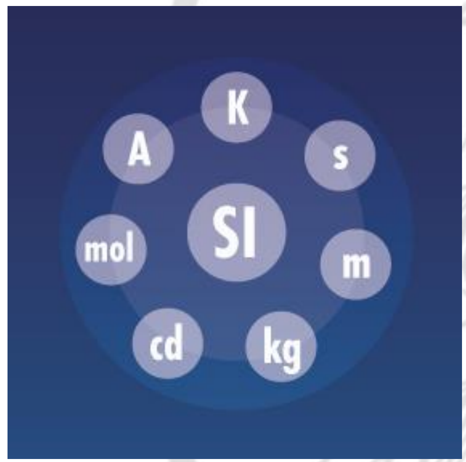
Units and Accurate Measurements in Chemistry



R.I. Wielgosz (BIPM)

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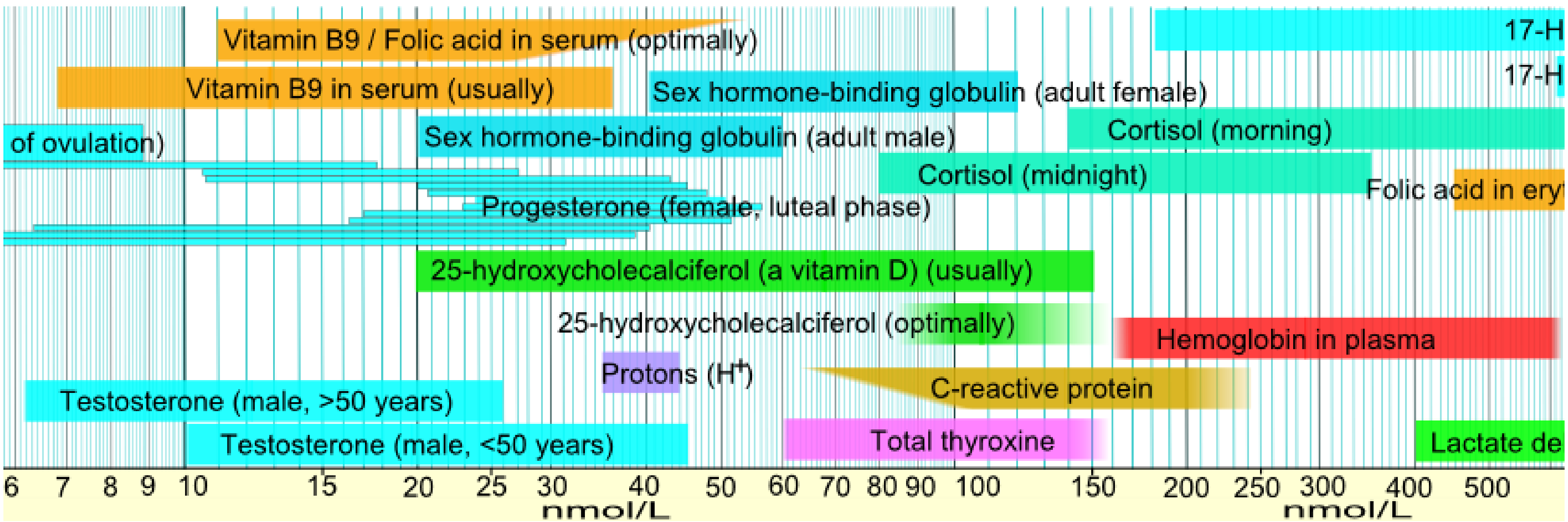
Outline

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}C and invariants of nature
8. Is ^{12}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

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The mole in use today: Atmospheric Monitoring

Air Quality

Greenhouse Gases

Pollutant	***Concentration***	***Averaging period***
Ozone	60 nmol/mol	Maximum daily 8 hour mean
Sulphur dioxide (SO_2)	120 nmol/mol	1 hour
	45 nmol/mol	24 hours
Nitrogen dioxide (NO_2)	100 nmol/mol	1 hour
	20 nmol/mol	1 year
Carbon monoxide (CO)	8 µmol/mol	Maximum daily 8 hour mean
Benzene	1.5 nmol/mol	1 year
Fine particles (PM2.5)	25 µg/m^3	1 year
PM10	50 µg/m^3	24 hours
	40 µg/m^3	1 year
Lead (Pb)	0.5 µg/m^3	1 year

