

## Avogadro's Number, the Mole and the Kilogram

The American Chemical Society Committee on Nomenclature, Terminology and Symbols met August 23, 2010 to discuss the definition of the mole. This was in anticipation of a later meeting by an international body, the Conférence Générale des Poids et Mesures, that will consider a number of definitions for measurement standards including the mole and the kilogram.

In 1983 the meter was redefined for the International System of Units (SI). Since then, it is defined as the distance travelled by light in vacuum in  $1/299,792,458$  of a second. This makes the speed of light,  $c$ , exactly  $299,792,458$  m/s. The second too has been defined exactly to be: the duration of  $9,192,631,770$  periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of a cesium 133 atom. This definition was made in 1960 and represented the limit of human time measuring ability available at that time. These two definitions make the meter  $9,192,631,770/299,792,458$  periods of vibration of a cesium atom (cesium clock). It is perhaps not surprising that this ratio is not a whole number but is instead:  $30.663318988498\dots$  a number that can be computed by Mathematica and is not a repeating decimal even after 5,632 decimal digits have been computed. Thus, using the definition of a meter would require counting  $30.6633\dots$  vibrations of the cesium clock to mark off one meter of distance traveled by a beam of light. Clearly a better standard for the unit of time than that given in 1960 would be needed to determine the duration of the fractional vibration (in 2010 an interval of about *twenty attoseconds* was measured). Determining a meter with light may not be trivial to do but at least the maintenance of the standard iridium-platinum meter stick in Paris is no longer necessary. By exactly defining the meter and the second, a conceptual advance has been made, and is manifested by an exact value for the speed of light. Implementation of these definitions by practical means will improve with time. The key point is that there is a difference between the conceptual definition and the practical implementation of that definition. What is the real conceptual value of a definition that is ultimately impractical?

A similar situation exists for the mole and the kilogram. The current definition (adopted in 1971) of the mole is tripartite [1]:

*The mole is the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon 12; its symbol is "mol".*

*When the mole is used, the elementary entities must be specified and may be atoms, molecules, ions, electrons, other particles, or specified groups of particles.*

*(Addendum in 1980) In this definition it is understood that unbound atoms of carbon 12, at rest and in their ground state, are referred to.*

Note that this definition is tied to the kilogram. Presently the kilogram is defined by a standard in Paris, *Le Gran K*, a cylinder of an iridium-platinum alloy. There are several problems with this standard not the least of which is that its mass fluctuates in value [2] depending on how it is cleaned and maintained. If that is so then the number of entities in a mole must also fluctuate according to the above definition. In 2009 I.M. Mills and M. Milton [3] proposed that we should make the definition of the mole independent of the definition of the kilogram. They wrote:

*“Given that: (a) a definition of the mole in a way that is independent of mass is desirable; (b) the mole is often thought of by chemists as an Avogadro number of entities; and (c) the name of the ISQ (International System of Quantities) base quantity “amount of substance” has been a source of much confusion, ICTNS recommends to the Bureau that:*

*The recommendation of the CCU (Consultative Committee on Units) of the BIPM, that the mole be defined as follows:*

*“The mole, 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, is such that the Avogadro constant is equal to exactly  $6.022\ 141\ 79 \times 10^{23}$  per mole.*

*Thus, we have the exact relation  $N_A = 6.022\ 141\ 79 \times 10^{23} \text{ mol}^{-1}$ . The effect of this definition is that the mole is the amount of substance of a system that contains  $6.022\ 141\ 79 \times 10^{23}$  specified elementary entities.”*

Their choice of numerical value for Avogadro’s number is based on the current NIST CODATA value [4]  $6.022\ 141\ 79 \times 10^{23}$  with a standard deviation of  $0.000\ 000\ 30 \times 10^{23}$ . Given this definition, one would also say, *a fortiori*, that a kilogram is defined exactly by:

$$0.012 \text{ kg} = 6.022\ 141\ 79 \times 10^{23} \text{ carbon 12 atoms}$$

unbound, at rest and in their ground state. How should we visualize this? Do we place the atoms in a sack or box? When carbon atoms get close to each other they spontaneously form bonds; i. e. *dangling bonds* are unstable, or said equivalently, *free radicals* are extremely reactive. How much does this affect the result of this definition? Again we have a conceptual advance but perhaps not a very practical one. Are unbound carbon atoms truly *elementary entities* as supposed in the last line of Mills and Milton’s definition? In practical terms methane molecules, being very stable, are more likely candidates for *elementary entities* than are unbound carbon 12 atoms, being highly reactive. Finally, how do we achieve the condition of pure carbon 12 isotopes when the natural state is one in which there is slightly more than one percent of carbon 13 present? Perhaps with time it will become possible to arrange for larger and larger amounts of pure carbon 12 and one day obtain and isolate as many as Avogadro’s number of them.

