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Amount of Substance and the Mole

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Abstract: The unit mole is very familiar amongst both chemists and physicists, but the name of the corresponding quantity 'amount of substance' is not so familiar and the concept is still a source of difficulty for many students. This paper reviews and clarifies these concepts and also discusses the definition of the unit mole, and its possible revision.

Keywords: Amount of substance · Molar mass constant · Mole · Redefinition · SI

1. Amount of Substance

Amount of substance is a quantity that measures the size of an ensemble of entities. It appears in thermodynamic relations such as the ideal gas law, and in stoichiometric relations between reacting molecules such as the Law of Multiple Proportions.[1,2] Familiar equations involving amount of substance (n) are

$$pV = nRT, \tag{1}$$

for an ideal gas, and the equation

$$c = n/V \tag{2}$$

for the amount of substance concentration (usually called simply the concentration) of a solution. Here V is the volume of a solution containing the amount of solute n. Another important relation is that between amount of substance n and mass m for a pure sample

$$n = m/M \tag{3}$$

where M is the mass per amount of substance, usually called the molar mass.

An important application of the quantity amount of substance in chemistry is to the way in which molecules react in a titration or more generally in any chemical reaction. This is the most fundamental concept for chemical reactions. Thus the ratio of volumes of solutions of X and Y that react together in a titration are given by

$$\left(\frac{V_X}{V_Y}\right) = \left(\frac{n_X / c_X}{n_Y / c_Y}\right) = \left(\frac{n_X / n_Y}{c_X / c_Y}\right) \tag{4}$$

where the quantity (n_X/n_Y) is a simple rational fraction. Hence the concentration of an unknown solution may be determined from the concentration of a standard solution by measuring the volumes in a titration. This is the Law of Multiple Proportions.

It is interesting to note that whilst the use of amount of substance in the sense of referring to a thermodynamic ensemble can be traced back to Boyle's research in the 17th century, the development of an understanding of stoichiometry dates to Lavoisier's work one hundred years later. Underlying both of the senses in which it is used, is the fact that the quantity amount of substance measures a number of entities. This insight can be traced directly to two developments made in the early 19th century: Dalton's explanation of his Law of Multiple Proportions and Avogadro's hypothesis that "samples of different gases at the same temperature, pressure and volume always contain the same number of molecules".[3,4] As discussed below, it is now being proposed that the link between the quantity amount of substance and the underlying concept of a number of entities should be strengthened by the introduction of a definition for the unit of amount of substance framed directly in terms of a fixed number of entities.

"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 entities may be atoms, molecules, ions, electrons, other particles, or specified groups of particles."

This definition emphasises the nature of amount of substance, which is distinct from a specific number of entities and from the definition of the unit for amount of substance.

The quantity amount of substance (n) is thus an alternative to using the quantity number of entities (N). They are related by the equation

$$n = N/N_A \tag{5}$$

where N_A is the Avogadro constant.

One might reasonably ask why we need the quantity amount of substance at all, when the number of entities could be used in its place? We propose three reasons for preferring to use n rather than N.

The first is that equations like Eqn. (3) can be used to determine molar mass M, or amounts in terms of moles, without knowing the value of the Avogadro constant. The atomic weights of atoms in the periodic table were known long before the value of the Avogadro constant was known with similar accuracy. Even today, the value of the Avogadro constant is only known to about one part in 10^7, whereas many atomic weights are known to about one part in 10^9 or better.

The second reason is practical; the number of entities is generally of the order 10^{23}, whereas n is generally a number of order 1 when expressed in moles. Thus, for example, in a chemistry laboratory the concentration of solutions is typically quoted in moles per litre, with numbers in the general order of magnitude 1. It would be inconvenient to quote concentrations in molecules per litre, with numbers of the order 10^{23}. Thus we find bottles labelled '0.1 M NaOH', where M is read as 'molar' and is an accepted shorthand for the unit $mol{\cdot}L^{-1} = mol{\cdot}dm^{-3}$. The quantity amount of substance may be seen as a device to handle the same quantitative information with much smaller numbers.