GAS	**Recent tropospheric concentration**
Carbon dioxide (CO_2)	392.6 µmol/mol
Methane (CH_4)	1874 nmol/mol
Nitrous oxide (N_2O)	324 nmol/mol
Tropospheric ozone (O_3)	34 nmol/mol
Halocarbons	(0.003 to 0.5) nmol/mol

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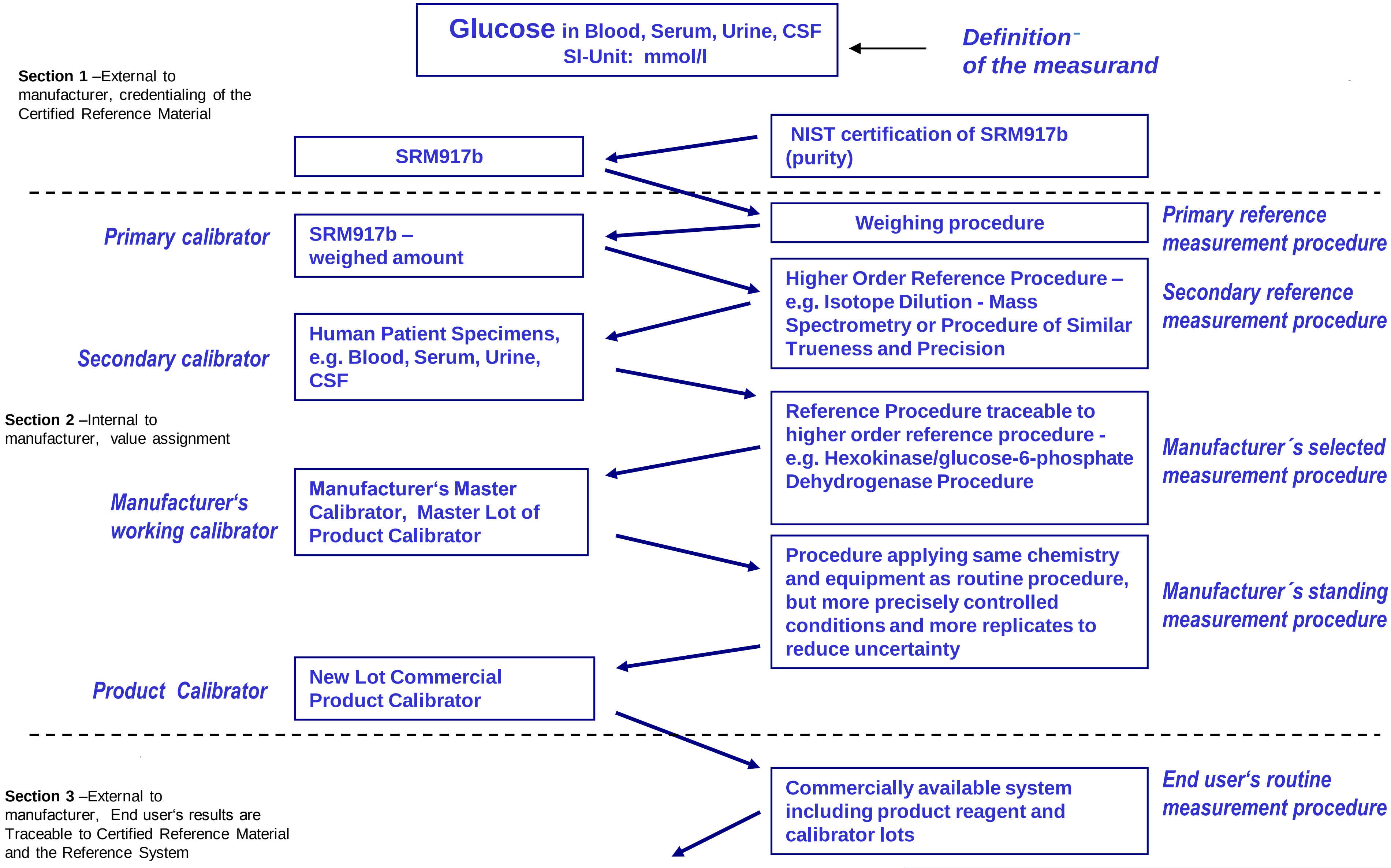
The mole in use today: Thermodynamic Quantities

