

Mise en pratique for the definition of the mole in the SI

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1. Introduction

The purpose of this *mise en pratique*, prepared by the Consultative Committee for Amount of Substance – Metrology in Chemistry and Biology (CCQM) of the International Committee for Weights and Measures (CIPM), is to indicate how the definition of the SI base unit, the mole, symbol mol, may be realized in practice.

In general, the term “to realize a unit” is interpreted to mean the establishment of the value and associated uncertainty of a quantity of the same kind as the unit that is consistent with the definition of the unit. The future definition of the mole does not imply any particular experiment for its practical realization. Any method capable of deriving an amount of substance value traceable to the set of seven reference constants could, in principle, be used. Thus, the list of methods given is not meant to be an exhaustive list of all possibilities, but rather a list of those methods easiest to implement and/or that provide the smallest uncertainties and which are officially recognized as primary methods by the relevant Consultative Committee.

A primary method is a method having the highest metrological properties; whose operation can be completely described and understood; for which a complete uncertainty statement can be written down in terms of SI units; and which does not require a reference standard of the same quantity.

2. Definition of the mole

The definition of the mole, SI base unit of amount of substance, is as follows [2.1]:

The mole, symbol mol, is the SI unit of amount of substance. One mole contains exactly $6.022\,140\,76 \times 10^{23}$ elementary entities. This number is the fixed numerical value of the Avogadro constant, N_A , when expressed in the unit mol⁻¹ and is called the Avogadro number.

The amount of substance, symbol n , of a system is a measure of the number of specified elementary entities. An elementary entity may be an atom, a molecule, an ion, an electron, any other particle or specified group of particles.

As a consequence of the definition of the mole, the Avogadro constant and the Avogadro number no longer have an experimental uncertainty in the SI.

This definition was agreed by the 26th General Conference on Weights and Measures (CGPM) in 2018, to take effect on 20 May 2019. It is now based on a fixed number of entities [2.2]. It replaces the definition adopted in 1971 which defined the mole as “the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon 12”.

The quantities used to characterize a sample of a pure chemical substance X are:

n	the amount of substance in the sample of X;
N	the number of elementary entities of the substance X in the sample;
m	the mass of the N elementary entities;
$A_r(\text{X})$	the relative atomic or molecular mass ¹ of X (depending whether X is an element or a compound, respectively)
M_u	the molar mass constant

Two widely used equations relate these quantities:

$$n = m / (A_r(\text{X})M_u) \quad (2.1)$$

and

$$n = N / N_A \quad (2.2)$$

These equations are valid under the 2019 definition as they previously were under the 1971 definition. This document explains how the measurement uncertainties of the quantities in these equations should be handled under the 2019 definition.

In Section 3, an example of the realization of the unit of amount of substance to the smallest possible uncertainty is given. It uses a method that helped motivate the development of the present definition and now demonstrates its realization on a primary level. In Section 4, some additional practical methods for realizing the mole are described. In Section 5, the issue of quantifying small numbers of entities is discussed. Finally, in Section 6, the continuity of measurement results expressed in moles with respect to the 1971 and 2019 definitions is explained.

In the future, this *mise en pratique* may be amended to include additional practical realizations or revised uncertainties. The *mise en pratique* is published uniquely as an on-line appendix to the latest edition of the SI Brochure. In this way, this appendix can be revised whenever necessary.

3. Practical realization of the definition of the mole with the smallest uncertainty

Currently, the most accurate realization of the mole results from an experiment that led to the determination of the Avogadro constant. This experiment was carried out within the framework of the International Avogadro Coordination and was fundamental to determining the best experimental values of both the Avogadro and Planck constants prior to fixing their numerical values. It involved the determination of the number of ²⁸Si atoms (N) in a single crystal of Si, enriched in ²⁸Si, using volumetric and X-ray interferometric measurements [3.1,3.2,3.3]:

$$N = 8V_s / a(^{28}\text{Si})^3 \quad (3.1)$$

where V_s is the crystal volume, 8 is the number of atoms per unit cell of crystalline silicon and $a(^{28}\text{Si})$ is the lattice parameter of the cubic unit cell. Equation (3.1) is strictly valid only for the hypothetical case a perfect crystal of pure ²⁸Si – hence, all elementary entities in the crystal were identified. This was achieved by determining and correcting for the amount of substance fraction of all impurities (elemental and isotope impurities, i.e. ²⁹Si, ³⁰Si) with sufficient accuracy [3.1,3.2]. This is consistent with the concept for the realization of the kilogram using the X-ray crystal-density (XRCD) approach as described in the *mise en pratique* for the kilogram [2.1].