Prior to the paper by Mills and Milton, T.P. Hill and R.F. Fox proposed an exact value for Avogadro’s number based on visualizing a cubic array of atoms [5]. Hill, a mathematician, envisaged an extended cubic array of carbon atoms with  $n$  atoms on a edge. We will consider the

real tetrahedral arrangement of carbon atoms in the diamond crystal structure in a moment. While *cubane* does have a cubic structure, the extended cubic structures Hill imagined do not exist. But they do have a conceptual advantage. An exact number such as  $6.02214179 \times 10^{23}$  is very difficult to comprehend, i.e. it is 602 214 179 000 000 000 000 000 (602 thousand billion billion). That's 15 zeros after the 9. Instead of this monumental number, our proposal based on the cubic structure implies that some number of atoms on a side, say  $n = 84\,446\,889$ , would yield a cube with

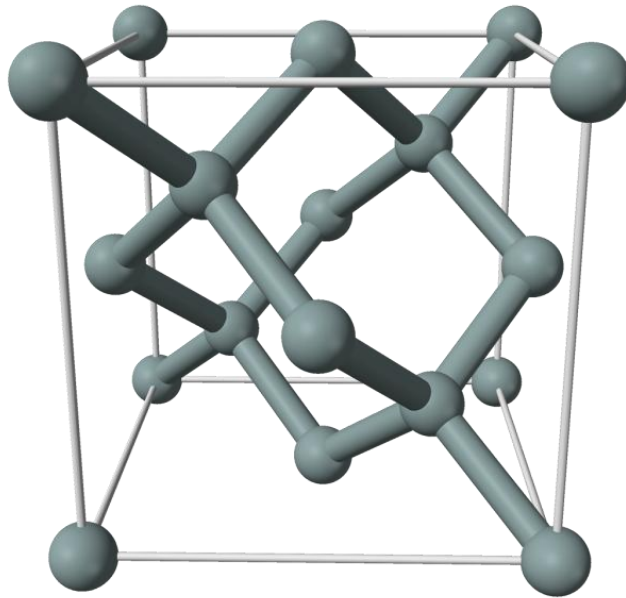
$$84446889^3 = 602\,214\,162\,464\,240\,016\,093\,369$$

atoms altogether. The number of atoms on a side,  $n$ , is the cube root of Avogadro's number and has only 8 digits as was initially observed by Fox. To say there are somewhat more than 84 million atoms on an edge is indeed comprehensible. This result is within one standard deviation of the value quoted from the NIST CODATA listing. The next bigger  $n$  gives the result

$$84446890^3 = 602\,214\,183\,858\,071\,454\,769\,000$$

This is a little bigger than the CODATA mean value and also within one standard deviation. Either choice is suitable for Avogadro's number and the uncertainty in the value of  $n$  is one part in  $10^8$ . Even though the second choice is closer to the CODATA mean value than the first choice, there is nothing sacred about the precise mean value, given the magnitude of the standard deviation. Mills and Milton chose the exact mean value as if it were special. We proposed a value for the cube root that was almost completely predetermined by the measured value. I must point out that when we made our original proposal the NISDT CODATA mean value for Avogadro's number was  $6.0221415 \times 10^{23}$  so that the cube root was better given by 84 446 888 and had more uncertainty. The key point is that if one imagines a cubic array of atoms then the number of atoms on an edge is 84 446 890, a large but comprehensible number. It implies the exact value for Avogadro's number given above.

Let us return to the issue of real crystal structures for carbon. We must also address the problem of the difference between unbound atoms and chemically bonded atoms in a crystal. Carbon can form a face centered cubic crystal structure based on the tetrahedral orbitals of carbon. The unit cell, a structure with a cubic envelope, is shown below



Note that there are 8 corner atoms, 6 face center atoms and 4 interior tetrahedrally coordinated atoms, for a total of 18. Only 4 of the corner atoms of the unit cell are bonded to the rest of the structure but become bonded as the number of unit cells is increased (except for some of the surface atoms). For example, this picture shows a unit cell for 2 atoms on an edge whereas with 3 atoms on an edge there would be 8 connected unit cells containing 27 unit cell corner atoms, 36 face center atoms and 32 interior tetrahedrally coordinated atoms, for a total of 95 atoms. This is perhaps not too easy for the reader to verify in his/her head but a simple drawing can be used to verify the result. In fact a little effort shows that if there are  $k$  atoms on an edge the total number of atoms in the face centered cubic structure is given by  $8 \times k^3 - 18 \times k^2 + 15 \times k - 4$ . Plugging in  $k = 2$  and  $k = 3$  yields 18 and 95 respectively. When  $k = 4$  the result is 280 which can be verified by a drawing with 4 atoms per edge. Now we can ask how big  $k$  needs to be to match Avogadro's number. We find that

$$8 \times 42223446^3 - 18 \times 42223446^2 + 15 \times 42223446 - 4 \\ = 602\,214\,194\,554\,987\,427\,447\,486$$

This is well within one standard deviation of the CODATA mean value. It provides yet another choice for the exact value of Avogadro's number. For large value of  $k$  such as used here, the leading term,  $8 \times k^3$  dominates the result implying that  $n \cong 2k$ . Only the last digit is slightly uncertain. We have ignored the fact that about half of the corner atoms on the surface are unbound but this only affects the 4 on 194 above since the number is of order  $k^2$ .