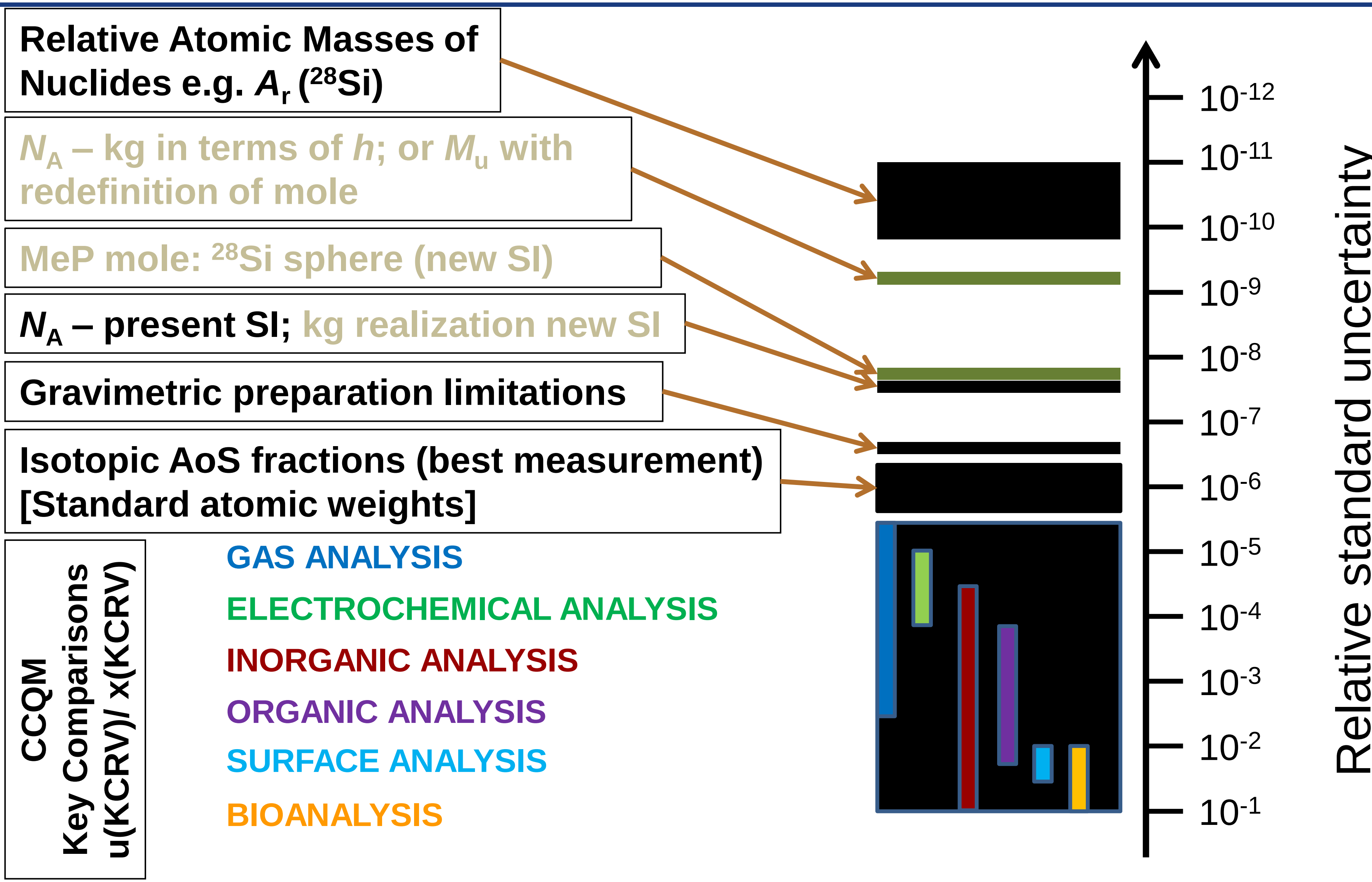
Molar quantities

Quantity	Symbol	Value
molar gas constant	R	8.314 472(15) J K^{-1} mol^{-1}
Molar volume of an ideal gas (p = 101.325 kPa, t = 0 °C)	V_m	22.412 996(39) dm^3 mol^{-1}
Standard partial molar enthalpy	$H_B°$	J mol^{-1}
Standard partial molar entropy	$S_B°$	J mol^{-1} K^{-1}

