On the redefinition of the mole

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Measuring mass and mass differences:

techniques change;
precision and accuracy improve

Unit of mass (kilogram)

This international prototype, made of platinum-iridium, is kept at the BIPM under conditions specified by the 1st CGPM in 1889

(Photograph courtesy of © BIPM)
(http://physics.nist.gov/cuu/Units/kilogram2.html)

CCQM Workshop 4/2014
“The redefinition and realization of the Mole”

The Mole is fundamental to Chemistry

(quantitative, historical* and actual)

$$\underline{2}\ H_2 + \underline{1}\ C \rightarrow \underline{1}\ CH_4$$

MICROSCOPIC: The reaction of two *molecules* hydrogen gas and one *atom* carbon combine to yield one *molecule* of methane. (Remember: Ostwald derived "Mol" from "Molekül", 1894)*

MACROSCOPIC: The reaction of two *parts* hydrogen gas and one *part* carbon combine to yield one *part* methane (with "part" to be defined via weighing (for mass) or measuring (for pressure and volume))

→ 1 mol = an agreed-upon number of entities (counts)

HOWEVER: In both cases, we will always need to ensure that the single particle carbon needs to meet its two molecules of hydrogen, there is no 'sum' reaction. Hence, the microscopic statement is fundamental. It describes what happens chemically. The macroscopic statement formulates what the chemist needs to provide for the reaction to happen.

* The name *mole* is an 1897 translation of the German unit *Mol*, coined by the chemist Wilhelm Ostwald in 1894 from the German word *Molekül* (molecule). However, the related concept of equivalent mass had been in use at least a century earlier. (Wikipedia)

Definitions of the mole:

current SI

"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.."

Hence: 1 mol = N_A number of ^{12}C atoms in 0.012 kg ^{12}C carbon

SI Brochure, 8th ed., BIPM (2006), p 115

Definitions of the mole:

New SI

"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 6.022 141 29 × 10^{23} when it is expressed in the unit mol^{-1}."

$$\text{mol} = \frac{6.022\,141\,29 \times 10^{23}}{N_\text{A}}$$

Hence: 1 mol = N_A number of entities (counts); 'mol' is a dimensionless unit

SI Brochure, 9th ed, Draft chapter 2 (Dec 16, 2013)

N_A: Visualizations of the mole:

