

Enthalpies of Formation: Validation of ATcT Data and a Recommendation for Best Practice in Determining the Energy Density of Compounds

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General aspects

The determination of the enthalpy of formation of a chemical compound was traditionally done experimentally by combustion calorimetry. This is no longer the case for a number of reasons including health and safety issues, expense, laboriousness and because it is an unfashionable research area.

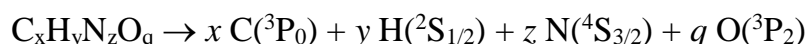
Fortunately computational quantum chemistry has emerged as an alternative methodology with the increases in computer performance and improvements in theoretical methods allowing the rapid and reasonably accurate determination for many different compounds including those which have only a transient existence.

One of the primary outcomes of determining the formation enthalpy of a compound is to be able to deduce its energy density which means in effect that one can measure the amount of energy that can be stored in that compound.

Computational methodology

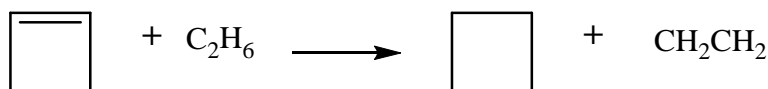
In this work the values present in the Active Thermochemical Tables of Ruscic [1] are treated as exact and compared to the mean value obtained from four theoretical methods. These include Petersson's G3 and G4 schemes [2] and Pople's CBS-QB3 and CBS-APNO model chemistries [3].

The approach is to use the atomisation method whereby one computes the enthalpy change for the reaction:



Since the enthalpies of formation of the atoms are very well-known the formation enthalpy of the target molecule can be deduced. This is the principal approach used here.

Confirmation or reassurance can be obtained by computing the enthalpy change for a working or isodesmic reaction such as:

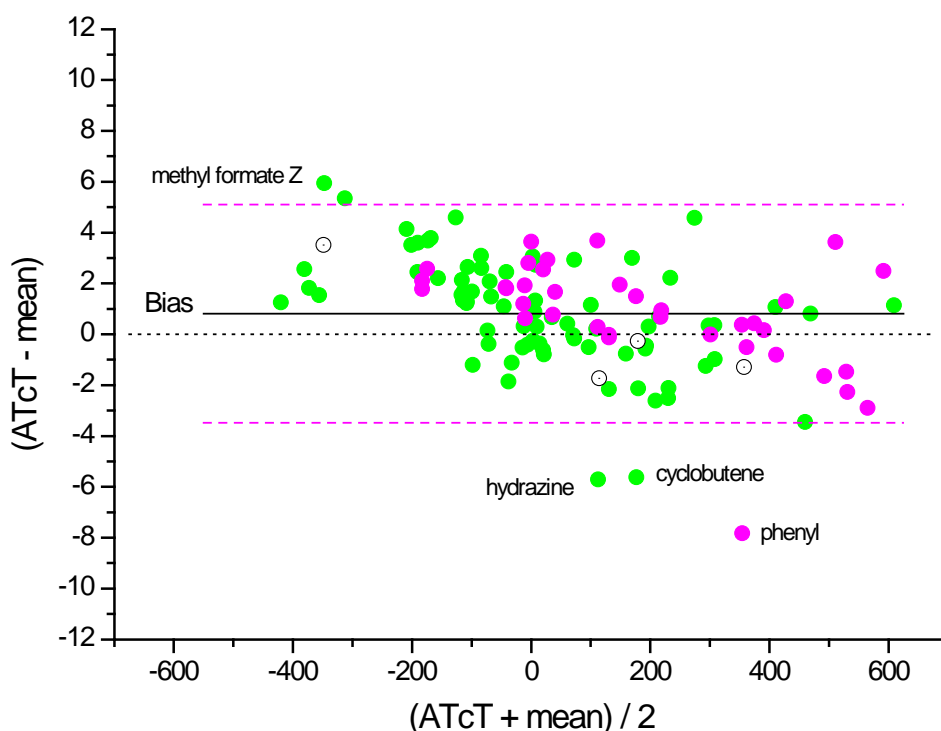


where error cancellation is anticipated to play a very big role in obtaining more precise results. However this approach is crucially dependent on accurate formation enthalpies

for the participating species or chaperons in order to compute a result for the target molecule.

Results

Preliminary results for 76 closed shell (green circles) and 36 open shell (magenta circles) species are shown in the Figure which is the form of a Bland Altman or Tukey mean difference plot. The data shown are for $\Delta_f H^\circ(0\text{ K})$ in kJ mol^{-1} and the bias is 0.80 kJ mol^{-1} and the 95% confidence limits are $\pm 4.3\text{ kJ mol}^{-1}$.



It is evident that the tabulated values for hydrazine, cyclobutene and methyl formate, and for the phenyl radical are outliers and deserve closer inspection.

When these changes are applied the open circles in the Figure are the result.

References

- [1] <http://atct.anl.gov/>
- [2] Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Rassolov, V.; Pople, J. A., Gaussian-3 Theory Using Reduced Moller-Plesset Order. J. Chem. Phys. 1999, 110 (10), 4703-4709; ibid, 2007, 126, 084108..
- [3] Montgomery, J. A.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A., A Complete Basis Set Model Chemistry. VII. Use of the Minimum Population Localization Method. J. Chem. Phys. 2000, 112, 6532-6542; ibid 1996, 104, 2598-2619.