

## Units for dimensionless counting quantities, enumeration, and chemical concentration

### 1. Amount of substance and number of entities

Amount of substance, AoS for brevity, is a **base quantity in the SI**, with the **symbol  $n$** . It is used for quantifying a chemical sample, particularly a pure chemical sample, in proportion to the number of **molecules or atoms** – or more generally the number of **entities** – in the sample, where the entity involved must be defined in any application. **The SI unit of AoS is the mole, symbol mol.**

Number of entities, NoE for brevity, with the symbol  $N$ , is **another quantity** used for essentially the same purpose as AoS. It is a counting quantity whose definition is implicit in the name: **number of entities** (or often **number of molecules**). It is a dimensionless quantity. **The SI unit of NoE is simply the number one, 1.**

NoE is not normally regarded as a base quantity of the SI, and it is not easy to see it as a derived quantity either (a derived quantity is defined as a product of powers of base quantities). Nonetheless NoE is a useful quantity. We could simply call it a dimensionless quantity, or a counting quantity, one of another class of quantities not covered by base and derived quantities. (Another name that I have used in my own notes for such quantities is to call them **pseudo-quantities**, and to call the corresponding units **pseudo-units**.)

The relation between the quantities AoS, symbol  $n$ , and NoE, symbol  $N$ , is given by the quantity equation

$$n = N/N_A \tag{1}$$

where the constant  $N_A$  is a fundamental constant which is the same for all entities, and is called the Avogadro constant. The entity is often, but not always, a single molecule or atom. But, for example, it may sometimes be convenient to use  $\frac{1}{2}\text{O}_2$  as an entity rather than an oxygen molecule  $\text{O}_2$ , or  $(1/5)\text{KMnO}_4$  rather than a potassium permanganate molecule  $\text{KMnO}_4$ , because the numerical factor makes the oxidation/reduction equations involving these molecules simpler (see for example the IUPAC Green Book, p.53 to 54 in the third edition 2007, or p.44 to 45 in the older second edition 1993).

The magnitude of the Avogadro constant is the same however the entity is chosen. **The numerical value of  $N_A$  determines the value of the unit mole.** For the accepted definition of the mole (either the current definition or the proposed new definition) the approximate value of the Avogadro constant is  $N_A = 6.022... \times 10^{23}$  molecules per mole, where I have introduced the dimensionless unit molecule which is actually equal to 1. The possible introduction of such units is the subject of these notes. Some argue that it is wrong to introduce such units, but others find them helpful. In what follows I shall use ‘molecule’ (or ‘entity’) as a dimensionless unit in this way, with the symbol ‘mcl’. Thus one might write the value of the Avogadro constant in the form:

$$N_A = 6.022... \times 10^{23} \text{ mcl/mol} = 6.022... \times 10^{23} \text{ mol}^{-1} \tag{2}$$

The equation in red is the expression usually used for  $N_A$  in the SI, avoiding the introduction of a dimensionless unit.

The Avogadro constant  $N_A$  is thus analogous to the Boltzmann constant  $k$  (or  $k_B$ ), which is a fundamental constant that may be regarded as the conversion factor between the quantities thermodynamic temperature  $T$  and energy  $E$  (energy per degree of freedom) in the equation  $E = kT$ . **The numerical value of  $k$  determines the value of the unit kelvin in terms of the joule.**

[In a similar way the Planck constant may be regarded as a conversion factor between the quantities frequency  $\nu$  and energy (quantum of energy)  $E$  in the equation  $E = h\nu$ . The magnitude of  $h$  may be thought of as determining the magnitude of the unit of energy  $E$  in terms of the unit of frequency  $\nu$ , the units being related by the factor  $J/Hz = kg\ m^2\ s^{-1}$ . Many, or perhaps all, of what we call fundamental constants may be thought of in a similar way, but this is a controversial statement which I do not wish to pursue here.]

