] [Emerson 2014] [Johansson 2014]

present concepts in the SI for amount of substance as well as for the 1971 and CCQM-envisaged "2015" definition of the mole not needed

9.7

No wonder that the IUPAC-ICTNS 2009 stated [IUPAC 2009]:

(b) the mole is often thought of by chemists as an Avogadro number of entities [IUPAC 2009] [(Lorimer, 2010]; and
(c) the name of the ISQ base quantity "amount of substance" has been a source of much confusion,

The 16th CCQM (2010) stated [CCQM 2010]:

" - prior to the change [of definitions], a more widespread understanding of the concepts and their acceptance within the chemical community must be achieved
- the level of awareness of the proposal to redefine the mole is low in the relevant community
- support for the proposal … is not yet unanimous

and recommended that:
- any decision be deferred until … full consideration is given to the interests of the chemical measurement community"

9.8

"There was no question of sending out the ICTNS resolution for public comment or formal review. Those aspects are the responsibility of BIPM which body asked ICTNS to give support, on behalf of IUPAC, to the CCU recommendation. This is not an official IUPAC Recommendation to be reviewed, but as an opinion forwarded to the Bureau (actually the Executive Committee) for approval or rejection, and sending this opinion to the BIPM.
ICTNS was following the approved protocol" [Karol 2014/1]

Conclusion:

there was no internal consultation within IUPAC, yet the CCU-requested support was given by IUPAC Bureau and interpreted in the outside world as an "IUPAC position" …

9.9

P Atkins defines the mole as a number: "1 mol of specified particles is equal to the number of atoms in exactly 12 g of carbon 12." [Atkins 1999] [Nelson 2013]. In other words, the mole is treated as a pure number; this is confirmed later when it is written:

"A mole is the analogue of the wholesaler's dozen … "
"The mole gives the number of atoms in a sample …"
"The mole is an SI base unit. The physical quantity to which it refers is called "amount of substance, *n*. "

"However, practicing chemists prefer to talk about the number of moles. Take the advice of your instructor on whether or not to use the official term" **[Atkins 1999]**

[Leonard 2010/1] and [Leonard 2010/2] conclude:
"if Da = g mol^{-1}, then mol = g/Da, confirming Atkins's (and, presumably, biophysicists') concept of the mole as a pure number: the gram-to-dalton mass-unit ratio."

10

The way forward:

choose as unit (= a matter of convenience):
a discrete unit "1" on the atomic level:
- it follows that -for thinking on the macroscopic level -
an integer multiple of the discrete unit "1"
(e.g. 6.022 14X YZ • 10^{23})
comes as a simple logical consequence:
- an Avogadro number of entities, symbol N_{avo} i.e. a direct value of the quantity concerned, is designated a unit
[Price 2011/2] for large numbers [Cooper 2010]

thinking of matter by way of its property of "inertia"
and having the characteristic of being continuous
is thereby replaced by

thinking of matter by way of its property of "numerosity"
[Rocha-Filho 1990] [Rocha-Filho 2011] [De Bièvre 2007/1]
and having the characteristic of being discrete
(particulate, granular, quantized …)

10.2

Proposal for a definition of the mole …

The mole, symbol mol, is equal to 6.022 14X YZ •10^{23} identical and specified entities exactly; see also [Karol 2014/2]
Note: it follows that the number of entities is an integer

[… and for a definition of the kilogram:

the kilogram, symbol $\mathcal{K}$, is the mass of 6.022 14X YZ •10^{23} atoms of ^{12}C in their nuclear ground state, multiplied by 1000/12]
also see [Karol 2014/2]

both proposals are consistent with the IUPAC-CIAAW and IUPAC-ACD positions in 2009 [Brand 2014] resp 2012 [Hibbert 2014] for their use in practice and in teaching;
these proposals are widely made [Isaev 2013] [De Bièvre 2007/2]

they are also consistent with:
"*h* may be calculated from *m* (^{12}C), and, hence, fixing *h*, or fixing *m* (^{12}C), are almost equivalent definitions" [Mills 2011]

10.3

The numerical value of the Avogadro number comes from its direct measurement in the "Avogadro Si project"

and fulfills what has been called the "fundamental mole-concept compatibility condition": N_{Avo} = g / Da

see the slide on the measurement of the N_{avo} number as well as [Rocha 1990] [Price 2011/1] [Baranski 2012] [Hill 2012] [Johansson 2014] and
-especially clarifying- [Baranski 2014]

this condition is violated in the present CCU redefinition proposals [Leonard 2011/1] [Leonard 2011/2] [Baranski 2013]

10.4

This definition enables to take (an integer number) "1" as unit

- for small numbers of entities [Chyla 2012]
- to define a(n integer) multiple of "1" such as 6.022 14X YZ • 10^{23} entities exactly
- meets seven meaningful conditions for a definition of the mole, described by Chyla [Chyla 2012]
- it is explicitly mentioned under entry 1.10 Note 3 in [VIM 2008 / 2012]
- for working with (up to very) large number of entities

it is immediately understandable, teachable and helpful, conforming to desires expressed in the 8th and 9th SI brochures:

