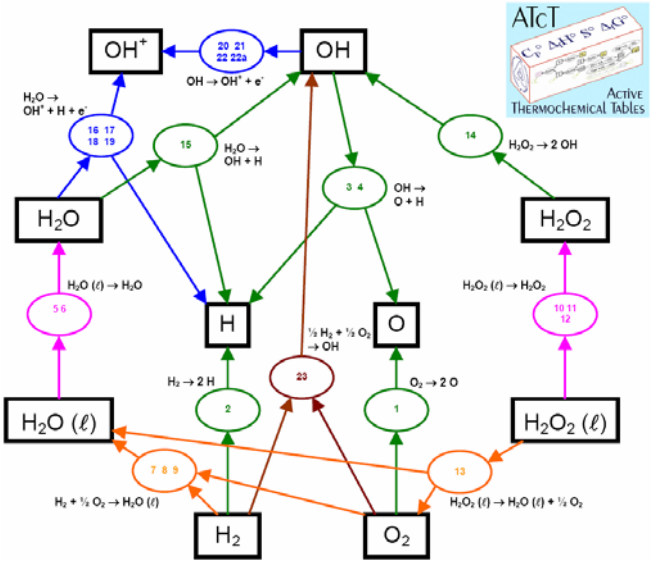
Active Thermochemical Tables – Thermochemistry for the 21st Century[1]

Highly accurate and internally consistent values for thermochemical properties of atoms and molecules, accompanied by quantified and understood uncertainties, are critical to many areas of chemical and engineering science, ranging from high-accuracy quantum computation of electronic-structures to construction of complex chemical reaction models for combustion, atmospheric chemistry, and industrial processes. However, these thermochemical values are highly interrelated, both by molecular relationships and in their interdependence on laboratory measurements or computations. Thus, when a critical value is updated, the same new information implicitly affects many other values, thus outdating whole sections of traditional thermochemical tables.

A team of researchers led by Dr. Branko Ruscic, have developed a new paradigm for providing accurate, reliable, and internally consistent thermochemical values for a comprehensive range of chemical species. Active Thermochemical Tables (ATcT) represent a synergism of breakthrough developments in the chemistry domain[2] with those in collaborative computer science by the Collaboratory for Multi-Scale Chemical Science (CMCS).[3] ATcT implements a Thermochemical Network (TN) concept that explicitly exposes the manifold of inherent interdependencies ignored in traditional approaches. The TN (see figure) is designed to incorporate all available experimental and computational data, which, through the collaboratory environment of CMCS, can be subjected to critical evaluation by recognized experts in the thermo-chemical field. The ATcT analysis, also accessible from the CMCS portal, produces a self-consistent TN from which it can generate, on demand, user-tailored and thoroughly documented thermochemical tables that optimally exploit all the available knowledge.

A stream of important scientific results is already flowing out of ATcT related research. A team of researchers at Argonne National Lab led by Dr. Ruscic have created a Core (Argonne) Thermochemical Network, C(A)TN, which is the primary TN that enables ATcT to extract new thermochemistry, and which currently encompasses over 350 chemical species and 1000 relevant measurements. Using ATcT, the Argonne research team has fully confirmed their recent revision[4,5] of the enthalpy of formation of the pivotal combustion and atmospheric radical, hydroxyl (OH). Furthermore, they have reduced its uncertainty by a factor of ~6.5, thus removing the thermochemistry of this chemical species from the list of potential sources of uncertainty in current chemical models. This achievement was singled out on the front cover (see figure) of the abstract compendium[6] of the 2004 Combustion Conference organized annually by Office of Basic Energy Sciences of the U. S. Department of Energy (see Fig. 1). This also resulted in new ATcT values for the combustion-related radical HO_2, and for nitrogen oxides (NO_x) that were used by kineticists at Argonne to analyze their latest experiments. The lead kineticist, Dr. J. Michael, who initially tried literature thermochemical values, was "extremely impressed by how perfectly the ATcT data fits the measurements", and was thus able to finally prove that the previous rate constant for the reverse of the important atmospheric reaction, $HO_2 + NO \rightarrow OH + NO_2$, must be in error by a factor of ~2.



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[6] 25th Annual Combustion Research Conference", Warrenton, VA, June 1-4, 2004