## 2. Units for concentration: the quantity ‘molecule’ or “entity” regarded as a unit

Atmospheric chemists describe the concentration of minor constituents in the atmosphere using the unit ‘molecules per centimetre cubed’, which I will write  $\text{mcl}/\text{cm}^3$ , using the symbol  $\text{mcl}$  for the unit molecule. Chemists more commonly use the concentration unit mole per litre,  $\text{mol}/\text{dm}^3$ . The conversion factor between these units involves the Avogadro constant, and is not dimensionless, so that the two quantities are dimensionally different and should really have different names and different symbols. I shall call them ‘molecular or entity concentration’,  $c_e = N/V$ , and ‘molar concentration’,  $c_m = n/V$ . The relation between these two quantities is

$$c_e = c_m N_A \quad \text{note the units: } \text{mcl}/\text{cm}^3 = (\text{mol}/\text{dm}^3)(\text{mcl}/\text{mol})(\text{dm}^3/\text{cm}^3) \quad (3)$$

It is tempting to write a relation between the corresponding units,  $\text{mcl}/\text{cm}^3$  and  $\text{mol}/\text{dm}^3$ , but that must be done with care and may be confusing because the two quantities  $c_e$  and  $c_m$  are dimensionally different. Instead it is best to give the corresponding values of the two different quantities  $c_e$  and  $c_m$ . Thus if a minor atmospheric pollutant were detected with the molecular concentration

$$c_e = 5000 \text{ mcl}/\text{cm}^3 = 5000 \text{ cm}^{-3} \quad (4)$$

then the corresponding molar concentration would be

$$c_m = c_e/N_A = \left( \frac{5000 \times 10^3}{6.022 \dots \times 10^{23}} \right) \text{ mol}/\text{dm}^3 = 8.302 \dots \times 10^{-18} \text{ mol}/\text{dm}^3 \quad (5)$$

where I have used the expression for  $N_A$  given in eq.(2) above. The factor  $10^3$  converts  $\text{dm}^3$  to  $\text{cm}^3$ .

Some would argue that the unit molecule (symbol  $\text{mcl}$ ) is equal to 1, and is not a unit, and should be omitted from these equations, and they would justify their view by saying that this is how the SI should properly be used. I have written in red the way in which they would like to see the equations written. I have written in black the way in which atmospheric chemists actually write their equations.

The symbol  $\text{mcl}$ , for ‘molecule’, appears in the place of a unit, which is why it seems reasonable to describe it as a unit. On the other hand the word ‘molecule’ in the unit

‘molecule per centimetre cubed’ is also conveying information about the quantity involved, molecular concentration. It seems that in the statement “ the concentration of the impurity was 5000 molecules per centimetre cubed” the word ‘molecule’ is serving two purposes: it both conveys information about the quantity, and it also plays the part of a unit in conveying the value of the concentration.

[ In describing current practice among chemists, they seldom introduce the quantity symbols  $c_e$  and  $c_m$  that I have used. They generally talk of ‘concentration’ without introducing any symbol for the quantities concerned. I believe they often do not realise that there are two different quantities involved, with different dimensions. Most chemists tend to use the units without mentioning the quantities involved. I hesitate to criticise them for this, because for the most part they get everything right nonetheless! However I personally believe it is helpful always to distinguish carefully between quantities and units, and to make use of both concepts. For that reason I tend to make a practice of introducing and using a symbol for each of the quantities that appear in the quantity equations involved, in addition to the names and symbols for the units. ]

### 3. Rate constants in chemical kinetics

The same problem appears in a more significant form in expressions for the value of rate constants in chemical kinetics. For example, the rate of a second order reaction may be expressed in the form

$$\frac{dc}{dt} = -k c^2 \quad (6)$$

where  $c$  is the concentration of (one of) the reactants,  $t$  is time, and  $k$  is a second order rate constant. This implies that  $k$  should have the dimensions  $(\text{concentration})^{-1} (\text{time})^{-1}$ , and the value of an experimentally-determined rate constant might thus be expressed in the form [3]

$$k = 10^{8.2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (7)$$

$$\text{or } \lg(k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = 8.2$$

However theoreticians calculate rate constants in terms of molecular concentration, in which the same rate constant (i.e. the same value of the constant) might be written

$$k = 10^{-12.6} \text{ cm}^3 \text{ mcl}^{-1} \text{ s}^{-1} \quad (8)$$

$$\text{or } \lg(k/\text{cm}^3 \text{ mcl}^{-1} \text{ s}^{-1}) = -12.6$$

The conversion factor between these different ways of expressing the same rate constant involves the Avogadro constant expressed in the form

$$N_A = 6.022 \times 10^{23} \text{ mcl/mol} = 10^{23.8} \text{ mcl/mol} \quad (9)$$

