Units and Accurate Measurements in Chemistry

R.I. Wielgosz (BIPM)
Outline

1. The mole in use today
2. Relative uncertainties in chemical standards and reference data
3. Amount of Substance
4. A short recent history of the mole
5. What we shouldn’t forget from 1971
6. Do we need the mole?
7. The Avogadro constant, molar mass of $^{12}\text{C}$ and invariants of nature
8. Is $^{12}\text{C}$ special?
9. The new proposed definition
10. Atomic mass, atomic weight and molar mass
11. Impact on ‘realizing’ the mole
12. What the publications say
13. A final look at uncertainties and definitions
The mole in use today: Clinical Chemistry

Clinical Chemistry:
Measurements of steroid hormone concentrations

Results expressed in units of nmol/L
The mole in use today: Atmospheric Monitoring

Air Quality

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Concentration</th>
<th>Averaging period</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ozone</td>
<td>60 nmol/mol</td>
<td>Maximum daily 8 hour mean</td>
</tr>
<tr>
<td>Sulphur dioxide (SO₂)</td>
<td>120 nmol/mol</td>
<td>1 hour</td>
</tr>
<tr>
<td></td>
<td>45 nmol/mol</td>
<td>24 hours</td>
</tr>
<tr>
<td>Nitrogen dioxide (NO₂)</td>
<td>100 nmol/mol</td>
<td>1 hour</td>
</tr>
<tr>
<td></td>
<td>20 nmol/mol</td>
<td>1 year</td>
</tr>
<tr>
<td>Carbon monoxide (CO)</td>
<td>8 µmol/mol</td>
<td>Maximum daily 8 hour mean</td>
</tr>
<tr>
<td>Benzene</td>
<td>1.5 nmol/mol</td>
<td>1 year</td>
</tr>
<tr>
<td>Fine particles (PM2.5)</td>
<td>25 µg/m³</td>
<td>1 year</td>
</tr>
<tr>
<td>PM10</td>
<td>50 µg/m³</td>
<td>24 hours</td>
</tr>
<tr>
<td></td>
<td>40 µg/m³</td>
<td>1 year</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>0.5 µg/m³</td>
<td>1 year</td>
</tr>
</tbody>
</table>

Greenhouse Gases

<table>
<thead>
<tr>
<th>GAS</th>
<th>Recent tropospheric concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide (CO₂)</td>
<td>392.6 µmol/mol</td>
</tr>
<tr>
<td>Methane (CH₄)</td>
<td>1874 nmol/mol</td>
</tr>
<tr>
<td>Nitrous oxide (N₂O)</td>
<td>324 nmol/mol</td>
</tr>
<tr>
<td>Tropospheric ozone (O₃)</td>
<td>34 nmol/mol</td>
</tr>
<tr>
<td>Halocarbons</td>
<td>(0.003 to 0.5) nmol/mol</td>
</tr>
</tbody>
</table>
## Molar quantities

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>molar gas constant</td>
<td>$R$</td>
<td>8.314 472(15) J K$^{-1}$ mol$^{-1}$</td>
</tr>
<tr>
<td>Molar volume of an ideal gas</td>
<td>$V_m$</td>
<td>22.412 996(39) dm$^3$ mol$^{-1}$</td>
</tr>
<tr>
<td>Standard partial molar enthalpy</td>
<td>$H_B^\circ$</td>
<td>J mol$^{-1}$</td>
</tr>
<tr>
<td>Standard partial molar entropy</td>
<td>$S_B^\circ$</td>
<td>J mol$^{-1}$ K$^{-1}$</td>
</tr>
</tbody>
</table>
Relative uncertainties in chemical standards and reference data

Relative Atomic Masses of Nuclides e.g. $A_r^{(28)Si}$

$N_A$ – kg in terms of $h$; or $M_u$ with redefinition of mole

MeP mole: $^{28}$Si sphere (new SI)

$N_A$ – present SI; kg realization new SI

Gravimetric preparation limitations

Isotopic AoS fractions (best measurement) [Standard atomic weights]

CCQM Key Comparisons $u(KCRV)/x(KCRV)$

GAS ANALYSIS
ELECTROCHEMICAL ANALYSIS
INORGANIC ANALYSIS
ORGANIC ANALYSIS
SURFACE ANALYSIS
BIOANALYSIS

Bureau International des Poids et Mesures
Amount of Substance


Amount of substance is proportional to the number of specified elementary entities considered. The proportionality factor is the same for all substances; its reciprocal is the Avogadro constant.

