

APPROXIMATIONS FOR HIGH-ACCURACY THEORETICAL THERMOCHEMISTRY

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The Active Thermochemical Tables (ATcT) approach by Ruscic^a incorporates data for a large number of chemical species from a variety of sources (both experimental and theoretical) and derives a self-consistent network capable of making extremely accurate estimates of quantities such as temperature dependent enthalpies of formation. The network provides rigorous uncertainties, and since the values don't rely on a single measurement or calculation, the provenance of each quantity is also obtained. To expand and improve the network it is desirable to have a reliable protocol such as the HEAT approach^b for calculating accurate theoretical data.

Anharmonic zero-point-energies are essential for accurate enthalpies of formation even at 0 K. Coupled Cluster based vibrational perturbation theory (VPT2) quickly becomes prohibitively expensive for larger, more chemically relevant molecules. Here we present benchmark work based upon testing the use of B3LYP and MP2 based VPT2 in-place of CCSD(T). The benchmark set includes some species from the original HEAT set^b, as well as some larger organic ($C_aH_bO_c$) species. We also consider scaled harmonic zero-point-energies based upon recent work^c with the B2PLYP double hybrid functional and comment on its outlook for the same benchmark set as the DFT and MP2 VPT2 approach. The derived methods are implemented in a fully automated computational workflow.

^aB. Ruscic, Active Thermochemical Tables (ATcT) values based on ver. 1.118 of the Thermochemical Network (2015); available at ATcT.anl.gov

^bA. Tajti, P. G. Szalay, A. G. Császár, M. Kállay, J. Gauss, E. F. Valeev, B. A. Flowers, J. Vázquez, and J. F. Stanton. JCP 121, (2004):11599.

^cM. Kesharwani, B. Brauer and J.M.L. Martin. J.Phys.Chem. A 119,(2015):1701