A critique on the definition of the SI Unit Mole

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Abstract

The Draft Chapter 2 for SI Brochure, following redefinition of the base units states, that the XXth CGPM adopted a new definition of the mole. A committee is set to redefine four base units – the ampere, the kilogram, the Kelvin and the mole. We find inconsistencies in the units of molar mass, molecular mass and the relation connecting them through Avogadro constant. There are also problems with the symbols and the terms 'entity' used in the definition of mole and the role of isotopes in the specification of an entity *X*. We give a critical analysis of these issues in this article.

Key words: Amount of substance, Mole, molar mass**,** molecular mass, units, entity, Avogadro constant, Molar mass constant, Unified atomic mass constant

Introduction

The 'Draft Chapter 2 for SI Brochure, following redefinition of the base units'[1] states, that the XXth CGPM (20XX, Resolution XX, CR, XXX and *Metrologia*, 20XX, **XX,** XX) adopted the following definition of the mole:

> **The mole, is the 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 14X x10^{23} when it is expressed in the unit mol^{-1}**.

We also find the following equations given in the draft,

$$M(X) = [A_r(X)/12]\, M(12_C) = A_r(X)M_u \tag{1}$$

$$M(X) = N_A\, m(X) = N_A\, A_r(X) m_u \tag{2}$$

$$M_u = N_A\, m_u \tag{3}$$

In these equations *Mu* is the molar mass constant, equal to $M(^{12}C)/12$, and m_u is the unified atomic mass constant, equal to $m(^{12}C)/12$. Avogadro constant N_A = 6.002 14X x10^{23} mol^{-1}, $M(^{12}C) = A_r(^{12}\text{C})$ = 0.012 kg/mol = 12 g/ mol and $m_u = m(^{12}C)/12$ = 1 u = 1 Da[2]. $A_r(X)$ is the recommended symbol for relative atomic mass (atomic weight) of an entity *X,* where the entity *X* should be specified, and the recommended symbol for relative molar mass is *M(X).*

Amount of substance, *n*, is defined to be proportional to the number of specified elementary entities N in a sample, the proportionality constant being a universal constant which is the same for all entities is the reciprocal of N_A so that $n = N/N_{A.}$, $n(X) = N(X)/N_A$.

New definitions of scientific units are on the horizon now[3]. A committee is set to redefine four basic units – the ampere, the kilogram, the Kelvin and the mole – using relationships to fundamental constants, rather than abstract or arbitrary definitions. The new definitions are expected to take effect in May 2019.

Analysis

In this background we find it necessary that we take note of the inconsistencies associated with the units of the quantities: molar mass $M(X)$, molecular mass $m(X)$ and N_A, related as shown in equations (1) and (2) or with M_u, m_u and N_A, related as shown in equations (3). Besides, there exist some problems with terminology and symbols: $A_r(X)$ and $M(X)$, the entity, and the role of isotopes in the specification of an entity X. We discuss these issues below, under four heads:

1. Inconsistency in the units of Molar mass $M(X)$ and molecular mass or $m(X)$. Or the inconsistency in the units of Molar mass constant M_u, and of Atomic mass constant $m_{u.}$
2. Terminology and symbols, $A_r(X)$ and $M(X)$
3. Entity
4. Isotope

1. Inconsistency in the units of $M(X)$ (or M_u), and $m(X)$ (or m_u), and the relation between them

Molar mass $M(X)$, and the molar mass constant $M_{u,}$ have the units: kg/mol (or g/mol). Molecular mass $m(X)$ and the unified atomic mass constant $m_{u,}$ have the units[2,4]: Da or kg or g. N_A has the units: mol^{-1}. $A_r(X)$ *as a relative mass (ratio of masses)* has no units or dimensions. Conventionally, we express it in grams and call it gram atomic weight.

The unit 'g/mol' indicates the quantity of which it is the unit is an intensive property. For example, $M(X)$, the molar mass of species X, is an intensive quantity. It refers to the relative mass of a mole of species X. Its value does not depend on the mass of the sample under consideration or on the number of moles of the sample.