SI traceable chemical measurement



Relative uncertainties in chemical standards and reference data



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Amount of Substance

IUPAC Green Book 3rd Edition, 2007

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)

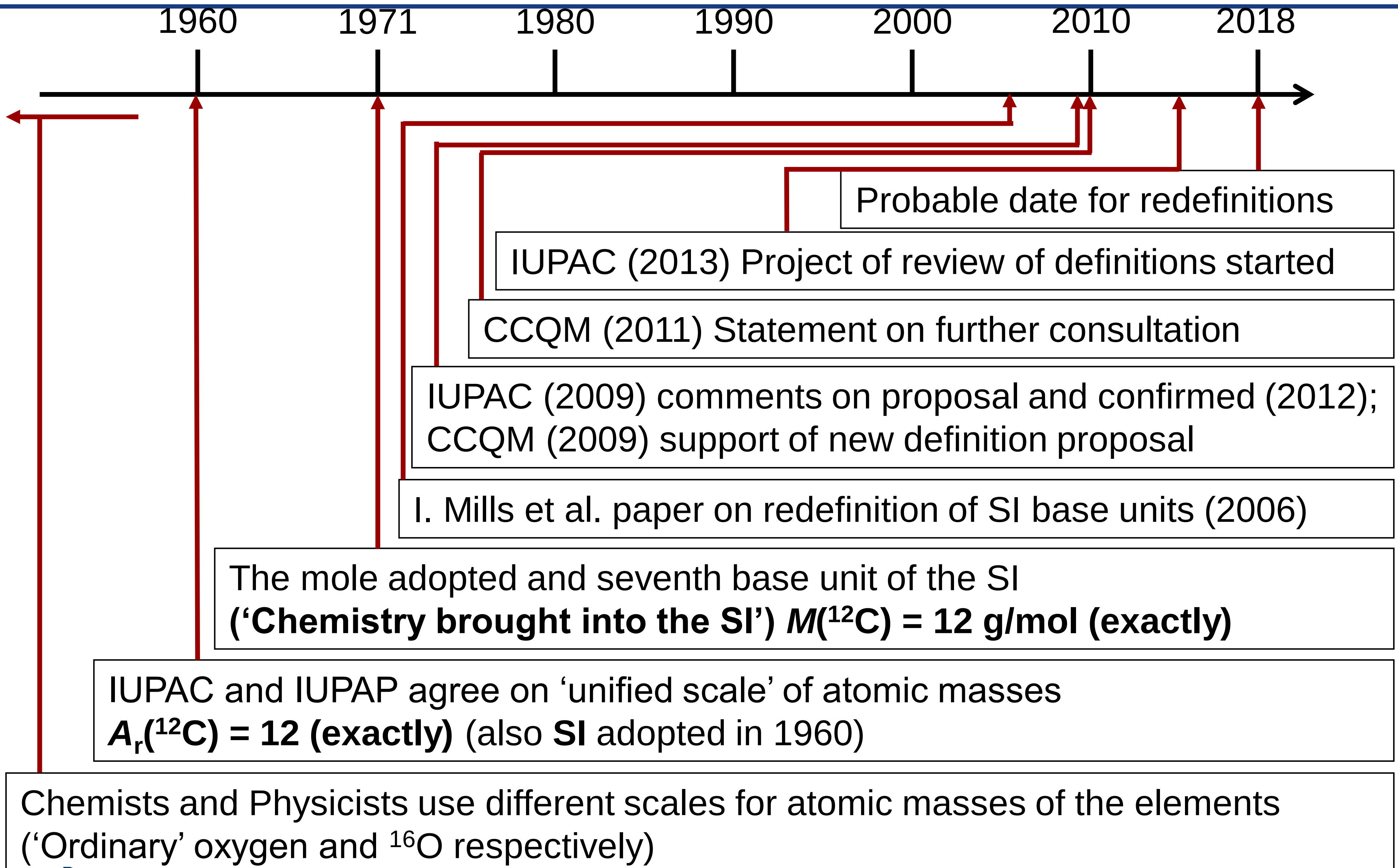
Amount of substance is a quantity that measures the size of an ensemble of entities. It is proportional to the number of specified entities and the constant of proportionality is the same for all substances. The substances may be atoms, molecules, ions, electrons, other particles, or specified groups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

