Quantification of the accuracy of detailed reaction mechanisms

István Gy. Zsély

Institute of Chemistry, Eötvös University (ELTE), Budapest, Hungary
Tel.: +36 1 372 2500 ext. 1109, Fax: +36 1 372 2592, E-mail: zsigy@chem.elte.hu

A large set of experimental data was collected for the combustion hydrogen. These data included ignition measurements in shock tubes (828 data points in 62 datasets), perfectly stirred reactor (PSR) measurements (152 data points in 9 datasets), flame velocity measurements (622 data points in 64 datasets), concentration–distance profiles in burner stabilized flames (43 data points in 3 datasets) and concentration–time profiles in flow reactor measurements (214 data points in 16 datasets). All experimental data were encoded in PrIMe format [1]. This is an XML scheme that is able to fully characterize different kind of combustion experiments.

A computer program was created [2] that carries out the simulations on the basis of all XML data files in a single round. For each experiment, plots are generated that compares the simulation results with the experimental data points. The agreement between the simulations and the measurements can be characterized with a least-squares deviation based objective function. In this objective function the least-square deviations are divided by the assumed standard deviations of the experiments. Using this measure, the different types of experiments become comparable. Therefore, a single value can be calculated which quantitatively describes the agreement / disagreement between the measurements and the simulation results using a reaction mechanism. The calculations can be repeated with any detailed reaction mechanism, allowing comparisons of detailed reaction mechanisms published by different authors.

In the recent years, several authors suggested detailed reaction mechanisms for the description of the combustion of hydrogen, including Li *et al*. (2004) [3], Ó Connaire *et al.* (2004) [4], Konnov (2008) [5], NUIG Natural Gas Mechanism III (2009) [6], Hong *et al.* (2011) [7], Burke *et al.* (2012) [8] and Keromnes *et al.* (2012) [9]. The performance of these mechanisms was tested against the experimental data and each other. A similar work is in progress for the comparative analysis of several wet CO combustion mechanisms published in the literature.

[1] PrIMe Database, http://www.primekinetics.org/
[2] T. Turányi, T. Nagy, I.Gy. Zsély, M. Cserháti, T. Varga, B.T. Szabó, I. Sedyó, P.T. Kiss, A. Zempléni and H.J. Curran, Int. J. Chem. Kinet. **2012**, *44*, 284–302.
[3] J. Li, Z. Zhao, A. Kazakov, F. L. Dryer, *Int. J. Chem. Kinet.* **2004**, *36*, 566-576.
[4] M. Ó Conaire, H. J. Curran, J. M. Simmie, W. J. Pitz, C. K. Westbrook, *Int. J. Chem. Kinet.* **2004**, *36*, 603-622.
[5] A. A. Konnov, *Combust. Flame* **2008**, *152*, 507-528.
[6] NUIG Natural Gas Mechanism III, http://c3.nuigalway.ie/naturalgas3.html
[7] Z. Hong, D. F. Davidson, R. K. Hanson, *Combust. Flame* **2011**, *158*, 633-644.
[8] M. Burke, M. Chaos, F.L. Dryer, Y. Ju, S.J. Klippenstein, *Int. J. Chem. Kinet.* **2011**, in press doi:10.1002/kin.20603
[9] A. Kéromnès, W.K. Metcalfe, N. Donohoe, A. K. Das, C.J. Sung, J. Herzler, C. Naumann, P. Griebel, O. Mathieu, M.C. Krejci, E. Petersen, W.J. Pitz, H.J. Curran, *Combust. Flame* **2012**, submitted