11

"because of the importance of a set of well defined and easily accessible units universally agreed for the multitude of measurements that support today's complex society, units should be chosen so that they are readily available to all, are constant throughout time and space, and are easy to realize with high accuracy" [SI 8 2006] sect 1.1, [SI 9 2014 section]

it is also fully consistent with Maxwell's well known statement:

"If, then we wish to obtain standards of length, time, and mass which shall be absolutely permanent, we must seek them not in the dimensions, or the motion, or the mass of our planet, but in the wavelength, the period of vibration, and the absolute mass of these imperishable and unalterable and perfectly similar molecules." [Maxwell J C 1870]

What is the proposal for a re-definition in the "New SI" ?

The proposal in the draft SI brochure, 9th edn [SI 9] is very complex: 11.2

"The mole, unit of amount of substance of a specified elementary entity, which may be an atom, molecule, ion, electron, any other particle or a specified group of such particles. ~~is such that the Avogadro constant is equal to exactly 6.022 141 79 ☒ 10^{23} per mole~~ Its magnitude is set by fixing the numerical value of the Avogadro constant to be exactly 6.022 141 29 x 10^{23} when it is expressed in the SI unit mol^{-1}.

Thus we have the exact relation $N_A = 6.022\ 141\ 29 \times 10^{23}\ mol^{-1}$.
Inverting this equation gives an exact expression for the mole in terms of the defining constant N_A:

$$mole = 6.022\ 141\ 29 \times 10^{23} / N_A$$

The effect of this definition is that the mole is the amount of substance of a system that contains 6.022 141 29 ☒ 10^{23} specified elementary entities"

the definition is built on the principle of fundamental constant-based units, rather than on constant-unit based units

the above version (without the deleted sentence and with the addition of the sentence in white, have not (yet ?) been submitted to either IUPAC nor CCQM.

12

The awareness in the chemical community for the problem of the re-definition of the mole, has now become considerable, as opposed to the lack of active interest during years, as the literature shows:

a number of critical papers about the "New SI" have been collected (see also a list of a number of literature references at the end of this presentation):

[ACQUAL 2011] Accred Qual Assur (16) (3) 117-174 (9 papers)

http://www.metrologybytes.net/documents2013.php

http://www.metrologybytes.net/opEds2014.php

Metrologia, in several issues over the last 10 years

Journal for Chemical Education (1992-2014):

Lectures and seminars by this author in more than 130 cities on the five continents (1998-2014)

A few quotations: 12.2

- "there is very little initiative for … a change from any of the communities of users of the mole." [Milton 2011] (meaning that chemists have ignored it)
- a study reveals that about 38.9 % of teachers (Spain) interpret amount of substance as a mass, and 44.4 % as a number of entities [Furio 2000]
- "… with only three [out of 28] of the educators articulating a conception that was consistent with the SI definition" [Fang 2014] [Strődmahl (1994]
- "… research has shown that the mole is one of the most perplexing concepts in the teaching and learning of chemistry" [Fang S C 2014]
- "… the way the mole is conceptualized in educational settings is inconsistent with the meaning of the mole expressed in the SI definition" [Fang S C 2014]

12.3

- 1971-2011: about 60 papers on the mole published in J Chem Educ [Fang S C 2014]
- " 'amount of substance' is mostly ignored in the chemical world" [Meinrath 2011]
- "a clear discrepancy exists between what is assumed as correct by the scientific community and the thinking of educators." [Furio 2002]
- "analysts need an Avogadro number of things" [Price G 2011/1]
- "… amount of substance is meaningless in all practical situations the chemist encounters;
  "chemists prefer to define the mole as Avogadro number without further discussion. That an alternative definition exists, is considered as a curiosity at best." [Meinrath 2011]
- "the scientific critique of the new SI by a number of writers and experts … has not been answered by the architects of the new SI and the BIPM. …correcting the deficiencies of the new SI units … will require the expenditure of much time and money, so it is better to make the necessary corrections before the new SI are adopted." [Hill 2013/2]

12.4
- the proposal for re-definition of the mole (as well as of other units) in the "New SI" are more difficult to teach although in section 1.1 of the 8th brochure [SI 8 2006], it is explicitly stated that "units should be chosen so that they are readily available to all, … and are easy to realize with high accuracy." [SI 8 2006]
- a review of ACS papers yields the following:
'amount of substance' is quoted 436 times,
'number of moles' is quoted 4 436 times [Karol 2014 /2]
"as far as meeting the CIPM goal of providing definitions that are understandable to students in all disciplines, the New SI fails miserably;
the pending proposal for redefinition of the SI base units should be withdrawn, and the open debate continued until the CCU and CIPM eliminate the confusion" [Hill 2012]
"the proposed New SI is poorly conceived, and should be withdrawn immediately" [Hill 2012]

