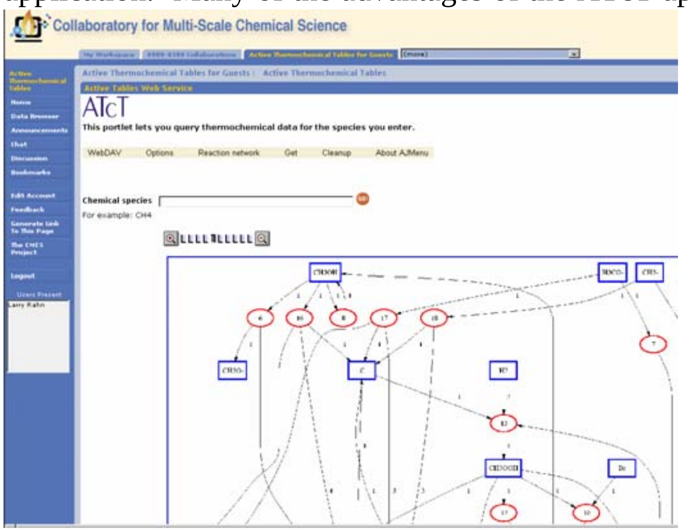
‘Weak Links’ Lead to New Science[1]

An exciting new paradigm for deriving values for the thermochemical properties of atoms and molecules, called Active Thermochemical Tables (ATcT), has been developed in a synergistic collaboration involving research in basic chemistry[2] and the latest developments in collaborative computer science.[3] This effort, led by Dr. Branko Ruscic of Argonne National Laboratory, is focused on improving the accuracy, reliability, and internal consistency of thermochemical values that are fundamental to many areas of chemical science and industrial application. Many of the advantages of the ATcT approach stem from its use of the Thermochemical Network (TN) that explicitly exposes the manifold of inherent interdependencies among thermochemical properties and the experiments and computations from which they are derived. Thus, ATcT provides quick and painless propagation of new knowledge to update all affected thermochemical values. Crucial collaborative capabilities are derived from the Collaboratory for Multi-scale Chemical Science (CMCS), which makes the ATcT application and associated data broadly available to collaborators and supports data evaluation and other community processes. The ATcT interface in the CMCS Portal with a visualization of a TN is shown in the figure.



Another new capability allows researchers to discover ‘weak links’ in the TN, where new experimental or theoretical determinations will significantly improve the TN. The first weak link related to the thermochemistry of N atom, and resulted from the development of the Core (Argonne) Thermochemical Network, (C(A)TN), which is the primary TN that enables ATcT. This finding prompted a collaborative experimental effort with Prof. C.-Y. Ng (UC Davis), resulting in new measurements. After insertion of these results into the C(A)TN, the uncertainty of the N atom thermochemistry improved by almost an order of magnitude, directly propagating through the TN into improvements for species in the N/O group.

The discovery of another weak link relating to gas phase C atom thermochemistry prompted collaborative high-fidelity calculations involving Profs. J. Stanton (UT Austin) and A. Csaszar (ELTE Budapest). This work is now addressing a 50-year old quandary on the correct value of the vaporization enthalpy of graphite. This is important since the majority of quantum-mechanical calculations use atomization energies as starting points.

A group of theorists in the U.S., Germany, and Hungary have been looking for high-quality thermochemical benchmarks to critically assess the accuracy of their newly developed high-accuracy computational method.[4] After trying the pertinent values from a number of standard compilations, they ended up rejecting them all, in favor of the ATcT values, for which, according to Prof. J. Stanton (UT Austin), they have found “outstanding agreement between the benchmarks and the theory.” Another request for the latest thermochemistry of ketene,[5] CH_2CO, has elicited the e-mail praise by Prof. P. Szalay (ELTE Budapest): “…Amazing! Using [the ATcT] ketene number, our fit became substantially better!”, but also a concern about the theoretical effort necessary to match ATcT results:"[Our calculations] are very expensive and you get the same quality results with ATcT!"

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[2] B. Ruscic, R. E. Pinzon, M. L. Morton, G. von Laszevski, S. Bittner, S. G. Nijsure, K. A. Amin, M. Minkoff, and A. F. Wagner, *J.Phys. Chem. A.* **108**, 9979 (2004).

[3] Myers, J. D., et al., "A Collaborative Informatics Infrastructure for Multi-scale Science," Proceedings of CLADE 04, Honolulu, Hawaii, 2004, p.24. http://csdl.computer.org/comp/proceedings/clade/2004/2115/00/2115toc.htm. Also see www.cmcs.org.

[4] A. Tajti, P. G. Szalay, A. G. Császár, M. Kállay, J. Gauss, E. F. Valeev, B. A. Flowers, J. Vázquez, and J. F. Stanton, *J. Chem. Phys.* **121**, 11599 (2004)

[5] P.G. Szalay, A. Tajti and J.F. Stanton, Ab initio determination of the heat of formation of ketenyl (HCCO) and ethynyl(CCH) radicals, *Mol. Phys.* in press