Milton and Mills (2009)

Amount of substance is a quantity that measures the size of an ensemble of entities. It is proportional to the number of specified entities and the constant of proportionality is the same for all substances. The substances may be atoms, molecules, ions, electrons, other particles, or specified groups of particles.

Simpler in equations than words to express:

‘A macroscopic measure of chemical amount which is proportional to the number of specified entities’

Other names for AoS have been proposed: Chemical amount, enplethy, ment... but none have led to popular use
Chemists and Physicists use different scales for atomic masses of the elements (‘Ordinary’ oxygen and $^{16}\text{O}$ respectively)

The mole adopted and seventh base unit of the SI (‘Chemistry brought into the SI’) $M^{(12}\text{C}) = 12 \text{ g/mol (exactly)}$

IUPAC and IUPAP agree on ‘unified scale’ of atomic masses $A_r^{(12}\text{C}) = 12 \text{ (exactly)}$ (also SI adopted in 1960)

I. Mills et al. paper on redefinition of SI base units (2006)

IUPAC (2009) comments on proposal and confirmed (2012); CCQM (2009) support of new definition proposal

CCQM (2011) Statement on further consultation

IUPAC (2013) Project of review of definitions started

Probable date for redefinitions

IUPAC (2012) Project of review of definitions started

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IUPAC (2009) comments on proposal and confirmed (2012); CCQM (2009) support of new definition proposal

The mole adopted and seventh base unit of the SI (‘Chemistry brought into the SI’) $M^{(12}\text{C}) = 12 \text{ g/mol (exactly)}$
A short history of the mole

The current definition:

1. The mole is the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon 12; its symbol is "mol".

2. When the mole is used, the elementary entities must be specified and may be atoms, molecules, ions, electrons, other particles, or specified groups of such particles.

   14th CGPM (1971, Resolution 3)

It follows that the molar mass of carbon 12 is exactly 12 grams per mole, \( M(^{12}\text{C}) = 12 \text{ g/mol} \).

In this definition, it is understood that unbound atoms of carbon 12, at rest and in their ground state, are referred to.

   CIPM (1980)
What we shouldn’t forget from 1971

From IUPAC and CCU documents:

1. Chemists expressed the need for a quantity which was defined as directly proportional to the number of entities in a sample of a substance.

2. It was preferable to adopt a convention with amount of substance having its own dimension. This convention was in wide use by Chemists and already recommended by IUPAC, IUPAP and ISO.

3. The wish for chemists to adopt the SI – but the need to incorporate a base unit for amount of substance into the SI to make this happen.
Do we need Amount of Substance and the mole?

Amount of substance has been assigned its own dimension, and is one of the seven base quantities in the received algebra of physical sciences

\( N_A, n, R, \text{mol} \) – could all be discarded from the equations of physical science – (move to entitic quantities) BUT it would not be very useful

e.g. Molar mass of \(^{28}\text{Si}\) is about \( \square \) g mol\(^{-1}\)

Entitic (nuclidic) mass of \(^{28}\text{Si}\) is about \( \square \) kg

Molar volume of \( \text{H}_2\text{O (l)} \) is about \( \square \) cm\(^3\) mol\(^{-1}\)

Molecular volume of \( \text{H}_2\text{O (l)} \) is about \( \square \) cm\(^3\)

Could amount of substance be treated as a number?
NO – would end up being very confusing as this would lead to dimensional departures from received algebra

M. McGlashan (1997)
Differing views:

‘The value of the Avogadro constant, \( N_A \), is a true constant of nature just like \( c \) and \( h \)’

‘The Avogadro constant is a fundamental constant of a lesser breed’

‘The Avogadro constant is nowhere provided by nature, we have to prepare this number using a balance’

\[
M(X) = N_A \, m(X)
\]
The Avogadro Constant

Macroscopic world

$M(^{12}\text{C})$ \hspace{1cm} A constant:

- Scientific understanding that the macroscopic world is composed of atoms

- A constant of proportionality which is the same for all substances

- Having chosen fixed point in the macroscopic world and the microscopic world, the constant is defined and applicable to all substances

- It has a unit and so cannot be called a number; it is a constant.

Microscopic/Atomistic world

$M(X) = N_A \cdot m(X)$
Is Carbon 12 special?

Used to fix conventions in two current definitions:

1. Relative atomic masses:

   Relative atomic mass of carbon 12, $A_r(^{12}\text{C})$, is exactly 12

   Atomic mass constant, $m_u = m_a(^{12}\text{C})/12$ (rel. uncertainty currently 12 parts in $10^9$)

2. Definition of the mole:

   Molar mass of carbon 12 is exactly 12 grams per mole, $M(^{12}\text{C}) = 12 \text{ g/mol}$

   Hence

   *Molar mass constant, $M_u$, equal to exactly $1 \text{ g mol}^{-1}$*

Non SI units accepted for use with the SI:

Unified atomic mass unit, $u (= m_a(^{12}\text{C})/12) = 1 \text{ Da}$

$= 1.660\,539\,040\, (20) \times 10^{-27} \text{ kg}$ (experimentally determined)
Is Carbon 12 special?