A short recent 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, $M(^{12}C) = 12$ 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*, 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}Si is about g mol^{-1}**

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

Molar volume of H_2O (l) is about cm^3 mol^{-1}

Molecular volume of H_2O (l) is about 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)

The Avogadro Constant

Macroscopic world

$M(^{12}\mathrm{C})$

↕ N_A

$m(^{12}\mathrm{C})$

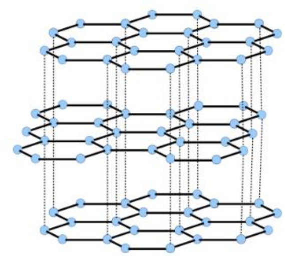
Microscopic/Atomistic world

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'



$$M(\mathrm{X}) = N_A\, m(\mathrm{X})$$

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The Avogadro Constant

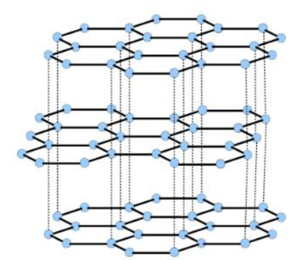
Macroscopic world

$M(^{12}\text{C})$ **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.**

N_A

$m(^{12}\text{C})$



$$M(X) = N_A\, m(X)$$

Microscopic/Atomistic world

Is Carbon 12 special?

Used to fix conventions in two current definitions:

1. Relative atomic masses:

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

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

2. Definition of the mole:

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

Hence

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

Non SI units accepted for use with the SI:

unified atomic mass unit, u (= $m_a(^{12}C)/12$) = 1 Da
= 1.660 539 040 (20) x 10^{-27} kg (experimentally determined)

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Is Carbon 12 special?

A note on Relative atomic masses:

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

Atomic mass constant, $m_u = m_a(^{12}C)/12$ (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 $m_a(X)/m_a(^{12}C)$**
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 new proposed defin

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.