¹ For historical reasons, the equivalent terms "atomic weight" and "molecular weight" are still in use [2.3].

Utilizing the fixed numerical value of the Avogadro constant [3.4] and (2.2), the amount of substance n of ^{28}Si in the macroscopic crystal is given by:

$$n = 8V_s / (a(^{28}\text{Si})^3 N_A) \quad (3.2)$$

This allows the definition of both the mole and the kilogram to be realized with a relative standard uncertainty below 2×10^{-8} [3.3, 3.5, 3.6] in a single crystal of Si, enriched in ^{28}Si .

This primary realization of the mole with the smallest uncertainty differs from methods generally used to realize the mole. It is presented here as the “state of the art” in determining the number of entities in a macroscopic sample, and hence the amount of substance in that sample. It is, at the same time, also a primary realization of the kilogram. It is a primary mass standard and the unit of mass, the kilogram, may be disseminated from this standard [3.7]. In the following sections, some of the more common and practical methods to realize the mole are described.

4. Common and practical realizations of the definition of the mole and derived units and dissemination of the mole

In practice, chemical measurements require the realization, across all types of chemical entities, of derived units involving amount of substance that are relevant to practical chemical measurement, such as the amount of substance concentration (mol/m^3), the amount of substance content (mol/kg) or the amount of substance fraction (mol/mol). This may be done by a variety of primary methods of measurement [4.1]. The present definition of the mole allows the number of entities N in a sample to be determined to the same accuracy as the amount of substance n in the sample because, from (2.2), $N = nN_A$ and N_A has an exact numerical value.

Similarly, the atomic or molecular mass $m_a(\text{X})$ and the molar mass $M(\text{X})$ of any entity X are known to the same relative uncertainty because:

$$m_a(\text{X}) = \frac{M(\text{X})}{N_A} \quad (4.1)$$

The atomic mass constant m_u is 1/12 of the mass of a free ^{12}C atom, at rest and in its ground state. Its present experimentally-determined value is approximately $1.660\,539\,067(1) \times 10^{-27}$ kg with a relative uncertainty less than 1 part in 10^9 and is identical to that of M_u . Note that $N_A m_u = M_u$ is a special case of (4.1). The advantages of these features of the present definition of the mole have been emphasized in the literature [4.2]. The most up-to-date values and uncertainties of m_u and M_u are the most recent recommendations of the CODATA task group on fundamental constants.

Three examples of methods to realize the mole (and the number of entities) follow:

4.1 Gravimetric preparation

Based on (2.1) and (2.2), the number of entities N of a substance X or its amount of substance n in a sample may be measured by determining the product of the mass fraction of X in the sample, $w(\text{X})$, and the mass m of the sample from the following equations²:

$$N = \frac{w(\text{X})m}{m_a(\text{X})} = \frac{w(\text{X})m}{A_r(\text{X})m_u} \quad (4.2)$$

$$n = \frac{N}{N_A} = \frac{w(\text{X})m}{A_r(\text{X})N_A m_u} = \frac{w(\text{X})m}{A_r(\text{X})M_u} \quad (4.3)$$

² Equation (4.2) assumes that N entities of X contribute a mass $N \times m_a(\text{X})$ to a sample whose total mass is m .

In (4.2) and (4.3), $A_r(\text{X})$ is the relative atomic or molecular mass of X as calculated from the chemical formula of the pure substance and tables of the relative atomic masses A_r of the elements. The relative atomic masses of the elements are tabulated [4.3] with uncertainties that, except for the mononuclidic elements, are dominated by the uncertainty in the spread of isotopes seen in naturally occurring elements from different environments. Because the reported values of A_r are mass ratios, they are unaffected by changes to the SI.