1 mol = N_A number of (countable) entities

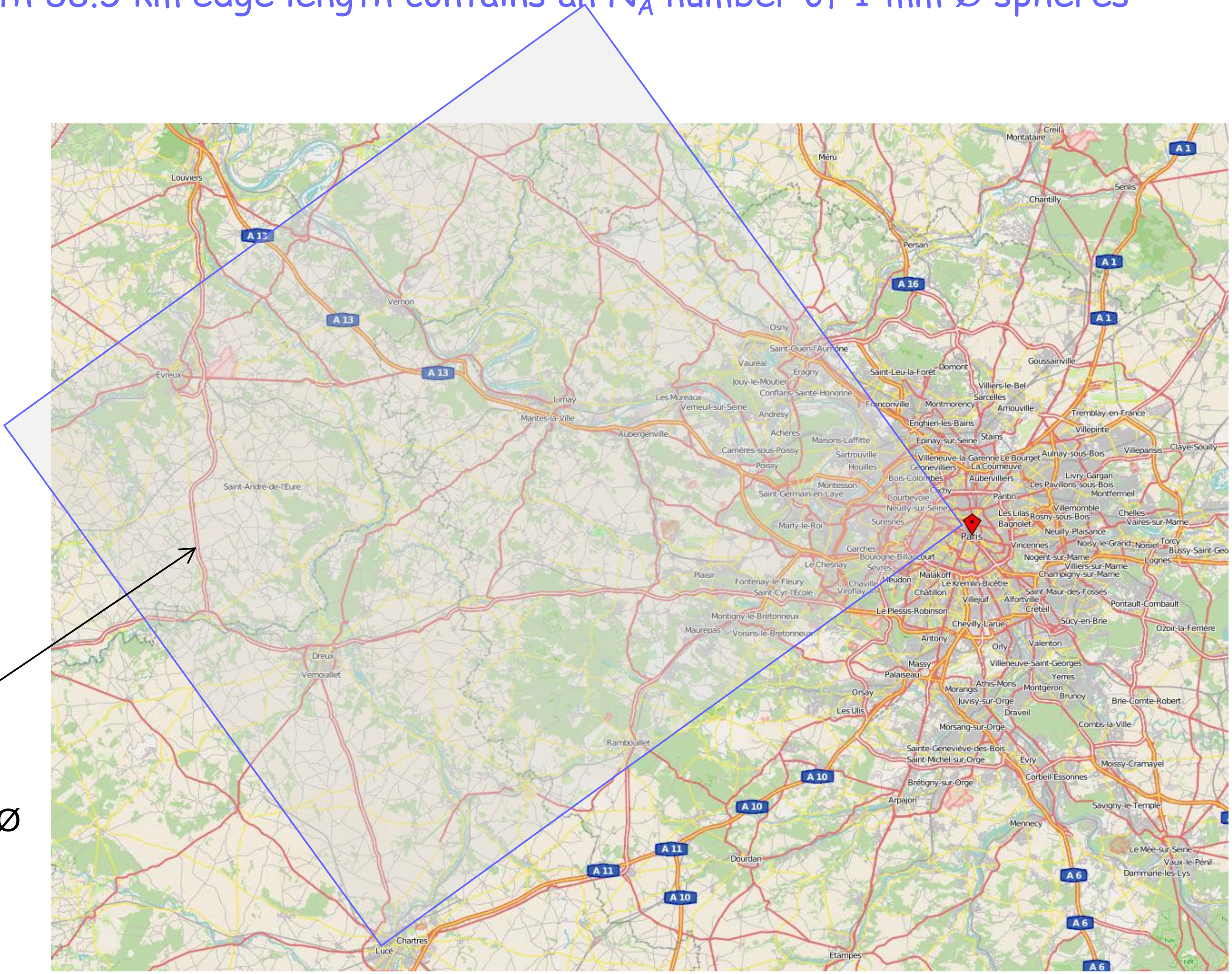
e.g. 6.022 141 29 x 10^{23} atoms of ^{12}C
6 x 10^{23} electrons, positrons
6 x 10^{23} quarks
6 x 10^{23} photons (?...probably ok)
6 x 10^{23} neutrinos (?...probably ok)
6 x 10^{23} Higgs-bosons (?)

6 x 10^{23} glass spheres of 1 mm diameter (*)

(*): Not really an elementary entity, but easy to visualize:

A cube with 88.5 km edge length contains an N_A number of such spheres

6×10^{23} is a pretty big number;
A cube with 88.5 km edge length contains an N_A number of 1-mm Ø spheres



Area holds 7.13×10^{15} spheres of 1 mm Ø

CODATA 2010

Invariant (true) constants:

Independent of any thinkable measurement system, we consider the following quantities to be constants of nature:

- Speed of light in vacuum (c = 299 792 458 m/s)
- Planck's constant (h = 6.62606957(29*) × 10^{-34} kg m^2/s)
- Elementary charge (e = 1.602176565(35) × 10^{-19} C)
- Atomic mass unit 1/12 m(^{12}C) (u = 1.660538921(73) × 10^{-27} kg)
- Microscopic scale masses like those of the electron, the proton, the neutron or the isotopes.
- And more like the fine structure constant α, the Rydberg constant R_∞, the Boltzman constant…