The third reason for introducing the quantity amount of substance, with the mole as a base unit, is that it extends the power of dimensional analysis to chemis-

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try, and to equations involving chemical quantities. This follows from the fact that n is a base quantity with its own dimension, whereas N is dimensionless.

2. The Mole

The mole is the SI unit for the quantity amount of substance.[5] It is currently defined by the statements:[6]

The mole is that amount of substance that contains the same number of elementary entities as there are atoms in 12 g of carbon-12. When the mole is used the entities must be specified and may be atoms, molecules, ions, electrons, other particles, or specified groups of such particles.

It follows that the numerical value of the Avogadro constant,[7] denoted $\{N_A\}$, expressed in the unit mol^{-1}, is simply the number of atoms in 12 g of carbon 12, so that the value of the Avogadro constant is directly related to the definition of the mole.

The effect of this definition is that the molar mass of carbon 12, $M(^{12}C)$, is exactly 12 $g{\cdot}mol^{-1}$, and the molar mass of any atom or molecule X is determined from its atomic or molecular weight by simply multiplying by the unit $g{\cdot}mol^{-1}$, without the need to know the value of the Avogadro constant. This is summarised in the relations

$$M(^{12}C) = A_r(^{12}C)\ g{\cdot}mol^{-1} = 12\ g{\cdot}mol^{-1} \quad (6)$$

$$M(X) = A_r(X)\ g{\cdot}mol^{-1} \quad (7)$$

Here $A_r(X)$ is the recommended symbol for the molecular weight of the entity X. The atomic or molecular weight of an entity is actually the relative atomic or molecular mass, relative to the value for the carbon 12 atom taken as exactly 12. (The names 'atomic weight' and 'molecular weight' are universally used, and have been officially sanctioned by IUPAC, although they refer to dimensionless quantities, which are neither masses nor weights.)

3. The Names 'Mole' and 'Amount of Substance'

The name 'mole' has been – and still is – the cause of some confusion. Its origin has been discussed in several publications.[3–5] The terms '*Kilogrammemolekuel*' and '*g-Molekel*' were used by German scientists in the 1880s and 1890s. The term "gramme-molecule" was first used in English in 1893 in an article in the *Encyclopaedia Britannica*. As the term implies, one gram molecular weight of a substance X is that amount in a mass equal to the molecular weight expressed in grams.

These terms proved too awkward for everyday use, and the abbreviation of "*g-Molekel*" to "*Mol*" was first recorded in 1898 by Nernst.[8] The term 'mole' appears in English for the first time in the translation of Ostwald's 'Principles of Inorganic Chemistry' published in 1902, in which he associated it with a standard number of molecules. Thus one gram molecule of X became one mole of X.

It must be admitted that the name 'amount of substance' is not well chosen, because the word 'amount' has a common dictionary meaning, and the additional words 'of substance' seem inadequate to imply the chemist's specialised use for the name. It was the original intention that the words 'of substance' should be replaced by the specification of the entity whenever possible, so that one would say (for example) 'amount of benzene, C_6H_6' or 'amount of hydrogen ions, H^+'.

Another name for n, which is the name that most chemists use, is simply 'number of moles'. However this is not a good name, because it confuses the name of the quantity with the name of the unit. A clear understanding requires that we always distinguish clearly between quantities and units. Thus mass is a quantity, for which kilogram (or gram, or milligram) are units, and similarly we wish to say that amount of substance is a quantity, for which mole (or millimole, or micromole) are units.

Setting aside the difficulties with the name amount of substance, it is important to realise that in the system of quantities and units that is now universally adopted in chemistry, amount of substance is regarded as a base quantity with its own dimension, whereas – by contrast – number of entities is regarded as a dimensionless quantity.

