Ask the Historian

# Why Has the Value of Avogadro's Constant Changed Over Time?

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### Question

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## Answer

As noted in an earlier column, the concept of Avogadro's constant or number ( $N_A$ ) was not introduced by Avogadro in 1811, but rather by the French physical chemist, Jean Perrin (figure 1), in 1908 (1). It may be formally thought of as the value of the conversion factor between the gram (g) and the unified atomic mass unit (u), as may be seen from the requirement that the molecular mass of a given atom, molecule, or ion, as expressed in atomic mass units per entity, must be numerically equal to the molar mass of the same substance as expressed in grams per mole. Thus for example:

### 207.2g/mol Pb =

 $(207.2 \text{ u/Pb atom})(1\text{g/N}_A \text{ u})(N_A \text{ Pb atoms}/1 \text{ mol Pb})$ 

There are two reasons why the value of  $N_A$  has changed over time. The first, and most obvious, is that any change in the standards used to define either the atomic mass unit or the gram will cause a shift in the value of their conversion factor and hence in the value of  $N_A$ . Such a change occurred in 1960 when the standard for the atomic mass unit was changed from the O = 16 scale to the  ${}^{12}C = 12$  scale. A similar shift would have occurred around 1900 with the shift from the H = 1 to the O = 16 scale, but, of course, the concept of  $N_A$ was not a part of chemistry at that time (2). The second reason for a shift in the value of  $N_A$  has to do with an ever increasing ability to accurately measure the value of this constant, as illustrated by the selected examples given in the accompanying table (3).



Figure 1. Jean Perrin (1870-1942).

The standard definition of  $N_A$  is that it is the same number of entities as there are carbon atoms in exactly 12 grams of carbon-12. Consequently students are often surprised when they are told that its numerical value is actually fixed by the conversion factor between the gram and the atomic mass unit. If chemists had failed to adopt the metric system and had instead continued to use some older conventional mass unit, such as the ounce, drachm or grain, to weigh chemicals in the laboratory, it would still have been expedient to maintain a numerical identity between atomic and molecular masses, as measured in atomic mass units, and the molar masses of the various substances as measured in the lab. Under such conditions, Avogadro's constant would have had a very different value, and it makes an interesting teaching exercise to assign

Year	Author	N <sub>A</sub> /10 <sup>23</sup>
1908	Perrin	6.7
1917	Mullikan	6.064
1929	Birge	6.0644
1931	Bearden	6.019
1945	Birge	6.02338
1951	DuMond	6.02544
1965	Bearden	6.022088
1973	Cohen	6.022045
1987	Deslattes	6.022134
1994	Basile	6.0221379
2001	De Bièvre	6.0221339

Table 1. Selected values reported for the value of  $N_A$  over time. A more complete listing may be found in reference 3.

students the task of calculating the corresponding values of  $N_A$  for each of these alternative macroscopic mass units. Likewise, students are often puzzled as to why Avogadro's constant has such an odd numerical value and it is also of interest to challenge them to invent a new macroscopic mass unit for laboratory use that would yield a more aesthetic number, such as  $1.0 \times 10^{24}$  for the value of  $N_A$ .

### Literature Cited

1. W. B. Jensen, "How and When Did Avogadro's Name Become Associated with Avogadro's Number?," *J. Chem. Educ.*, **2007**, *84*, 223.

2. Estimates of the number of molecules per given volume (though not the number per mole) were made by various 19th-century physicists and can be retrospectively used to calculate estimates of  $N_A$ . See, for example, R. W.

Hawthorne, "Avogadro's Number: Early Values by Loschmidt and Others," J. Chem. Educ., **1970**, 47, 751-755.

3. Based on the values reported in P. Becker, "History and Progress in the Accurate Determination of the Avogadro Constant," *Rep. Prog. Phys.*, **2001**, *64*, 1945-2008. The author would like to thank Juris Meija of the Institute for National Measurement Standards of Canada for bringing this report to his attention. Readers should be warned, however, that the author of this report makes numerous incorrect historical statements about the origins of Avogadro's work and related concepts, such as the false implication that Avogadro derived his hypothesis from the kinetic theory of gases.

Do you have a question about the historical origins of a symbol, name, concept or experimental procedure used in your teaching? Address them to Dr. William B. Jensen, Oesper Collections in the History of Chemistry, Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172 or e-mail them to jensenwb@ucmail.uc.edu

# Update

The fact that the numerical value of  $N_A$  is ultimately fixed by the conversion factor between the gram and the atomic mass unit was first pointed out in the *Journal of Chemical Education* by F. E. Brown in 1933:

\* F. E. Brown, "Molecular and Atomic Weights," J. Chem. Educ., **1933**, *10*, 308-309.

yet 40 years later Hawthorne was describing this view as "remarkable" by which he obviously meant "eccentric:"

\* R. M. Hawthorne Jr., "The Mole and Avogadro's Number: A Forced Fusion of Ideas for Teaching Purposes," *J. Chem. Educ.*, **1973**, *50*, 282-284.

That an experienced teacher like Hawthorne had difficulty grasping this point says much about how this concept is or is not taught in the average chemistry textbook.