* Uncertainties arise from the kg and N_A

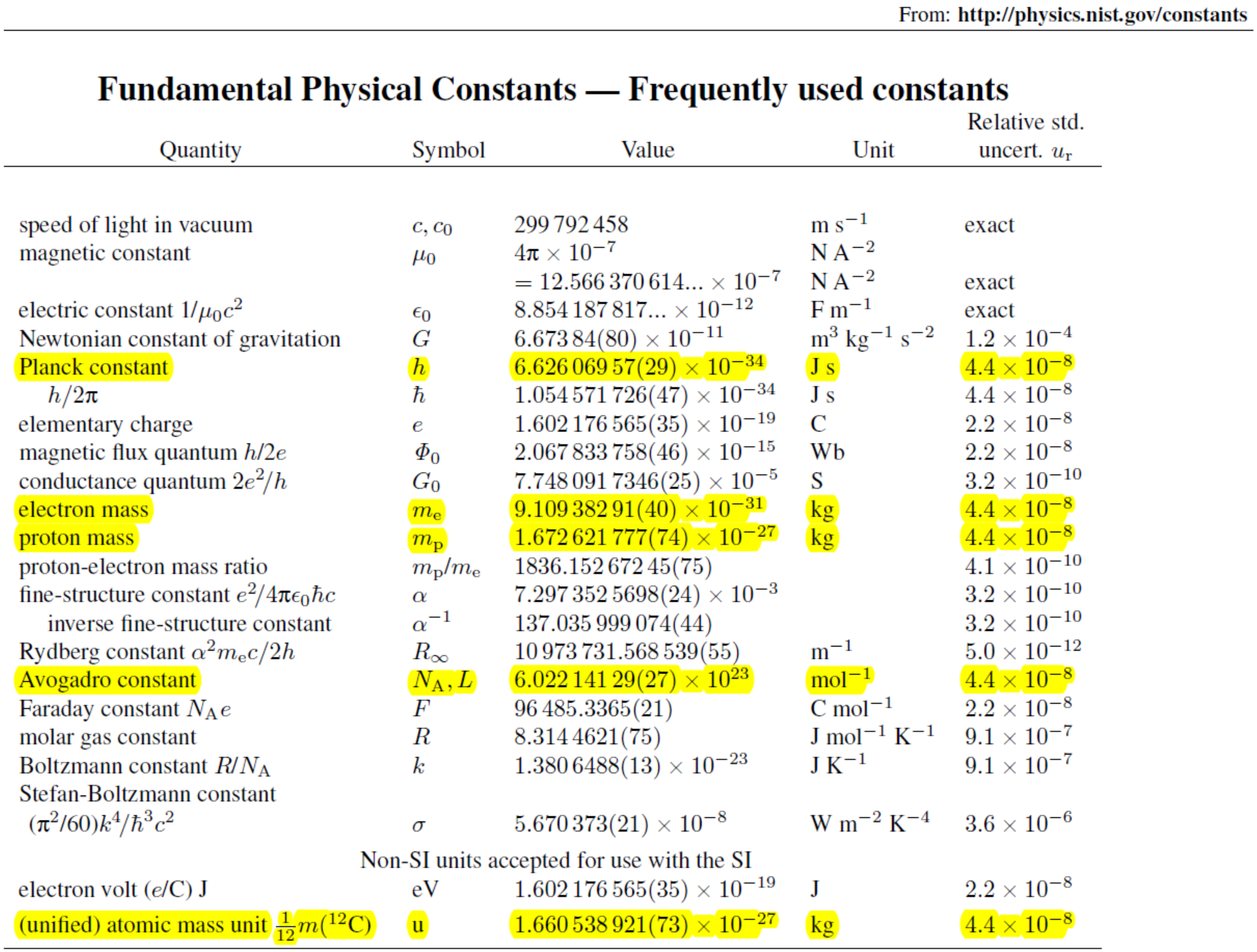
Non-invariant quantities:

Some quantities can not be considered invariant in nature:

- Second (originating from historic time concepts; fixed by a frequency difference in the ^{133}Cs spectrum)
- Meter (originating from the meter-bar at BIPM; fixed by c)
- Kilogram (defined through the artifact $\mathfrak{K}$; to be fixed by the new SI)
- Avogadro's number $(6.02214\ldots)\times 10^{23}$; tied to the kg, to be fixed by the new SI)
- Molar gas constant R … and many more …

Fundamental quantities with large uncertainties:

