

Mise en pratique of the definition of the mole

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(**Note:** this text will not come into force until a re-definition of four of the base units of the SI has been agreed by the General Conference on Weights and Measures and takes effect. Certain numerical values are [indicated here in blue](#), because they will not be known until that time.)

1. Introduction

This document explains the definition of the mole and how it can be put into practice. The process of putting a definition into practice is often referred to as “realization”, and following the French translation, this document is called the “*mise en pratique*” for the mole.

The mole, symbol mol, is the SI unit of amount of substance. It is defined in Chapter 2 of the *SI Brochure* with the words:

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 N_A to be **6.022 141 29 $\times 10^{23}$** when expressed in the SI unit mol⁻¹.

The number of entities in one mole is equal to the numerical value of the Avogadro constant which is known as the Avogadro number. As a consequence of the definition of the mole, the Avogadro constant, and the Avogadro number have no uncertainty.

The definition given here was agreed by the 26th CGPM in 2018. It replaced the definition agreed 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;
$A_r(X)$	the relative atomic or molecular mass of X (in case that X is an element or compound, respectively)
M_u	the molar mass constant

Two widely used equations relate these quantities:

	$n = m / A_r(X)M_u$	(1.1)
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and

	$n = N / N_A$	(1.2)
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These equations were valid under the 1971 definition, and remain valid under the 2018 definition. This document explains how the measurement uncertainties of the quantities in these equations should be handled under the 2018 definition.

In Section 2 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 to motivate the development of the present definition. In Section 3, some more practical methods for realizing the mole are described. In Section 4, the issue of quantifying small numbers of entities is discussed. Finally, in Section 5, the continuity of measurement results expressed in mol with respect to the 1971 and 2018 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 as an on-line appendix to the current SI *Brochure*. The appendix is revised whenever necessary without necessarily being accompanied by a new edition of the *Brochure*.

2. Realization of the definition of the mole with smallest uncertainty

Currently, the most accurate realization of the definition of the mole results from an experiment that led to the determination of the Avogadro constant. This experiment was carried out in 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 current values. It involved the determination of the number of ^{28}Si atoms (N) in a single crystal of Si enriched in ^{28}Si using volumetric and X-ray interferometric measurements [1,2] using :

$$N = 8V_s / a(^{28}\text{Si})^3 \quad (2.1)$$

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 2.1 is strictly only valid for the hypothetical case of a pure ^{28}Si crystal – 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. ^{29}Si , ^{30}Si) with sufficient accuracy [1,2]. 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.

Utilising the fixed value of the Avogadro constant and (1.2) the amount of substance n of ^{28}Si in the macroscopic crystal is given by:

$$n = 8V_s / (a(^{28}\text{Si})^3 N_A) \quad (2.2)$$

This allows the definition of both the mole (and the kilogram) to be realized with a relative standard uncertainty of $2 \cdot 10^{-8}$ [3] in such a single crystal of Si enriched in ^{28}Si .

This primary realization of the mole with smallest uncertainty differs from methods generally used to realize the mole in practice. 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. In the following section some practical methods to realize the mole are described.

3. Common methods for the realization and dissemination of the mole

In practice, chemical measurements require the realization of the unit for amount of substance for all types of chemical entities and often of derived units such as the amount of substance concentration (mol/m^3), amount of substance content (mol/kg) or amount of substance fraction (mol/mol). This may be done by a variety of primary methods of measurement [5]. 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 (1.2), $N = nN_A$ and N_A has an exact 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:

$$m_a(\text{X}) = \frac{M(\text{X})}{N_A} \quad (3.1)$$

In particular, it is shown in Section 5 that the molar mass constant M_u is 1 g/mol to within a relative standard uncertainty which is less than 10^{-9} .

The atomic mass constant m_u is 1/12th the mass of a free ^{12}C atom, at rest and in its ground state is $1.660\,538\,921(\text{XX}) \cdot 10^{-27}$ kg with a relative uncertainty less than 1 part in 10^9 and identical to that of M_u . Note that m_u is equal to the SI value of the dalton and that $N_A m_u = M_u$ is a special case of (3.1). Advantages of these features of the present definition of the mole have been emphasized in the literature [6].