In the current definition of the mole, and also in the definition proposed by Mills and Milton, there is reference to unbound atoms. We have already stated that this is a fiction, perhaps of conceptual simplicity, but a fiction nevertheless. It is not unlike our fiction of an extended cubic array of carbon atoms. With the diamond structure, at least the imagined arrangement of atoms is real, but it does involve atomic bonds. By the way, silicon allows the same face centered cubic unit cell structure as diamond. If we want to use our defined value of Avogadro's number to define the mole and then to define the kilogram we must account for the amount of mass lost

as a result of chemical bonding. Each carbon-carbon single bond lowers the energy by  $5.76 \times 10^{-10} nJ$ . This is 347 kJ/mol, or 82.935 kcal/mol. Using Einstein's mass-energy identity,  $E = mc^2$  implies that the bonding energy decreases the effective mass of the diamond. Each bulk atom makes 4 covalent bonds but these are shared, half and half, with other atoms so that there are 2 bonds per atom throughout the structure. On the surface half of the bonds are missing or dangling as free radicals. In diamond they are usually bonded to hydrogens and not left dangling. First of all the amount of mass equivalent is given by

$$-\Delta m = \frac{347 \text{ kJ/mol}}{c^2} = \frac{347 \times 10^{10} \text{ erg/mol}}{299792458^2 \text{ m}^2/\text{s}^2} = 38.6 \times 10^{-10} \text{ gm/mol}$$

If we have pure carbon 12 then one mole of carbon, as diamond, has a mass of almost 12 gm (60 carats), or exactly 12 gm minus the lost mass equivalent of the bonding energy, i.e. about 38.6/12 parts in  $10^{10}$ . This error is smaller than the other uncertainties we have mentioned. So why don't we define the kilogram in terms of a cubically cut 60 carat diamond with 42,223,446 atoms on an edge. This is a little bit different than using a mole of unbound carbon 12 atoms to get exactly 12 gm but it is more realistic. The surface atom issue affects roughly  $2 \times 6 \times 42,223,446^2$  atoms. This is roughly  $2 \times 10^{16}$  atoms. The factor of 6 is for the 6 faces of a cube and the factor of 2 is for the face centered atoms in addition to the edge atoms that number 42223446 (for 42223446 edge atoms there are 42223445 face centered atoms but this difference is truly minor). The bulk atoms are over  $10^7$  times as abundant as the surface atoms and dominate the result. Nevertheless this error is bigger than the others and could add  $2 \times 10^{16}$  atoms of hydrogen to the surface and to the mass of the Avogadro diamond. While important, this is still nothing compared the the isotopic purity problem. Perhaps future technology can be used to reduce the amount of surface atoms bound to the free radical surface carbon atoms.

In summary, we propose fixing Avogadro's number,  $N_A$ , to be exactly

$$N_A = 602\,214\,194\,554\,987\,427\,447\,486$$

This corresponds to the face centered crystal structure of diamond. If made from pure carbon 12 isotopes the mass of this structure would be defined to be exactly 0.012 kg provided there are no atoms bound to the dangling bonds on the surfaces of the structure. This new definition includes the chemical bond energy, just as does the current accepted definition wherein the energy of bound electrons on carbon nuclei is included as well as the electron masses (carbon 12 has 6 protons, 6 neutrons and 6 electrons that are bound together by nuclear forces and chemical forces, all of which is included). The two definitions give slightly different values but no greater than the change from oxygen 16 to carbon 12 did. A look at the face centered crystal structure unit cell above verifies that adjacent atoms on the edge of the structure are not directly covalently bonded to each other. Instead they are 3.567 angstroms apart, not the covalent C-C bond spacing of 1.54 angstroms, making an edge

$$42223445 \times 3.567 \text{ \AA} = 150,611,028.315 \text{ \AA}$$

long. This is 1.50611028315 *cm*. Combining the meter and time standards, it may be possible to determine a length with this precision using light. Of course the atom spacing at the surfaces

will be slightly different from the bulk spacing so that less precision may be adequate. In the end the conceptual gain is that the number of atoms on the edge of such a crystal, 42,223,446, is comprehensible.

### References

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- [4] <http://physics.nist.gov/cuu/Constants/index.html>.
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