CODATA 2010



From: **http://physics.nist.gov/constants**

Fundamental Physical Constants — Frequently used constants

Quantity	Symbol	Value	Unit	Relative std. uncert. u_r
speed of light in vacuum	c, c_0	299 792 458	$\mathrm{m\ s^{-1}}$	exact
magnetic constant	μ_0	$4\pi \times 10^{-7}$	$\mathrm{N\ A^{-2}}$	
		$= 12.566\,370\,614... \times 10^{-7}$	$\mathrm{N\ A^{-2}}$	exact
electric constant $1/\mu_0 c^2$	ϵ_0	$8.854\,187\,817... \times 10^{-12}$	$\mathrm{F\ m^{-1}}$	exact
Newtonian constant of gravitation	G	$6.673\,84(80) \times 10^{-11}$	$\mathrm{m^3\ kg^{-1}\ s^{-2}}$	1.2×10^{-4}
Planck constant	h	$6.626\,069\,57(29) \times 10^{-34}$	J s	4.4×10^{-8}
$h/2\pi$	$\hbar$	$1.054\,571\,726(47) \times 10^{-34}$	J s	4.4×10^{-8}
elementary charge	e	$1.602\,176\,565(35) \times 10^{-19}$	C	2.2×10^{-8}
magnetic flux quantum $h/2e$	Φ_0	$2.067\,833\,758(46) \times 10^{-15}$	Wb	2.2×10^{-8}
conductance quantum $2e^2/h$	G_0	$7.748\,091\,7346(25) \times 10^{-5}$	S	3.2×10^{-10}
electron mass	m_e	$9.109\,382\,91(40) \times 10^{-31}$	kg	4.4×10^{-8}
proton mass	m_p	$1.672\,621\,777(74) \times 10^{-27}$	kg	4.4×10^{-8}
proton-electron mass ratio	m_p/m_e	$1836.152\,672\,45(75)$		4.1×10^{-10}
fine-structure constant $e^2/4\pi\epsilon_0\hbar c$	α	$7.297\,352\,5698(24) \times 10^{-3}$		3.2×10^{-10}
inverse fine-structure constant	α^{-1}	$137.035\,999\,074(44)$		3.2×10^{-10}
Rydberg constant $\alpha^2 m_e c/2h$	R_∞	$10\,973\,731.568\,539(55)$	$\mathrm{m^{-1}}$	5.0×10^{-12}
Avogadro constant	N_A, L	$6.022\,141\,29(27) \times 10^{23}$	$\mathrm{mol^{-1}}$	4.4×10^{-8}
Faraday constant $N_A e$	F	$96\,485.3365(21)$	$\mathrm{C\ mol^{-1}}$	2.2×10^{-8}
molar gas constant	R	$8.314\,4621(75)$	$\mathrm{J\ mol^{-1}\ K^{-1}}$	9.1×10^{-7}
Boltzmann constant R/N_A	k	$1.380\,6488(13) \times 10^{-23}$	$\mathrm{J\ K^{-1}}$	9.1×10^{-7}
Stefan-Boltzmann constant $(\pi^2/60)k^4/\hbar^3 c^2$	σ	$5.670\,373(21) \times 10^{-8}$	$\mathrm{W\ m^{-2}\ K^{-4}}$	3.6×10^{-6}
		Non-SI units accepted for use with the SI		
electron volt (e/C) J	eV	$1.602\,176\,565(35) \times 10^{-19}$	J	2.2×10^{-8}
(unified) atomic mass unit $\frac{1}{12}m(^{12}\mathrm{C})$	u	$1.660\,538\,921(73) \times 10^{-27}$	kg	4.4×10^{-8}

CODATA 2010

Uncertainties of the electron mass:

CODATA 2010

Electron, e^-

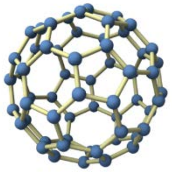
electron mass	m_e	$9.109\,382\,91(40) \times 10^{-31}$	kg	4.4×10^{-8}
		$5.485\,799\,0946(22) \times 10^{-4}$	u	4.0×10^{-10}
energy equivalent	$m_e c^2$	$8.187\,105\,06(36) \times 10^{-14}$	J	4.4×10^{-8}
		$0.510\,998\,928(11)$	MeV	2.2×10^{-8}

CODATA 2010

Fundamental quantities with small uncertainties:

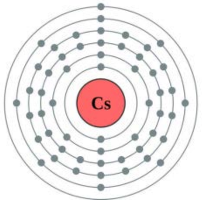
Quantity	Symbol	Value	Unit	Relative std. uncert. u_r
Faraday constant[6] $N_A e$	F	$96\,485.3365(21)$	$\mathrm{C\ mol^{-1}}$	2.2×10^{-8}
molar Planck constant	$N_A h$	$3.990\,312\,7176(28) \times 10^{-10}$	$\mathrm{J\ s\ mol^{-1}}$	7.0×10^{-10}
	$N_A hc$	$0.119\,626\,565\,779(84)$	$\mathrm{J\ m\ mol^{-1}}$	7.0×10^{-10}
quantum of circulation	$h/2m_e$	$3.636\,947\,5520(24) \times 10^{-4}$	$\mathrm{m^2\ s^{-1}}$	6.5×10^{-10}
	h/m_e	$7.273\,895\,1040(47) \times 10^{-4}$	$\mathrm{m^2\ s^{-1}}$	6.5×10^{-10}

Influence of uncertainties from N_A or kg cancel.