Similarly, $m(X)$ represents the relative mass of *one* entity of X. Its value does not depend on the mass of the sample under consideration or on the number of entities of X present in the sample. Therefore, it is an intensive quantity. As such, its units must reflect that fact. The units, Da or kg or g cannot do that. On the other hand, they give an impression that $m(x)$ with units of Da or kg or g is an extensive quantity, which it is not. Consistency requires $m(x)$ and m_u to have units Da/molecule or kg/molecule or g/molecule.

Both M_u and m_u represent an intensive property of species X at the macro and atomic levels respectively.

The units of g/mol for M_u, and Da or kg or g for m_u, reflect an inconsistency.

This issue should be addressed before the draft is finalized. In fact, this problem permeates chemical thermodynamics, where the units of properties of state functions such as standard enthalpy, standard free energy are given in text books variously in kJ/mol and kJ. The problem of units of equilibrium constant and its relation to standard free energy change are byproducts of this problem. The definition of entropy S in statistical mechanics: S = k ln W is another instance where the problem appears in disguise.

2. Terminology and symbols $A_r(X)$ and $M(X)$

The recommended symbol for relative atomic mass (atomic weight) of an entity X is $A_r(X)$ and the recommended symbol for molar mass of entity X is $M(X)$ where the entity X should be specified,.

Let us specify the entity to be HCl. Then, $A_r(HCl)$ represents the relative atomic mass of HCl. It is rather odd to talk of atomic weight of HCl which is not an atom but a molecule. Thus whenever, the entity X is a molecule, $A_r(X)$ gives a poor representation of the term – it talks about the mass of an atom when there is a molecule but not an atom. Similarly, when we specify the entity X to be an atom, say, 'He', $M(He)$ represents the molar mass of He, which doesn't sound odd since we are used to using molar mass of any species unmindful of the fact whether it is atom, molecule or ion etc. However, when we consider, *m(He)*, we mean molecular mass of He. That sounds odd since we are not talking about a molecule but about an atom.

Relative atomic mass (atomic weight) applies only to atoms. Relative molecular mass or relative molar mass applies to molecules.

3. Entity

(a) In the definition of mole[1], we find the phrase: 'elementary entity'. What is elementary entity? How is it different from entity? If both are same we can remove the adjective 'elementary' from the phrase in definition of mole.

(b) The definition of mole[1] further says, an entity may be an atom, molecule, ion, electron, any other particle or A SPECIFIED GROUP OF SUCH PARTICLES. The question naturally arises: How to specify a group of particles? Can a given group of particles have unique values for properties? Let us say, we have a group of particles consisting of atoms of He, Ar, molecules of N_2, O_2, CO_2, in certain proportion; does such a group of particles qualify to be an entity?

What is it we want to be included under the head 'specified group of particles'?

(c) In the explanation following the definition, we find this: ' ………. mole is the amount of substance of A SYSTEM that contains …... . 'Why 'a system'?

4. Isotope

Isotopes of a given element have same chemical properties, since the nucleus does not take part in a chemical reaction. For example ^{16}O or ^{17}O do not have different chemical properties. Each of them reacts with two atoms of hydrogen to form a water molecule. It is the ratio of these numbers that a chemical reaction (chemistry) is concerned with: $H:O:H_2O = 2:1:1$. This ratio does not depend on the kind of isotopes of the different elements that take part in the reaction.

More importantly, if isotopes are brought into the discussion or given any significance in the discussion of definition of mole, then insurmountable problems arise. Just to give an example, it becomes impossible to specify a chemical entity uniquely – Water molecules with different isotopes of oxygen become different entities; similarly, water molecules with different isotopes of hydrogen become different entities. Thus water molecule loses identity as a single entity. The specification of the entity H_2O becomes ambiguous unless one specifies the isotopic composition. Imagine specification of N_A entities giving details of isotopic composition of each water molecule in a mole!

Specific isotope of an element may be good for a standard unit of mass, but as a unit of standard of a chemical substance, it creates many avoidable problems.

Many problems that arise in chemistry can be resolved by recognizing that *'equivalent of a reaction'* is the basic unit of a chemical reaction.

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