

# Effect of the uncertainty of kinetic and thermodynamic data on methane flame simulation results

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A method for assessing and comparing the impact of uncertainties in both kinetic and thermodynamic parameters on the predictions of combustion chemistry models has been developed. Kinetic, thermodynamic and overall uncertainty parameters are defined, which allow tracking the sources of uncertainties for a particular model result. The method was applied to premixed laminar methane-air flames using the Leeds Methane Oxidation Mechanism (K. J. Hughes *et al.*, *Int. J. Chem. Kinet.*, 2001, **33**, 513). Heat of formation and rate coefficient data for species and elementary reactions, respectively, related to methane combustion were collected from several recent reviews and critically assessed error limits were assigned to them. Local rate coefficient sensitivities and heat of formation sensitivities were calculated for lean ( $\phi = 0.62$ ), stoichiometric ( $\phi = 1.00$ ) and rich ( $\phi = 1.20$ ) laminar atmospheric premixed methane-air flames. Uncertainties of flame velocity, maximum flame temperature and also the value and location of maximum concentration of radicals H, O, OH, CH and CH<sub>2</sub> were obtained from the sensitivities and the uncertainties of thermodynamic and chemical kinetic data. The uncertainty of the calculated flame velocity is typically 2–5 cm s<sup>-1</sup>. Maximum flame temperature and concentration of H, O, and OH can be calculated accurately, while there is high uncertainty in the calculated maximum concentration of CH and CH<sub>2</sub>. The calculations have revealed that the uncertainty of the calculated flame velocity is caused mainly by errors of the input rate coefficients. This is the case also for the calculated concentration of CH and CH<sub>2</sub>. The uncertainty of the location of concentration maxima is also of kinetics origin and it is caused by the very same rate coefficients that affect flame velocity. Uncertainty of maximum adiabatic flame temperature and maximum concentration of H, O and OH originates mainly from errors of the input heat of formation data. In order to obtain good simulation results for methane flames, accurate heats of formation are required in particular for radicals OH, CH<sub>2</sub>(S), CH<sub>2</sub>, CH<sub>2</sub>OH, HCCO and CH<sub>2</sub>HCO. Simulation results could be improved by better knowledge of the reaction rate parameters for the reactions O<sub>2</sub> + H = OH + O, O<sub>2</sub> + H + M = HO<sub>2</sub> + M, CO + OH = CO<sub>2</sub> + H, H + CH<sub>3</sub>(+M) = CH<sub>4</sub>(+M), CH<sub>3</sub> + OH = CH<sub>2</sub>(S) + H<sub>2</sub>O, C<sub>2</sub>H<sub>2</sub> + OH = C<sub>2</sub>H + H<sub>2</sub>O and C<sub>2</sub>H<sub>2</sub> + CH = C<sub>2</sub>H + CH<sub>2</sub>. This conclusion is somewhat surprising since at least the first three reactions are among the most frequently studied ones in chemical kinetics. The calculations demonstrate that all simulation results of chemical kinetic modelling studies should be accompanied by uncertainty information (*e.g.* standard deviation) for the model outputs to indicate which results are well supported by the model and which ones are merely nominal values that were obtained using the selected set of input parameters.

## Introduction

A great part of our understanding of the chemistry of combustion processes comes from computer modelling studies that are ultimately limited by our knowledge of the chemical kinetics of the underlying elementary reactions and the thermodynamics of the reacting species.<sup>1</sup> Combustion models require reliable reaction rate parameters and thermodynamic data as input parameters. Uncertainties of rate coefficients and thermodynamic data may have significant impact on the output of the models but this aspect of modelling has been largely overlooked in practice. The ignorance of the impact of the errors of input parameters on simulation outputs in regular combustion modelling studies can be due, at least in part, to the lack of easily applicable uncertainty analysis methods. Objectives of this work were to develop an effective method for the estimation of the uncertainty of combustion simulation results and to apply it to methane flame modelling.