Combining $E = h \times v$
and $E = m \times c^2$:

$h/m = c^2/\nu = c \times \lambda$

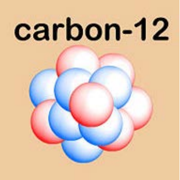


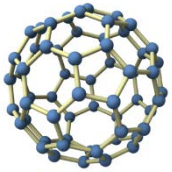
	$\lambda_{\text{De Broglie}}$ [m]	ν_{Compton} [Hz]
m = 1 kg:	2.2102×10^{-42}	1.3564×10^{50}
m = 1 g = 1 mol u:	2.2102×10^{-39}	1.3564×10^{47}
m = 720 u (C_{60} ^{12}C-Buckminster-Fullerene)	1.8486×10^{-18}	1.6217×10^{26}
m = 133 u (^{133}Cs)	1.0015×10^{-17}	2.9935×10^{25}
m = u; unified atomic mass unit (= dalton (Da)):	1.3311×10^{-15}	2.2523×10^{23}
m = m_e; mass of the electron:	2.4260×10^{-12}	1.2356×10^{20}

$\lambda_{\text{De Broglie}}$ is the wavelength of the (hypothetical) photon with energy = h × v generated from a given mass in $E = m \times c^2$ by annihilation. ν_{Compton} is the corresponding frequency.

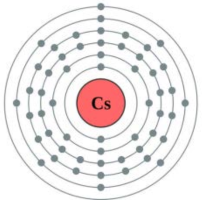
For the electron, the Compton frequency of 1.2356×10^{20} corresponds to the better known 0.511 MeV photon energy needed twice for pair formation. Likewise, 931.5 MeV is the single-photon energy equivalent of the dalton.

The 1-kg wavelength of 2.2×10^{-42} m is 27 orders of magnitude smaller then a proton! For the proton, $\lambda_{\text{De Broglie}}$ is about 1.5 times the diameter.





Measurements of h/m



- Annihilation $e^- + e^+ \rightarrow 2\gamma$ ($2 m_e c^2 = 1.022$ MeV; precision still lacking ?)

- ^{133}Cs as a source for mass definition using a Compton clock:
  ^{133}Cs: $\omega_0 = mc^2/\hbar$
  ($\omega_0 / 2\pi = 2.\,993\,486\,252(12) \times 10^{25}$ Hz)

* "Using an atom interferometer and an optical frequency comb."
Lan et al., A Clock Directly Linking Time to a Particle's Mass, *Science* **399**, 554 (2013)

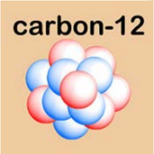
- Quotient h/m(^{133}Cs)*:

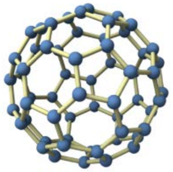
$$\frac{h}{m(^{133}\mathrm{Cs})} = 3.002\,369\,432(46) \times 10^{-9}\ \mathrm{m^2\,s^{-1}}$$
$$[1.5 \times 10^{-8}].$$

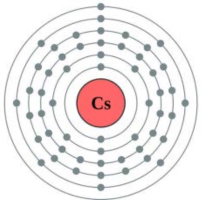
- Quotient h/m(^{87}Rb)*:

$$\frac{h}{m(^{87}\mathrm{Rb})} = 4.591\,359\,2729(57) \times 10^{-9}\ \mathrm{m^2\,s^{-1}}$$
$$[1.2 \times 10^{-9}].$$

* PJ Mohr, BN Taylor, and DB Newell, CODATA recommended values of the fundamental physical constants: 2010; DOI: 10.1103/RevModPhys.84.1527