This method of realizing the mole is commonly used because measuring the mass of a sample is relatively simple and accurate. The knowledge of the mass fraction w is a prerequisite for its use. When very high purity substances are available, the uncertainty of the determination of the mass m is often the limiting factor and the mole may be realized with a relative standard uncertainty of less than 1×10^{-6} . It is important to note that there are relatively few substances (e.g. pure gases or pure metals), where the mass fraction of the substance (traditionally called its “purity”) can be assigned with sufficiently small uncertainty to permit a realization of the mole with a relative uncertainty at the 1×10^{-6} level. Experimental verification that the isotopic composition of the substance is equivalent to that used for the calculation of the molar mass must also be undertaken if uncertainty at this level is to be achieved.

Realization of the mole for a pure organic or inorganic substance will usually be limited by the uncertainty of the mass fraction assignments to the substance rather than the uncertainty of mass determinations. As there are very few organic substances whose mass fraction (“purity”) is assigned with relative standard uncertainty below 1×10^{-4} , achieving a relative standard uncertainty of 1×10^{-4} for a realization of the mole based on a pure organic or inorganic substance is the limit in most cases.

This method of realization is used for most chemical entities. However, there are other methods that can be used for certain restricted classes of substances. These are described in 4.2 and 4.3.

4.2 Equations of state for gases

The amount of substance n of a sample of a pure gas may be determined by solving the equation of state for the gas:

$$pV = nRT \left[1 + B(T) \left(\frac{n}{V} \right) + \dots \right] \quad (4.4)$$

where p is the pressure, V is the volume, T is the temperature, and R is the molar gas constant. The value of R is known exactly ($R = N_A k$, k is the Boltzmann constant and its numerical value is fixed). The SI coherent unit of the molar gas constant is $\text{Pa m}^3 \text{ mol}^{-1} \text{ K}^{-1}$ or $\text{J mol}^{-1} \text{ K}^{-1}$, *i.e.* $\text{kg m}^2 \text{ s}^{-2} \text{ mol}^{-1} \text{ K}^{-1}$ when expressed in base units. The terms involving the second virial coefficient $B(T)$ and possible higher-order terms are generally small corrections. Virial coefficients expressed in SI units are tabulated for a number of simple gases. The uncertainty in a measurement of n made this way depends on the uncertainty in measuring p , V and T , and in the tabulated values of $B(T)$. This method of realizing the mole for a gas relies on the use of a pure sample of the gas. The number of molecules in the gas is nN_A , which has the same relative uncertainty as the determination of n .

4.3 Electrolysis

In a chemical electrolysis experiment, the number N of entities that have reacted at an electrode equals the charge Q passed through the system divided by ze , where z is the charge number of the ions reacted and e is the elementary electrical charge. Thus:

$$N = \frac{Q}{ze} \quad (4.5)$$

where e has a fixed value. In terms of amount of substance n :

$$n = \frac{Q}{zN_A e} = \frac{Q}{zF} \quad (4.6)$$

The Faraday constant F has the unit C/mol and is known exactly ($F = N_A e$). The uncertainty of this method of realizing the mole depends on the reaction efficiency of the ion of interest and no interfering ions present.

5. Small numbers of entities

In cases where the number of entities being considered is small, quantities are commonly expressed as numbers of entities instead of amount of substance [5.1]. The Avogadro constant is the constant of proportionality that links amount of substance to the number of entities. However, the number of entities and amount of substance may only be equated in this way if the entities considered in both quantities are elementary entities of the same type. The unit for the number of entities is one, symbol 1, although this unit is rarely stated explicitly. An example of its use is: the number concentration of ozone molecules in air has the unit $1/\text{m}^3$.

6. Continuity with previous definition

Note that the 1971 definition of the mole made a direct link between the mole and the mass of a particular nuclide. This allowed traceability to the mole to be established via mass measurements and established a simple relation between macroscopic measurements and microscopic entity numbers such as atoms or molecules via the molar mass constant. The mass of one mole of ^{12}C was fixed at exactly 12 g. This meant that $M(^{12}\text{C})$ was exactly 12 g/mol and M_u was exactly 1 g/mol.

