Active Thermochemical Tables: A Divertimento in Thermochemistry for the 21st Century

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Active Thermochemical Tables (ATcT) have been hailed in the scientific literature as the most significant improvement in thermodynamics in several decades. The availability of reliable, high-quality thermochemical values is critical in many areas of chemistry and technology, and is a particularly important ingredient in the development of realistic predictive models of complex chemical environments, ranging from combustion and atmospheric chemistry to astrochemistry, as well as in the development and improvement of the latest round of state-of-the-art electronic structure computational treatments that are now capable of sub-kJ/mol accuracies. ATcT are a new paradigm of how to obtain accurate, robust, and internally consistent thermochemistry and overcome the serious limitations that are intrinsic to the traditional sequential approach to thermochemistry. In contrast to the latter, ATcT utilize the Thermochemical Network (TN) approach. The TN contains all available thermochemical interdependencies between the targeted chemical species, such as reaction enthalpies, reaction Gibbs energies, constants of equilibria, adiabatic ionization energies and electron affinities, etc., that were either experimentally determined (actual measurements) or accurately computed (virtual measurements). The determinations that are included in the TN effectively represent a set of qualified constraints that must be simultaneously satisfied by the resulting enthalpies of formation. ATcT construct and statistically analyze the TN, trying to identify and correct the constraints that may be - because of finite measurement accuracies - inconsistent with the prevailing knowledge content of the TN. The end result is the extraction of the best possible thermochemistry, based on using optimally all of the currently available knowledge, and characterized by significantly enhanced accuracy and robustness compared to conventional tabulations of thermochemical values, making the latter obsolescent. Moreover, ATcT offer a number of additional features that are neither available nor possible in the traditional approach. With ATcT, new knowledge can be painlessly added and propagated through all affected thermochemical values, a feat that is nearly impossible in traditional tabulations. ATcT also allow hypothesis testing and evaluation, as well as discovery of weak links in the TN. The latter provide pointers to new experimental or theoretical determinations that can efficiently improve the underlying thermochemical body of knowledge. While ATcT focus on optimally utilizing the available thermochemically-relevant knowledge and deliver the best currently possible thermochemical parameters for a broad range of chemical species, the underlying Active Tables approach is more general in nature, and could in principle be applied to a variety of other scientific and technological problems.

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