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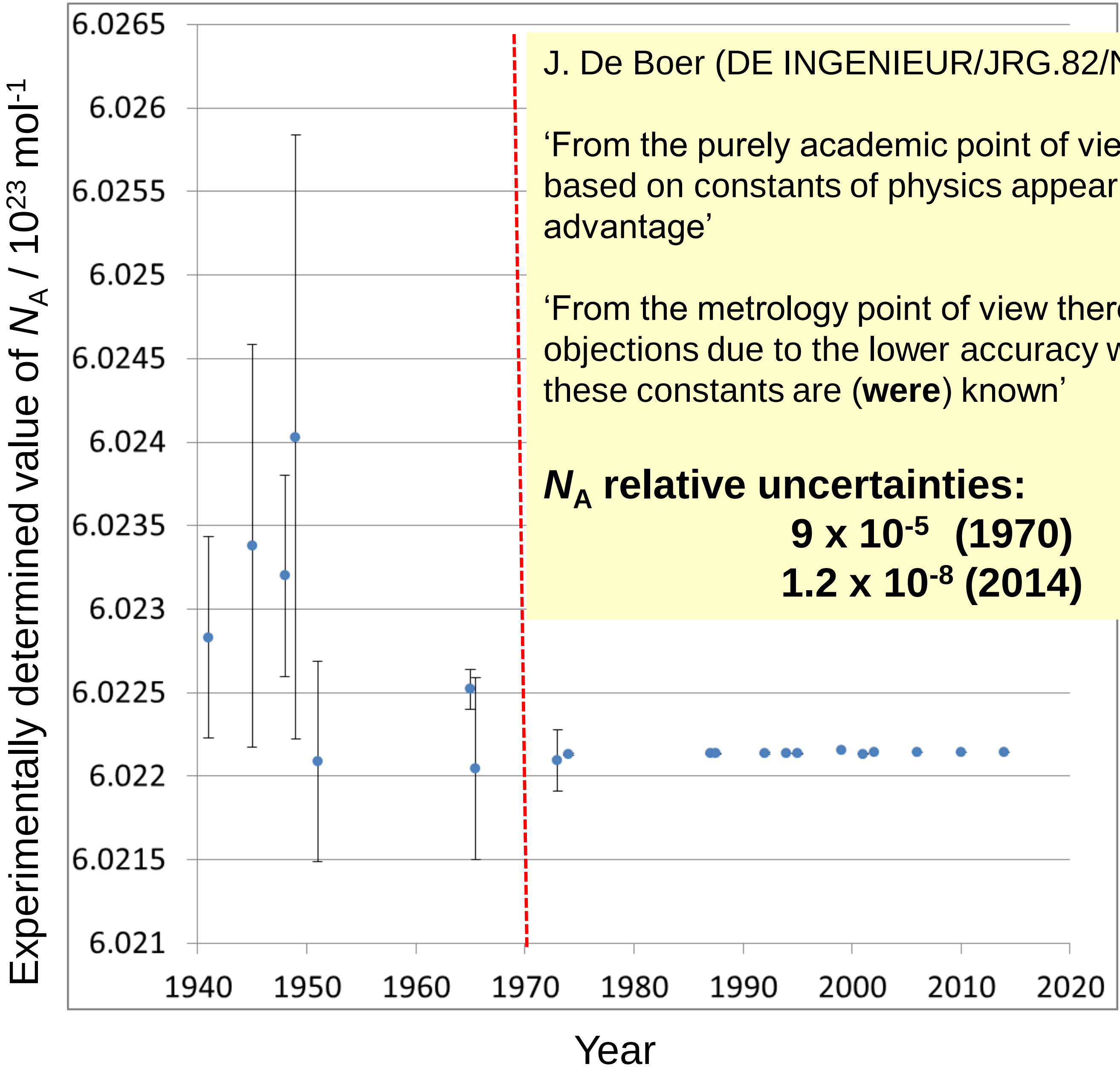
Evolution in measurement uncertainty of N_A



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:

9×10^{-5} (1970)

1.2×10^{-8} (2014)

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Impact on: Atomic mass, Atomic Weight, Molar Mass

$$m_a(^{12}C)/12 = m_u = 1\ u$$

Atomic mass — **Atomic mass constant** — **Atomic mass unit (Dalton)**

$$m_a(^{12}C) = 12\ u$$

No Change

Atomic weight (Relative Atomic Mass)

$$A_r(^{12}C) = 12$$

No Change

Atomic mass constant Expressed in SI units

m_u = 1.660 539 040 (20) x 10^{-27} kg

Relative uncertainty now is 1.2 x10^{-8}
With redefinition of kg reduced to 0.45 x 10^{-9}

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Impact on: Atomic mass, Atomic Weight, Molar Mass

$$M_\mathrm{B} = A_\mathrm{r}(\mathrm{B})M_\mathrm{u}$$

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

$$M_\mathrm{u} = m_\mathrm{u}N_\mathrm{A}$$

Current SI, M_u is exactly 1 gmol^{-1}

With redefinition, M_u is 1 gmol^{-1}, but with same relative uncertainty as for m_u

Current SI	**With redefinitions**
$M(^{12}\mathrm{C})$ = 12 g/mol	**$M(^{12}\mathrm{C})$ = 12.000 000 000(5) g/mol**

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Impact on: Molar masses of mono-isotopic elements

Element	Present rel unc. /(10^{-9})	Rel unc. after revision*/(10^{-9})
Be	330	330
F	26	26
Al	30	30
Na	0.87	1.32
P	65	65
Cs	1.50	1.8