13
The designers of the New SI themselves concede that key aspects of the proposed New SI are confusing. Coupled with the unanswered published scientific criticisms of the New SI, and the fundamental new scientific discoveries directly related to the SI, this certainly calls into question the wisdom of pressing for a complete restructuring of the SI at this time [Hill 2013/1]
the SI itself admits that
"… the Avogadro constant N_A, has the character of conversion factor to convert … the mole into the counting unit 1"
see pp 18 / 29 in [SI 9 2013] and [Johansson 2014]
"It is something of a paradox that such concepts as the quantity 'amount of substance' and its unit 'mole', so widely used by practicing chemists, are also the subjects of wide misunderstanding"
[Mills 2009]
we must investigate the reasons for such a paradox in the present discussions of the definition of the mole

14

OVERALL CONCLUSIONS & KEY QUESTIONS:

given that it is likely that (analytical) chemists e.g. IUPAC-CIAAW and IUPAC-ACD, will continue to use

- the dalton [Baranski 2013] [Atkins 2002] and
- their perception of the mole [Atkins 2002]

as they did so far, do we face the probability that they will (continue to work) with units which go "with the SI" rather than "in the SI"?

See also the recommendation in [Hill 2013/1]:
"… when *m* (^{12} C) and N_{Avo} are fixed, we have a single fixed value of *m* (^{12}C) and … a fixed value of the amu or dalton: Da = *m* (12 C)/12"

with a defined value of the Avogadro number N_{avo}, practicing chemists have all they need

14.2

The desirable qualities for a good invariant, should be available to anyone at any time, should be realizable as accurately as the best measurements require, and should preferably be as simple as possible to comprehend and to realize" [Mills 2011]

"As "12" and "dozen" are synonymous, Avogadro's number and one mole (mol) are synonymous
Conclusion: ban the use of the ambiguous and misguided expression "amount of substance" [Karol 2014/2]

"The SI was declared in 1960 as an 'evolving' and 'practical' system of units. 'Practical', however, seems to have often been interpreted as 'pragmatic', … with disregard for consistency and uniqueness. … The result is that the SI contains significant inconsistencies and contradictions, which detract from its definition, utility and usability." (Foster 2010]

In addition, "the SI Brochure and the well known ISO 80000 are inconsistent" and "the concept and definition of amount of substance and mole are problematic" [Foster 2010]

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THE CONSEQUENCES MUST NOW BE EXAMINED WITH THE HELP OF A FEW KEY QUESTIONS:

1. metrological traceability (see definition in entry in [VIM 2008 / 2012] of measurement results for relative atomic masses and counting can be validly established to “their” units (Da and unit 1)

2. what is now the task for a Consultative Committee which carries the confusing concept ‘amount of substance’ in its title (hence, in its task) and has never described it? [De Bièvre 2014]

3. is the mole not a unit that serves to count particles? [Furio 2000]

4. is amount of substance indeed a quantity invented for the unit mole? [Furio 2000] [Furio 2002] Mills 2009]

15.2

5. is amount of substance proportional to a number of entities? [Furio 2000] [SI 8 2006] [SI 9 2013] why is it then not simply a number of entities, the correct symbol of which is N ? The symbol N_A for a reciprocal number, is inconsistent with internationally accepted rules for symbols [IUPAC 1993] [IUPAC 2007]

6. is amount of substance a mass or a number of entities? [Furio 2000]

7. “… an ‘amount of substance’, which is merely a number of moles, is not a quantity, and certainly not a base quantity” [Emerson 2012]

8. “practicing chemists prefer to talk about the number of moles. Take the advice of your instructor on whether or not to use the official term” [Atkins 1999]; why is his question not resolved ?

9. “… a change in the definition of the mole may be seen as taking it … closer to the established approaches of physics and further from its ubiquitous implementation in chemical measurement” [Milton 2011]

that statement is probably correct and explains much of the confusion : we have been using two different moles since 1971 (!)

16

Are the "Laws of Terminology" respected ? [Karol 2014/2]:

- **1st law: definitions must be exact and understandable**
- **2nd law: definitions must be unambiguous and exception-free**
- **3rd law: the number of people who understand a definition approaches zero as the number of words used to satisfy the first and second laws of terminology approach infinity**

17

Finally:
The measurement of a number of entities has great similarity with the measurement of time i.e. with the duration of an event (time is measured by the duration of an event):

atomic scale:

one natural unit = the existence of one event (the duration of an electronic transition in the ^{133}Cs atom)	one entity (atom, molecule) = the existence of one entity the reality of one atom/molecule

macroscopic scale:

a defined multiple of one natural event: the duration of a large number of events: 9 192 631 770 events exactly	a defined multiple of one natural entity the collection/ensemble of a large number of entities: 6.22 14X YZ entities

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