4. A Possible New Definition for the Mole

The current definition of the seven base units of the SI is given in the SI Brochure {SI brochure}. However there are proposals at present under discussion to adopt new definitions for four of the base units.[9,10] This follows from a desire to define each of the base units in relation to one of the fundamental constants of physics or the properties of a simple atom, because we believe these to be the most stable and reliable constants of nature available. Specifically, new definitions are being considered for the kilogram, ampere, kelvin and mole. This is the subject known as quantum metrology, and the proposals are discussed in detail elsewhere.[9,10] However the proposed new definition of the mole is the subject of the present discussion,[4] and the suggestion is that it should simply specify the number of entities in a mole. This new definition might then read as follows.

The mole is that amount of substance of a system that contains exactly 6.022 141 79 × 10^{23} specified elementary entities, which may be atoms, molecules, ions, electrons, other particles or specified groups of such particles.

The effect of this new definition would be to fix the value of the Avogadro constant to be 6.022 141 79 × 10^{23} mol^{-1} exactly. The number would be chosen to be the best estimate of the numerical value of the Avogadro constant at the time the new definition is adopted, thus ensuring continuity in the value of the mole.[9]

This new definition would be conceptually simpler than the current definition, which is chosen to fix the molar mass of carbon 12 rather than the number of entities in a mole. Also the new definition would no longer be dependent on the kilogram, so that uncertainties in realising the definition of the kilogram would no longer be transmitted to the mole – as they are at present.

5. The Molar Mass Constant M_u

Many of the relations between the quantities discussed here can be simplified by introducing the molar mass constant M_u, defined as one twelfth of the molar mass of the carbon 12 atom. This is the natural analogue on the macroscopic scale of the unified atomic mass constant m_u on the atomic scale, defined as one twelfth of the mass of a carbon 12 atom. The quantity m_u is often used as a unit of atomic mass, denoted either u (for 'unified') or Da (for Dalton). For example, it is more convenient to write Eqns (6) and (7) as

$$M(^{12}C) = A_r(^{12}C)\ M_u \quad (8)$$

and

$$m(^{12}C) = A_r(^{12}C)\ m_u \quad (9)$$

The molar mass M(X) of any entity X is then given in terms of the molecular weight $A_r(X)$ by the equation:

$$M(X) = A_r(X)\ M_u \quad (10)$$

just as the atomic mass of the entity X is given by

$$m(X) = A_r(X)\ m_u \quad (11)$$

Eqns (8) and (9) can be re-written with explicit use of N_A as

$$M(^{12}C) = N_A\ m(^{12}C) \quad (12)$$

and

$$M_u = N_A\ m_u \quad (13)$$

At present in the SI, $M_u = 1$ g·mol^{-1} exactly, and the Avogadro constant is an experimentally determined quantity (the number of atoms in 12 g of carbon 12), whose value is currently known with a relative standard uncertainty of about 5×10^{-8}.[7] With the new definition proposed above, M_u will initially have the same value of 1 g·mol^{-1}, but it will be an experimentally determined quantity, with an uncertainty, and its value may change slightly from 1 g·mol^{-1} due to future adjustments in the values of other constants. However the relative change of M_u from the value 1 g·mol^{-1} is unlikely ever to be greater than a few parts in 10^9, and this is so much smaller than the uncertainty with which chemical measurements are likely to be made that for all practical purposes chemists may still treat M_u as being equal to 1 g·mol^{-1}.

The Figure provides a diagrammatic representation of how this proposal would work. In the proposed system, it is the two factors $A_r(^{12}C)$ and N_A indicated by the ellipses that would be exact, and the four masses at the apexes that would all have the same uncertainty.

