ACTIVE THERMOCHEMICAL TABLES: ON THE ACCURATE SEQUENTIAL BOND DISSOCIATION ENERGIES OF WATER

BRANKO RUSCIC, REINHARDT E. PINZON, ABEL FERNANDEZ, MELITA L. MORTON, *Chemistry Division, Argonne National Laboratory, Argonne, IL, USA*; DEEPTI KODEBOYINA, and GREGOR von LASZEWSKI, *Mathematics and Computer Science Division, Argonne National Laboratory, Argonne, IL, USA*.

Active Thermochemical Tables (ATcT), which have been recently developed at Argonne National Laboratory in conjunction with the Collaboratory for Multi-Scale Chemical Science, are a new paradigm of how to obtain accurate, reliable, and self-consistent thermochemical values for the targeted chemical species. As opposed to conventional sequential thermochemistry, the ATcT approach is based on constructing, manipulating, statistically evaluating, and solving the Thermochemical Network (TN) Graph. The TN Graph incorporates all relevant spectroscopic measurements, together with all other thermochemically-relevant determinations, including other experiments and high-level electronic structure theory. The advantages of ATcT over the conventional approach are numerous. The resulting thermochemical values are inherently superior and more accurate, since they exploit all the knowledge existent in the TN Graph. Exacly for the same reason, the associated uncertainties properly reflect the inherent confidence that one may place in the resulting values. Very importantly, the TN Graph is easily updated with new knowledge as it becomes available, and its consequences are automatically propagated through all affected chemical species - which is something that is virtually impossible to accomplish using the traditional approach. ATcT also offers a number of new features that were so far unavailable in thermochemistry, such as the availability of the full covariance matrix, hypothesis testing (”what if” scenarios), and isolation of ”weak links” in the TN Graph that point to new experiments or computations that will most efficiently enhance the current thermochemical knowledge. The main features of the ATcT approach will be illustrated using as example the latest ATcT results on the sequential bond dissociation energies of water, $D_0(H_2O)$ and $D_0(OH)$, and their thermochemical implications. This work was supported by the U.S. Department of Energy, Division of Chemical Sciences, Geosciences and Biosciences of the Office of Basic Energy Sciences, and by the Mathematical, Information, and Computational Science Division of the Office of Advanced Scientific Computing Research, under Contract No. W-31-109-ENG-38.