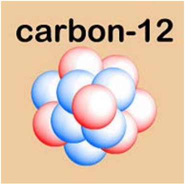


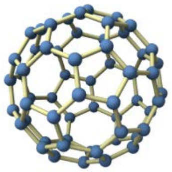


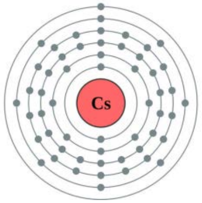


Preference for fixing u (the dalton) rather than h:

- kg/u must be constant. The proportionality factor of the (old) SI used to be N_A exactly.
  Fixing the kg and Na in the new SI leads to an ambiguity, when u is not fixed as well. With u changing upon new determinations of h/m, the number of particles in a kg must change as well, i.e. N_A is no longer constant.
- The atomic mass unit is easy to comprehend as an existing mass. In contrast, the mass definition via h is made through the virtual mass of a photon by combining $E=mc^2$ and $E=h\nu$. The related wavelength of the kg ($> 10^{50}$) is beyond any direct measurability.
- The established SI relations remain largely valid. Textbooks on the mole and Avogadro number need to be revised only marginally.







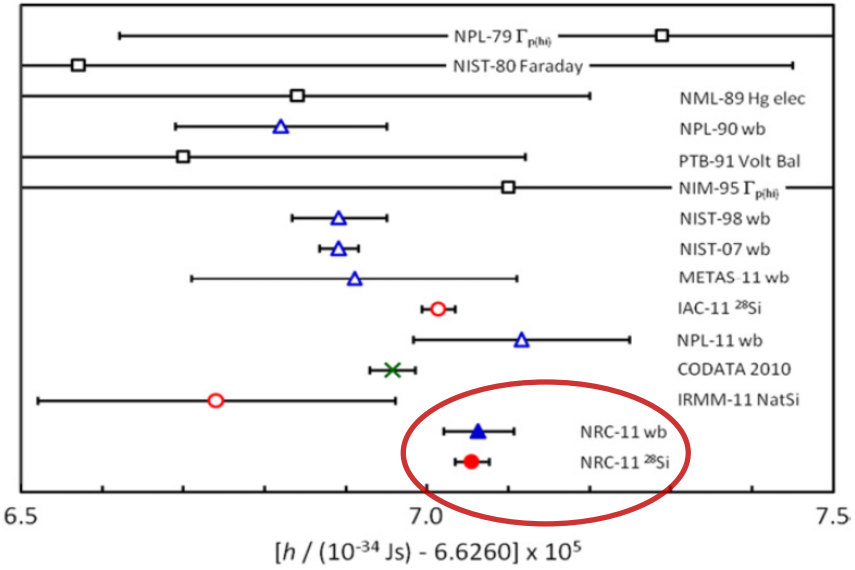
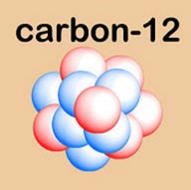


Figure 1. Experimental determinations of the Planck constant with sufficient precision to be relevant when computing a statistical value for *h* by the Committee on Data for Science and Technology (CODATA) Task Group on Fundamental Constants. The error bars indicate standard uncertainties, approximately equivalent to 68% confidence intervals. Watt balance results are shown with triangles, silicon results with circles, and other techniques with squares. The CODATA 2010 value [12] is shown as a cross.

A G Steele etal.
Metrologia 49 (2012) L8–L10

Recent Watt Balance and IAC data have removed the experimental discrepancy for h (or N_A), leaving an uncertainty of ~ 1 × 10^{-8}.

→ u or h as well as N_A can be fixed to define a new kg.



Commission on Isotopic Abundances and Atomic Weights, CIAAW, Calgary 2011*

The CIAAW, considering that

1. the non-SI unit of mass, the dalton (symbol Da), is defined as 1/12th of the mass of a single ^{12}C atom,
2. *atomic-mass values of the elements are commonly expressed in daltons, not in kilograms,*
3. all atomic-weight values of the elements have traditionally been published as ratios to atomic-mass values,
4. all molecular-weight values for large molecules such as proteins are increasingly expressed in daltons,
5. numerous chemical measurements consist of measurement of ratios of number of entities (atoms, molecules, …)…