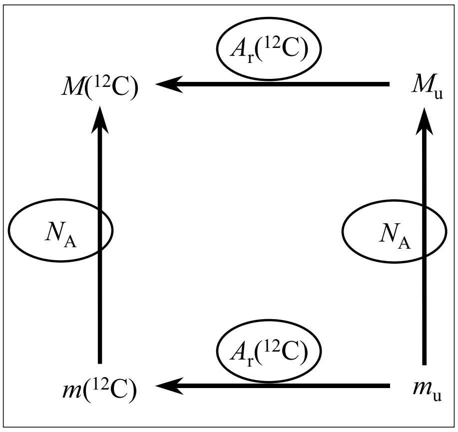

Fig. Diagrammatic representation of Eqns (8, 9 10 and 11) subject to the proposed re-definition of the mole such that $A_r(^{12}C)$ and N_A are fixed. The quantities at the apexes of the four-sided figure all have the same uncertainty. The quantities within ellipses are all fixed.

The relation between the Avogadro constant and the Planck constant, which would be used to determine M_u from the theoretical expression for the Rydberg constant R_∞, remains true under both the current and the new definition of the mole (Eqn. (14)):

$$\left(\frac{M(^{12}C)}{12}\right) = M_u = \left(\frac{2R_\infty N_A h}{\alpha^2 c A_r(e)}\right) \qquad (14)$$

In this equation α is the fine structure constant, c is the speed of light in vacuum, h is the Planck constant, and $A_r(e)$ is the relative mass of the electron on the unified atomic mass scale.

The molar mass constant M_u has not been much used in the established literature. It can of course always be replaced by the expression $M(^{12}C)/12$, which is how it is defined. We recommend that this constant could be used with advantage more widely than it is at present, in teaching chemistry for example, to simplify the expression for calculating the molar mass of atoms and molecules.

6. Realising the Mole

There is an important difference between the way the mole is realised and the way the other base units of the SI are realised. Whilst the definition of the other base units and their associated *mise en pratiques* provide specific information about how they should be realised, the use of the mole does not depend on a particular method of realisation. For example, the use of the mole according to its current definition does not depend on the use of an experimental method that determines the number of entities in 0.012 kg of carbon-12 or one that compares the number of entities in an unknown sample with the number of entities in 0.012 kg of carbon-12. Clearly both of these would be impractical. If a new definition based on a fixed number of entities, such as the one discussed here, is adopted, it will still not require the use of such hypothetical methods that count the number of entities in a sample directly. The challenge of realising the mole would be unchanged under the new definition.

The challenge of realising the mole has been discussed elsewhere.[4,11] The recognised solution is that it is realised by the valid use of a primary method of measurement,[12] which has been defined by the CCQM as

"a method having the highest metrological qualities, whose operation can be completely described and understood, for which a complete uncertainty statement can be written down in terms of SI units."

By far the most widely used example of a primary method is by the weighing a sample of material of known purity and hence known relative molecular mass (A_r(X)) and then use of the formula for the amount of substance (Eqn. (15)):

$$n = \frac{m}{M_u A_r(\mathrm{X})} \qquad (15)$$

where m is the mass of the sample in kg (after correction for the mass of impurities). The use of this formula will continue to be extremely wide and will only differ by the introduction of the very small additional uncertainty associated with M_u as described in this paper.

7. Summary and Conclusions

It is something of a paradox that a concept such as the quantity 'amount of substance', and its unit 'mole', so widely used by practical chemists, are also the subject of widespread misunderstandings. We have presented a proposal to re-define the mole on the basis of a fixed number of entities. The basis for such a proposal is that the atomic weight of carbon 12 ($A_r(^{12}C)$) is defined to be exactly 12 by IUPAP/IUPAC and any revision of the definition of the mole must retain complete consistency with this.

There are strong arguments in favour of the proposal to fix N_A as part of a revised definition for the mole. This is most easily achieved by allowing M_u to have some very small uncertainty (equal to the uncertainty in the mass of the electron in the proposed system). This approach would have the advantage of allowing existing equations to be retained and used without alteration.

It would also introduce the same (relative) uncertainties for the parallel systems of atomic and molar masses. (*i.e.* The mass of one mole of X and one molecule of X would have the same relative uncertainty $u_r(M_u) = u_r(m_u)$).

The proposed new definition for the mole would simplify the link between the mole and the Avogadro constant, which has its own long and rich history.

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