As a result of gas kinetics research, detailed mechanisms and measured rate parameters are available for many important

combustion reactions. Kinetic parameters of elementary reactions of combustion and atmospheric relevance have been critically evaluated in permanently updated periodicals.<sup>2–4</sup> These critical data evaluations provide not only recommended kinetic parameters, but also assess the accuracy of the data and assign error limits to them. Nevertheless, usually only the recommended data are used in modelling studies and the information on the uncertainty of kinetic parameters has almost never been utilised.

Thermodynamic data are indispensable for combustion modelling. In many combustion systems, the temperature range spans from 300 to about 2300 K and therefore enthalpy, entropy and heat capacity data for each species are needed for a wide temperature range. This is usually achieved by representing the thermodynamic data in the form of polynomials, fitted to experimentally measured or calculated values. During the combustion simulations, the required thermodynamic data at any temperature can be evaluated from the fitted polynomials. For adiabatic simulations, the maximum attainable temperature is calculated from reaction heats and the heat

capacity of the gas mixture. Exact calculation of temperature is very important because of the strong temperature dependence of the rate controlling elementary reactions of combustion processes. Rate coefficients of many elementary reactions can be measured with sufficient accuracy in one direction only, and the rates of reverse reactions are calculated from the equilibrium constants, derived from heat of formation and entropy data.

Until quite recently, most kineticists and combustion modelers assumed the thermodynamic data to be well known and while a few percent change of rate coefficients of certain elementary reactions were heavily debated, unchecked and outdated thermodynamic data were used in many simulations. On the other hand, attention has been increased by specialists in the field concerning the accuracy of thermodynamic data, in particular for free radicals. This was prompted and made possible by the more accurate experimental data being published (see *e.g.* ref. 5), the elaboration of new theoretical methods (see in refs. 6 and 7) and the appearance of several new review papers (*e.g.* refs. 8 and 9). Also, it is now clear that raising the quality of thermodynamic data is an unexplored area of improving the accuracy of combustion simulations. Other parameters used in chemical kinetic simulations (*e.g.* diffusion coefficients) also have uncertainties. However, the effect of the uncertainty of parameters other than kinetic and thermodynamic has not been dealt with in this study.

The model calculations to be discussed were performed with the Leeds Methane Oxidation Mechanism.<sup>10,11</sup> The Leeds mechanism has been preferred because it contains more species and reactions than many other methane combustion mechanisms in use and because it has recently been extensively validated against experimental data.<sup>10</sup>

There are only few applications<sup>12–14</sup> of uncertainty analysis to the investigation of complex combustion mechanisms, which will be discussed in the next sections. Uncertainty analysis is more frequently used in conjunction with the derivation of rate coefficients from kinetic measurements<sup>15–18</sup> and it is a frequently applied tool in atmospheric chemistry modelling.<sup>19–22</sup>

## Thermodynamic data for methane combustion modelling

In most combustion simulation codes, including the generally used CHEMKIN-II programme package,<sup>23</sup> the temperature dependence of thermodynamic properties is described by the so-called NASA polynomials. For species *j*, these generalized polynomials are given in the following forms:

$$\frac{C_{p,j}^{\circ}}{R} = a_{1,j} + a_{2,j}T + a_{3,j}T^2 + a_{4,j}T^3 + a_{5,j}T^4 \quad (1)$$

$$\frac{H_j^{\circ}}{RT} = a_{1,j} + \frac{a_{2,j}}{2}T + \frac{a_{3,j}}{3}T^2 + \frac{a_{4,j}}{4}T^3 + \frac{a_{5,j}}{5}T^4 + \frac{a_{6,j}}{T} \quad (2)$$

$$\frac{S_j^{\circ}}{R} = a_{1,j} \ln T + a_{2,j}T + \frac{a_{3,j}}{2}T^2 + \frac{a_{4,j}}{3}T^3 + \frac{a_{5,j}}{4}T^4 + a_{7,j} \quad (3)$$