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

3.1 Gravimetric preparation

Based on (1.1) and (1.2), 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 equations¹:

$$N = \frac{w(\text{X})m}{m_a(\text{X})} = \frac{w(\text{X})m}{A_r(\text{X})m_u} \quad (3.2)$$

$$n = \frac{N}{N_A} = \frac{w(\text{X})m}{A_r(\text{X})N_A m_u} = \frac{w(\text{X})m}{A_r(\text{X})M_u} \quad (3.3)$$

In (3.2) and (3.3) $A_r(\text{X})$ 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 with a relative standard uncertainty of less than 10^{-4} in most cases, and in some cases less than 10^{-8} . Reported values of A_r are mass ratios and are thus unaffected by changes to the SI.

This method of realizing the mole is mostly 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

¹ Equation (3.2) assumes that N entities of X contribute a mass $N \times m_a(\text{X})$ to a sample whose total mass is m .

uncertainty of less than $1 \cdot 10^{-6}$. 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 $1 \cdot 10^{-6}$ 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.

A realization of the mole for a pure organic or inorganic substance will usually be limited by the uncertainty of the mass fraction assignment of 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 $1 \cdot 10^{-4}$, achieving a relative standard uncertainty of $1 \cdot 10^{-4}$ 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 several other methods that can be used for certain restricted classes of substances.

3.2 Use of the ideal gas law

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

$$pV = nRT \left[1 + B(T) \left(\frac{n}{V} \right) + \dots \right] \quad (3.4)$$

where p is the pressure, V is the volume, T is the temperature, and R is the molar gas constant ($R = N_A k$, k is the Boltzmann constant; the value of k is fixed). The value of R is known exactly. 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.* $\text{kg m}^2 \text{s}^{-2} \text{mol}^{-1} \text{K}^{-1}$ in base units. The term 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 .

3.3 Electrolysis

In a chemical electrolysis experiment, the number N of entities 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:

$$N = \frac{Q}{ze} \quad (3.5)$$

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

$$n = \frac{Q}{zN_A e} = \frac{Q}{zF} \quad (3.6)$$

The Faraday constant F has the unit C/mol and is known exactly ($F = N_A e$). This method of realizing the mole depends on reaction efficiency for the ion of interest being 100% with no interfering ions present.

4. 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. The Avogadro constant is the constant of proportionality that links amount of substance to the number of entities. However, 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 '1', although this unit is only explicitly stated with some intensive quantities of this type, for instance: the number concentration of ozone molecules in air, with the unit $1/\text{m}^3$.

5. 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 establishes 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 value of N_{A} . Therefore from:

$$M_{\text{u}} = m_{\text{u}} N_{\text{A}} \quad (4.1)$$

M_{u} and m_{u} now have the same uncertainty.

In (4.1) m_{u} is the atomic mass constant. The atomic mass unit u (also known as the dalton) and the atomic mass constant m_{u} are defined in terms of the mass of the ^{12}C isotope.

$$1 \text{ u} = m_{\text{u}} = m(^{12}\text{C})/12 \quad (4.2)$$

The molar mass constant M_{u} and the atomic mass constant m_{u} are determined to the same relative uncertainty [6], for example from the equation:

$$M_{\text{u}} = N_{\text{A}} m_{\text{u}} = \frac{2N_{\text{A}} h}{c} \frac{R_{\infty}}{\alpha^2 A_{\text{r}}(e)} \quad (4.3)$$

where the Rydberg constant (R_{∞}), the fine structure constant (α) and the relative atomic mass of the electron ($A_{\text{r}}(e)$) are determined experimentally. The values of the speed of light (c), the Planck constant (h) and the Avogadro constant are fixed by the definitions of the metre, kilogram and the mole respectively.

Continuity conditions imposed on redefinitions of SI base units have ensured that M_{u} is still 1 g/mol but now with finite, but very small, experimental uncertainty. The currently accepted value of the molar mass constant is $M_{\text{u}} = 1.000\,000\,000 \cdot 10^{-3} \text{ kg mol}^{-1}$ with a relative standard uncertainty of $7.0 \cdot 10^{-10}$ based on (4.3) and additional independent experimental methods [7,8]. The present uncertainty is more than sufficient for the needs of chemical measurements, being approximately thirty times smaller than the relative uncertainty achievable in the most accurate realization of the mole [1-3], and several orders of magnitude smaller than the uncertainties in examples of more common realizations of the mole described above.

References

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