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

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

$$A_r(\mathrm{E})_P = \sum [x(i\mathrm{E})_P \times A_r(i\mathrm{E})]$$

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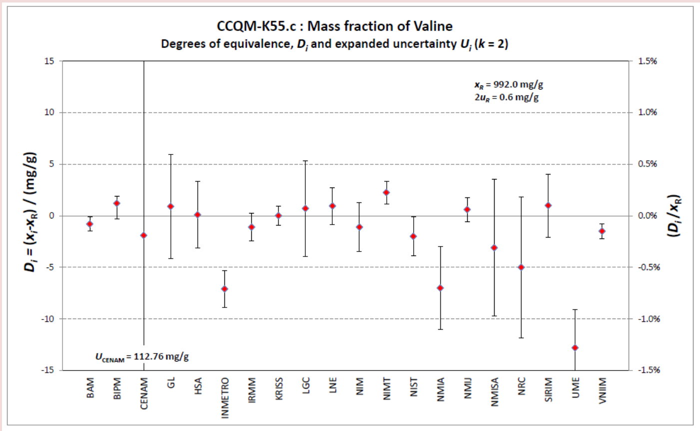
Impact on: Realizing the mole



Relative Uncertainties

Buoyancy corrected weighing (10's of mg)

Parts in 10^3

Parts in 10^4

$$n = \frac{N}{N_A} = \frac{w(X)m}{A_r(X)N_A m_u} = \frac{w(X)m}{A_r(X)M_u}$$

Parts in 10^5

Parts in 10^9

Conventional atomic weight values (2011)

IUPAC tables of atomic weights

$$A_r(E)_P = \sum [x(iE)_P \times A_r(iE)]$$

Preparation of Primary Organic Calibrator material (Valine)

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Comments from IUPAC (2009)

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 1.4×10^{-9} (*0.45 x* 10^{-9} *in 2015*)

Further IUPAC activities

IUPAC Project (2013-2015):

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

http://www.iupac.org/fileadmin/user_upload/projects/2013-048-1-100_2014-July-meeting-minutes-final2.pdf

What the publications say

Basic views expressed	Publication(s)
(1) Establishment of current definition of the mole	M. McGlashan (1994,1997), J. Lorimer (2010)
(2) Support the proposed redefinitions of both the mole and the kilogram	Milton and Mills (2009, 2009), I.M. Mills(2010), P. Atkins(2011), M. Milton(2013), R.S. Davis and M. Milton(2014),
(3) Concede the utility to the scientific community and to electrical metrology of redefining the kilogram in terms of *h*, but see no need to redefine the mole	H. Andres(2009), Y. Jeannin (2010), G. Meinrath (2011), P.G. Nelson (2013-CCQM),
(4) Argue for rejecting the proposed redefinition of the kilogram. Prefer kilogram defined in terms of the mass of a carbon-12 atom and the definition of the mole to follow from this.	B.P. Leonard(2010, 2012), T.P. Hill et al(2011), IUPAC CIAAW (2011), I. Johansson(2013-CCQM),
(5) Express discontent with the mole, the term “amount of substance” or the SI	I. Johansson(2011), B.P. Leonard(2013-CCQM (2)), M.P. Forester(2013), P. De Bievre(2011)

A closer look at definitions and uncertainties

h	$M_u = M(^{12}C)/12$	N_A	$1\ Da = m(^{12}C)/12$	Comments
12	**0**	**12**	**12**	**Present SI**
0	**0.45**	**0**	**0.45**	**Proposed New SI**
0	**0**	**0.45**	**0.45**	**New kg def.** and keep **present mole def.**
0.45	**0**	**0**	**0**	**Define kg wrt dalton, define value of N_A**
0	**0**	**0**	**0**	overdetermined…

relative standard uncertainties in parts per billion (parts in 10^9)

A closer look at definitions and uncertainties

$M_u = M(^{12}C)/12$	N_A	Comments
0.45	**0**	**Proposed New SI**
0	**0.45**	**New kg definition** and keep **present mole definition**

Rydberg Energy Relation

$$\frac{h}{m\left(^{12}\mathrm{C}\right)/12} = \alpha^2 \frac{A_r(\mathrm{e})}{R_\infty}\frac{c}{2} = \frac{N_A h}{M\left(^{12}\mathrm{C}\right)/12}$$

$$\frac{M\left(^{12}\mathrm{C}\right)}{m\left(^{12}\mathrm{C}\right)} = N_A$$

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

relative standard uncertainties in parts per billion (parts in 10^9)

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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}Si sphere with relative standard uncertainty 2 x 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. $M(^{12}C)$ 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}Si sphere: uncertainty negligibly larger than 2 x 10^{-8}
7. M_u equal to exactly 1 g mol^{-1} (N_A with uncertainty of parts in 10^{10})