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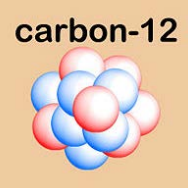
* Letter W.A. Brand to R. Kaarls, September 2011



Commission on Isotopic Abundances and Atomic Weights, CIAAW, Calgary 2011*

(CIAAW) recommends

1. changing the name of the quantity “amount of substance” to “number of entities”,

2. the following future definition of the mole:

> ***Mole, the unit of number of entities, symbol ‘mol’, is a number of specified entities equal to 6.022 14X ×10^{23} entities exactly.***

3. that, in addition, together with the fixed value of the Avogadro constant, the dalton could serve to redefine the kilogram in a way that would suit the needs of the chemists:

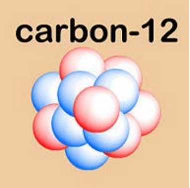
> ***Kilogram, the unit of mass, symbol ‘kg’, is the mass of 6.022 14X ×10^{23} atoms of ^{12}C in their nuclear ground state multiplied by 1000/12,***

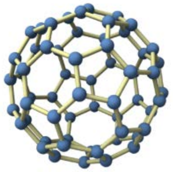
or

> ***Kilogram, the unit of mass, symbol ‘kg’, is the mass of one mole of ^{12}C atoms in their nuclear ground state multiplied by 1000/12.***

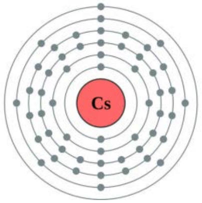
4. that any decision on the redefinition of the mole be deferred until full consideration is given to the interests of the chemical and isotopic measurement communities.

* Letter W.A. Brand to R. Kaarls, September 2011



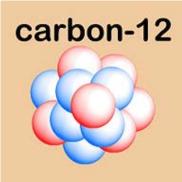


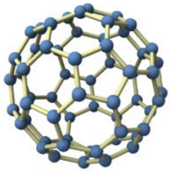
SI Base units

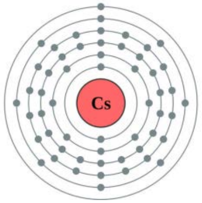


Quantity	Unit symbol	SI	New SI (h-fixed)	Alternative New SI (u-fixed)
Time	s	fixed; $\Delta\nu(^{133}Cs)_{hfs}$ = 9 192 631 770 Hz	ditto	ditto
Length	m	fixed by c: c = 299 792 458 m/s	ditto	ditto
Mass	kg	fixed by $\mathfrak{K}$* 1 kg = 1000 N_A u (u = 1.660538921(73) × 10^{-27} kg)	fixed by h; (u variable) ** 1 kg is defined to satisfy h = 6.626 069X × 10^{-34} kg m^2/s	fixed by u; (h variable)*** 1 kg = 1000 N_A u (u = 1.660538922 × 10^{-27} kg)
Amount of Substance	mol	Amount containing the same # of entities as 0.012 kg of ^{12}C	Amount containing a fixed N_A # of entities	Amount containing a (fixed) N_A # of entities as found in 0.012 kg of ^{12}C

*$\mathfrak{K}$ = international Prototype
** h/u = 1000 N_A h = 3.9903 e^{-7}; u_r~ 7 e^{-10}; h, N_A fixed
*** h/u = 1000 N_A h = 3.9903 e^{-7}; u_r~ 7 e^{-10}; u, N_A fixed

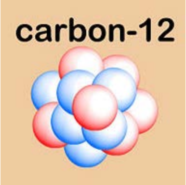






Summary and conclusions:

- The mole is a very important concept in chemistry, brdging the gap between the atomic realm and the daily macroscopic environment
- The quantity relation h/m with m being m_e or u is known with an uncertainty of $< 10^{-9}$. Through fixing either h or u, the other constant automatically has to take the uncertainty, independent of N_A or the kg.
- The mass defining the new fixed kg may be generated from an invariant, elementary mass (the unified atomic mass unit, u or Da).
- The mole can be regarded as a simple proportionality factor, fixed as a whole number to represent the new kg exactly.
  Thus: 1 mol = N_A entities and 1 kg = 1000 $N_A \times$ u are still valid.
- New techniques for determining h/m may improve the remaining uncertainty of h in the future.



(Foto: PTB)