However, the present definition of the mole fixes the numerical value of N_A . Therefore from:

$$M_u = m_u N_A \quad (6.1)$$

M_u and m_u now have the same relative uncertainty.

In (6.1) m_u is the atomic mass constant. The atomic mass unit u (also known as the dalton, a non-SI unit whose symbol is Da) and the atomic mass constant m_u are defined in terms of the mass of the ^{12}C isotope. The unit u is related to the constant m_u by

$$1 \text{ u} = m_u = m(^{12}\text{C})/12 \quad (6.2)$$

The molar mass constant M_u and the atomic mass constant m_u are determined to the same relative uncertainty for example from the equation:

$$M_u = N_A m_u = \frac{2N_A h}{c} \frac{R_\infty}{\alpha^2 A_r(e)} \quad (6.3)$$

where the Rydberg constant (R_∞), the fine structure constant (α) and the relative atomic mass of the electron ($A_r(e)$) are determined experimentally. The speed of light (c), the Planck constant (h) and the Avogadro constant have fixed numerical values [2.1].

Continuity conditions imposed on redefinitions of SI base units have ensured that M_u , now determined experimentally, is still 1×10^{-3} kg/mol within a relative standard uncertainty of 4.5×10^{-10} based on (6.3) and additional independent experimental methods [6.1]. The present

uncertainty is more than sufficient for the needs of chemical measurements, being an order of magnitude smaller than the relative uncertainty achievable in the most accurate realization of the mole [3.1-3.3], and several orders of magnitude smaller than the uncertainties in examples of more common realizations of the mole described above.

References

- [2.1] BIPM, The International System of Units (SI Brochure) [9th edition, 2019], <https://www.bipm.org/en/publications/si-brochure/>.
- [2.2] IUPAC Recommendation, *Pure Appl. Chem.* **90**, (2018) 175-180
- [2.3] IUPAC Quantities, Units and Symbols in Physical Chemistry, third ed. (2007) RSC Publishing, Cambridge UK https://www.iupac.org/fileadmin/user_upload/publications/e-resources/ONLINE-IUPAC-GB3-2ndPrinting-Online-Sep2012.pdf
- [3.1] Fujii K, Bettin H, Becker P, Massa E, Rienitz O, Pramann A, Nicolaus A, Kuramoto N, Busch I and Borys M, *Metrologia* **53** (2016) A19-A45.
- [3.2] Bartl G, Becker P, Beckhoff B, Bettin H, Beyer E, Borys M, Busch I, Cibik L, D'Agostino G, Darlatt E, *Metrologia* **54** (2017) 693-715.
- [3.3] Kuramoto N, Mizushima S, Zhang L, Fujita K, Azuma Y, Kurokawa A, Okubo S, Inaba H, Fujii K, *Metrologia* **54** (2017) 716-729.
- [3.4] Newell D B, Cabiati F, Fischer J, Fujii K, Karshenboim S G, Margolis H S, de Mirandés E, Mohr P J, Nez F, Pachucki K, Quinn T J, Taylor B N, Wang M, Wood B M and Zhang Z, *Metrologia* **55** (2018) L13-L16.
- [3.5] Cladé P, Biraben F, Julien L, Nez F and Guellati-Khelifa S, *Metrologia* **53** (2016) A75-A82.
- [3.6] Fujii K, Massa E, Bettin H, Kuramoto N and Mana G *Metrologia* **55** (2018) L1-L4.
- [3.7] <https://www.bipm.org/utis/en/pdf/si-mep/MeP-kg-2018.pdf>
- [4.1] Milton M and Quinn T, *Metrologia* **38**, (2001) 289-296.
- [4.2] Milton M, and Mills I, *Metrologia* **46** (2009) 332-338.
- [4.3] Commission of Isotopic Abundances and Atomic Weights, <http://ciaaw.org/atomic-weights.htm>
- [5.1] Brown R J C, *Metrologia* **55** (2018) L25–L33.
- [6.1] Mohr P J, Newell D B, Taylor B N and Tiesinga E, *Metrologia* **55** (2018) 125-146.