Letter

# The Mythical Dependence of Boiling Points on Molecular Mass

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The myth that molecular mass, as such, greatly affects boiling points, persists and even seems to gather strength. This conventional 'wisdom' was disposed of long ago[1] but keeps popping up all over, as will be shown below, albeit for brevity, with a narrow set of examples.

Some writers note that gravity is not crucial, but they still allege the importance of mass itself. Others however, even in some secondary physics textbooks, have actually stated that gravity makes the difference.

***Is boiling like escaping from gravity?***
Laing examined the boiling points of small molecules versus molecular mass.[2] However, a molecule escaping from a liquid is not closely analogous, as claimed, to 'a satellite breaking free from the earth's gravitational field' with the requirement of 'a minimum escape velocity', such that the required kinetic energy is proportional to the mass of the satellite at that escape velocity.

The difference is that all the mass of the satellite is acted upon by the restraining force (or curved space-time) of gravity, while the mass of the boiling molecule is practically irrelevant to the crucial van-der-Waals, London, or mutual-polarization forces in the liquid. Thus germanium tetrachloride, hexafluorobenzene, pentacarbonylruthenium, and tetrapropyltin do not boil appreciably higher than carbon tetrachloride, benzene, pentacarbonyliron, or tetrapropylmethane, respectively, where, in most cases, the additional potentially polarizing and polarizable electrons, not to mention additional nucleons, of the heavier molecules are buried in the center.

Much more information is available elsewhere[3] and in references therein. The unknown boiling points of a great variety of substances are also predicted there.

***What does $H_2$ prove?***
In the paper 'A Thermodynamic Analysis to Explain the Boiling-Point Isotope Effect for Molecular Hydrogen'[4] the title is just right, but we need to point out clearly, and perhaps often, that the mass effect, which is mentioned repeatedly and properly throughout the article is very small in the rest of chemistry. Too many otherwise well-prepared chemists still teach and write about a supposed general dependence of boiling point on molecular 'weight' or mass, and some readers may take this article as supporting that.

Even for molecular hydrogen, the difference in boiling points between 20.4 K for $H_2$ and 23.5 K for $D_2$, although important at these low temperatures, is perhaps not striking for a mass ratio of 1 to 2.

***Does mass directly affect melting points?***
For the related variable of melting point, the molecular mass as such is cited currently[5] and repeatedly as a relevant independent variable. This is misleading for melting points too, although the importance of symmetry is well elucidated in that paper.

Let's give students the useful and interesting information in both of these articles[4, 5], together with a perspective[3] that incidentally exposes the uniqueness of molecular hydrogen with regard to the importance of mass.

***How decisive is molecular surface area?***
Mebane et al. correlate the physical properties of organic molecules with computed molecular surface areas.[6] This should recall the earlier general (not just for organics) correlation of boiling points with the ¾ power of the polarizabilities of the outer atoms.[3] Polarizability, as noted there, is closely related to volume, and of course surface area is proportional to the ⅔ power of volume for any given shape.

The ¾ and ⅔ powers differ only slightly, but the former, applied to polarizability (as London theory suggests and as Mebane et al. mention in passing) rather than to volume itself, covers all types of volatile molecules having low polarity, and over a wider range of boiling temperatures, although it has not yet been used for a great variety of physical properties. Students and teachers may wish to be alerted to this related but different work.[3]

Another point is that entirely different functions had to be chosen to correlate boiling points for different classes of substance, i.e. a logarithmic one for the alkanes, and a second-order polynomial for the alcohols.[6] At least with these related (organic) molecules, we might have expected a single type of function to work if it were potentially more fundamental than empirical.

### *Conclusion*

Students are found to be well able to understand that molecular mass per se has a nearly always negligible influence on boiling temperatures. This result is supported both by theory and by the observations of nearly constant boiling points in various series of both organic and inorganic substances whose masses vary greatly while their polarizabilities at their molecular surfaces are nearly constant. We need to bury once and for all the contrary but false conventional wisdom, however entrenched it may be. Polarizability is found to be much more useful for the practical prediction of unknown boiling points for all sorts of only slightly polar substances.

### References

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