A note on Relative atomic masses:

Relative atomic mass of carbon 12, \( A_r(^{12}\text{C}) \), is exactly 12

Atomic mass constant, \( m_u = m_a(^{12}\text{C})/12 \) (rel. uncertainty currently 12 parts in \( 10^9 \))

1. Relative atomic masses \( A_r(X) \) are indeed relative
2. The uncertainties in their values are related to determining the ratio \( m_a(X)/m_a(^{12}\text{C}) \)
3. This allows the relative atomic masses of some nuclides to be known to parts in \( 10^{11} \)
4. Uncertainties in Relative Atomic Masses unaffected by any of the redefinitions

However:

1. Atomic masses \( m_a(X) \) and molar masses \( M(X) \) of nuclides and elements are subject to the same uncertainties arising from \( h \) and \( N_A \)
2. Redefinition of the kg reduces the relative uncertainty in \( m_u \) to 4.5 parts in \( 10^{10} \), with or without the proposed redefinition of the mole
The mole, symbol mol, is the SI 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; its magnitude is set by fixing the numerical value of the Avogadro constant to be equal to exactly $6.022\ 140\ 86 \times 10^{23}$ when it is expressed in the SI unit mol$^{-1}$.

This results in the exact relation $N_A = 6.022\ 140\ 86 \times 10^{23}$ mol$^{-1}$.

The effect of this definition is that the mole is the amount of substance of a system that contains exactly $6.022\ 140\ 86 \times 10^{23}$ specified elementary entities.
Evolution in measurement uncertainty of $N_A$

J. De Boer (DE INGENIEUR/JRG.82/NR.27/1970)

‘From the purely academic point of view units based on constants of physics appear to be an advantage’

‘From the metrology point of view there are objections due to the lower accuracy with which these constants are (were) known’

$N_A$ relative uncertainties:

- $9 \times 10^{-5}$ (1970)
- $1.2 \times 10^{-8}$ (2014)
Impact on: Atomic mass, Atomic Weight, Molar Mass

\[ m_a(\text{^12C})/12 = m_u = 1 \text{ u} \]

Atomic mass

Atomic mass constant

Atomic mass unit (Dalton)

\[ m_a(\text{^{12}C}) = 12 \text{ u} \]

No Change

\[ A_r(\text{^{12}C}) = 12 \]

No Change

Atomic mass constant Expressed in SI units

\[ m_u = 1.660 \ 539 \ 040 \ (20) \times 10^{-27} \text{ kg} \]

Relative uncertainty now is \(1.2 \times 10^{-8}\)

With redefinition of kg reduced to \(0.45 \times 10^{-9}\)
Impact on: Atomic mass, Atomic Weight, Molar Mass

\[ M_B = A_r(B)M_u \]

- Molar mass (B)
- Relative atomic mass (B)
- Molar mass constant

Current SI, \( M_u \) is exactly 1 g mol\(^{-1} \)

With redefinition, \( M_u \) is 1 g mol\(^{-1} \), but with same relative uncertainty as for \( m_u \)

**Current SI**

\( M^{(12)C} = 12 \text{ g/mol} \)

**With redefinitions**

\( M^{(12)C} = 12.000 000 000(5) \text{ g/mol} \)
### Impact on: Molar masses of mono-isotopic elements

<table>
<thead>
<tr>
<th>Element</th>
<th>Present rel unc. $(10^{-9})$</th>
<th>Rel unc. after revision $(10^{-9})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>330</td>
<td>330</td>
</tr>
<tr>
<td>F</td>
<td>26</td>
<td>26</td>
</tr>
<tr>
<td>Al</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Na</td>
<td>0.87</td>
<td>1.32</td>
</tr>
<tr>
<td>P</td>
<td>65</td>
<td>65</td>
</tr>
<tr>
<td>Cs</td>
<td>1.50</td>
<td>1.8</td>
</tr>
</tbody>
</table>

*assuming an additional uncertainty of 1 part in $10^9$

Molar masses of non-monoisotopic elements are dominated by uncertainty in measured isotopic abundance

$$A_r(E) = \sum [x(iE) \times A_r(iE)]$$
Impact on: Realizing the mole

Relative Uncertainties

- Buoyancy corrected weighing (10’s of mg)
- Parts in $10^3$
- Parts in $10^4$
- Parts in $10^5$
- Parts in $10^9$

IUPAC tables of atomic weights

$$A_r^{(E)} = \sum \frac{x(iE)}{P} \times A_{r}^{(iE)}$$

Preparation of Primary Organic Calibrator material (Valine)

Conventional atomic weight values (2011)
IUPAC (2009) and confirmed in 2012:

Supports redefinition of the mole

With the following suggestions:

1. The greatest effort should be made to change the name of the ISQ base quantity ‘amount of substance’ at the same time that a new definition of the mole is approved.