The symbol mcl is used here for the dimensionless unit ‘molecule’, but most kineticists would write out the word ‘molecule’ for the unit mcl. These equations break two of the formal rules for the use of the SI, in that the pseudo-unit ‘molecule’ should be set equal to one, and should not appear, and also the dimension of the molecular rate constant is not the same as the dimension of the molar rate constant, so that it should strictly have a different symbol to go with the different definition. However if you delete the unit ‘molecule’ or ‘mcl’ from the above equations, and use the same symbol for the molecular and molar rate constants (which is what I have actually done in eq.s (7) and (8) above!),

there is no doubt that the results become more difficult for students – and for many of their teachers – to understand.

This is an example of a case where scientists working in a specialised field have discovered what suits them best, and they act accordingly. They are not concerned with the fact that they are breaking the rules of the SI. I believe it is a case where the SI should somehow be adapted to their needs, and that it would be pointless to suggest that they should adopt the formal rules of the SI in their present form. They would simply ignore the rules, which is what happens at present.

#### 4. How might we offer advice on the use of units for dimensionless quantities

Our objective is to perhaps offer advice on the use of units for dimensionless quantities, like the example of number of entities  $N$  considered in the example of molecular concentration considered here.

My own conclusion from all this is to introduce the dimensionless unit ‘molecule’ when it is helpful to do so, and to omit it otherwise. I am not sure how else to meet the needs of practising scientists.

As an example of situations where it would *not* be helpful to require the inclusion of this extra dimensionless unit, suppose we wish to express the value of an atomic mass. Are we to say, for the mass of the proton,

$$m_p = 1.672\,623 \times 10^{-27} \text{ kg} \quad (10)$$

or should we always write the unit: kg/mcl? Are we to write the value of the Boltzmann constant

$$k = 1.380\,658 \times 10^{-23} \text{ J/K} \quad (11)$$

or should we always write the unit: J mcl<sup>-1</sup> K<sup>-1</sup>? Compare the unit for  $k$  with the unit for the molar gas constant,  $R = 8.315 \text{ J mol}^{-1} \text{ K}^{-1}$ , and the equation

$$R = N_A k \quad (12)$$

The choice is equivalent to the choice between writing  $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$ , or  $N_A = 6.022 \times 10^{23} \text{ mcl/mol}$ . The only solution to these problems that I can see at present is to treat the dimensionless unit ‘molecule’ as a unit that may be included whenever it clarifies the meaning, but may be set equal to one and omitted when there seems no reason to include it.

I am tempted to say that we should not discourage the use of the dimensionless unit ‘molecule’ (or ‘entity’) in the manner illustrated in equations (7), (8), and (9). Instead I would prefer to give the advice that such units may be introduced when they aid understanding, but they may alternatively be omitted and replaced by the number one when they are not needed, as in equations (10), (11), and (12). My reasons are:

1. The chemists argue that it is easier to understand the equations as they write them. When the dimensionless unit is omitted, as in the red equations, they say they are more difficult to understand. We should listen; they perhaps have a point!
2. Even those that listen with attention to the arguments for the SI will almost certainly continue to adopt their current practice in this example. We shall achieve nothing by

recommending a revised way of doing things that they find more difficult, when they are happy with their current practice, and they follow it without making errors.

3. I think it is a mistake for committees of (so-called) wise experts to lay down rules that the community do not really like. Our objective should be to persuade the community of the advantages of the SI, rather than to lay down rigid rules. We are not dictators! The strongest argument for rigid adherence to the rules of the SI is that it makes it easier for those coming from other specialist fields if we all follow the rules. That seems perhaps not to be an effective argument in the examples considered here.

However I do strongly believe in encouraging the use of the recommended quantity names and symbols, and quantity equations as in (1) and (3) above, in addition to the use of the appropriate unit names and symbols. Quantity equations remain true regardless of the units used, and help to provide a clear understanding of the science involved.

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