2. A note should accompany the new definition to explain that the molar mass of $^{12}$C will be an experimental quantity with a relative measurement uncertainty of about $1.4 \times 10^{-9}$ ($0.45 \times 10^{-9}$ in 2015).
Further IUPAC activities

A critical review of the proposed definitions of fundamental chemical quantities and their impact on chemical communities

Project No.: 2013-048-1-100
Start date: 2013-12-01

In the end of December of 2013, IUPAC approved a project proposal which aims to critically review the definitions for the quantity amount of substance and its SI unit, mole. At the present meeting, the Task Group focused mainly on the scientific and technical aspects as well as on the reasons of the current and the proposed definitions of the mole.

REMIT
This project aims to achieve internal IUPAC consensus on the definition of the mole. The outcome of this project is an IUPAC Technical Report which may or may not change the official IUPAC position on the mole which has been ratified by the IUPAC Council in 2011

## What the publications say

<table>
<thead>
<tr>
<th>Basic views expressed</th>
<th>Publication(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(3) Concede the utility to the scientific community and to electrical metrology of defining the kilogram in terms of $h$, but see no need to redefine the mole</td>
<td>H. Andres (2009), Y. Jeannin (2010), G. Meinrath (2011), P.G. Nelson (2013-CCQM),</td>
</tr>
</tbody>
</table>
A closer look at definitions and uncertainties

<table>
<thead>
<tr>
<th></th>
<th>$h$</th>
<th>$M_u = M^{(12)C}/12$</th>
<th>$N_A$</th>
<th>$1 \text{ Da} = m^{(12)C}/12$</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>0</td>
<td>12</td>
<td>12</td>
<td></td>
<td>Present SI</td>
</tr>
<tr>
<td>0</td>
<td>0.45</td>
<td>0</td>
<td>0.45</td>
<td></td>
<td>Proposed New SI</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0.45</td>
<td>0.45</td>
<td>New kg def. and keep present mole def.</td>
<td></td>
</tr>
<tr>
<td>0.45</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>Define kg wrt dalton, define value of $N_A$</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>overdetermined...</td>
<td></td>
</tr>
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relative standard uncertainties in parts per billion (parts in $10^9$)
## A closer look at definitions and uncertainties

<table>
<thead>
<tr>
<th>$M_u = M(^{12}C)/12$</th>
<th>$N_A$</th>
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<tr>
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<tr>
<td>0</td>
<td>0.45</td>
<td>New kg definition and keep present mole definition</td>
</tr>
</tbody>
</table>

### Rydberg Energy Relation

\[
\frac{h}{m(^{12}C)/12} = \alpha^2 \frac{A_r(e)}{R_\infty} \frac{c}{2} = \frac{N_A h}{M(^{12}C)/12}
\]

\[
\frac{M(^{12}C)}{m(^{12}C)} = N_A
\]

Based on modern formulation of the Bohr model for the hydrogen atom.

Relative standard uncertainties in parts per billion (parts in $10^9$)
## Summary and consequences

### Redefinition, $N_A$ fixed

1. $N_A$ fixed numerical value
2. Conceptually easier to understand
3. No need to specify energetic state of entities
4. No impact on Relative Atomic Masses
5. No impact on practical chemical measurements
6. Realization of the mole with $^{28}\text{Si}$ sphere with relative standard uncertainty $2 \times 10^{-8}$
7. $M_u$ may no longer equal exactly 1 g mol$^{-1}$ (within parts in $10^{10}$)

**PREFERRED BY CCQM (2009)**

### Current definition (with $h$ fixed)

1. $M^{(12}\text{C})$ fixed numerical value
2. Familiarity with definition
3. Energetic state of entities needs to be specified (effect of parts in $10^{10}$)
4. No impact on Relative Atomic Masses
5. No impact on practical chemical measurements
6. Realization of the mole with $^{28}\text{Si}$ sphere: uncertainty negligibly larger than $2 \times 10^{-8}$
7. $M_u$ equal to exactly 1 g mol$^{-1}$ ($N_A$ with uncertainty of parts in $10^{10}$)