Here  $C_{p,j}^{\circ}$  is the heat capacity at constant pressure, the temperature dependence of which (*i.e.* coefficients  $a_{1,j}$  to  $a_{5,j}$ ) can usually be estimated with good accuracy using the methods of statistical thermodynamics. Moreover, entropy,  $S_j^{\circ}$ , and thus coefficient  $a_{7,j}$  can be calculated in a similar way.  $H_j^{\circ}$  is the ‘absolute enthalpy’ of the species, which includes the heat of formation.<sup>1</sup> Usually this is the most uncertain thermodynamic data in combustion simulations, especially for free radicals. Provided coefficients  $a_{1,j}$  to  $a_{5,j}$  are known, coefficient  $a_{6,j}$  is usually obtained from the standard heat of formation,  $\Delta_f H_{298}^{\circ}(j)$ .<sup>6,7,9</sup>

In combustion modelling studies, the thermodynamic database<sup>24</sup> distributed with the CHEMKIN-II package<sup>23</sup> is used most often. This data collection is based mainly on the JANAF tables.<sup>25</sup> Data not found there were taken from the 1984 version of the thermodynamic database of Burcat<sup>26</sup> or were calculated by the Sandia group using the BAC-MP4 method of Melius and co-workers (see *e.g.* ref. 27). Some of the thermodynamic data were occasionally updated, but no systematic revisions were implemented in CHEMKIN-II. Burcat continuously updates his database, which is available on the Internet;<sup>28</sup> a most recent version has been published also as a printed report.<sup>29</sup> A permanently updated database/website is the NIST Computational Chemistry Comparison and Benchmark Database;<sup>30</sup> the NIST Webbook<sup>31</sup> is another convenient Internet source for thermodynamic data. Critically evaluated or compiled thermodynamic data are available from numerous recent publications. These include the latest editions of CRC,<sup>32</sup> JANAF,<sup>33</sup> TRC<sup>34</sup> and Gurvich *et al.*<sup>35</sup> handbooks, and the reviews of McMillen and Golden,<sup>36</sup> Berkowitz *et al.*<sup>9</sup> and Tsang.<sup>8</sup> Evaluations of rate coefficients for atmospheric chemical modelling<sup>2,3</sup> also include recommended heat of formation data.

The Leeds Methane Oxidation Mechanism version 1.4<sup>10</sup> utilises the thermodynamic database provided by the CHEMKIN-II programme suite.<sup>24</sup> As a continuation of the development of the mechanism, and for the purpose of the current uncertainty analyses, we have surveyed all pertinent heats of formation and updated them by creating a new recommended data set. At the selection of the ‘best available’ heat of formation values, usually the recent review of Atkinson *et al.*<sup>3</sup> and the recent measurements of Ruscic and co-workers<sup>37–39</sup> were preferred. Note that significantly different values can be found in the literature for CHO, HO<sub>2</sub>, CH, CH<sub>2</sub>CO, CH<sub>2</sub>OH, C<sub>2</sub>H<sub>3</sub> and C<sub>2</sub>H<sub>5</sub> and that the heats of formation for H<sub>2</sub>CCCH and HCCO are known only with very large uncertainty. Then, NASA polynomials for the appropriate atoms, radicals and molecules were downloaded from the Internet database of Burcat<sup>28</sup> and  $\Delta_f H_{298}^{\circ}$  values were calculated. If the agreement between the calculated value and our recommendation was found to be good, the original Burcat polynomial was accepted. Otherwise, the polynomials were modified by the program MECHMOD<sup>40</sup> to reproduce the standard heat of formation value that we considered the best. In this way, the original polynomials for the following species were modified: OH, CH<sub>3</sub>, HO<sub>2</sub>, CH<sub>2</sub>(S), CH, CH<sub>2</sub>CO, CH<sub>2</sub>OH, C<sub>2</sub>H, CH<sub>2</sub>HCO, H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>CCCH, C<sub>2</sub>H<sub>5</sub> and CH<sub>3</sub>O. Most reactions in the Leeds Methane Oxidation Mechanism version 1.4 are regarded as ‘reversible’, *i.e.* for these reactions the ‘reverse’ rates were calculated in the simulation program by means of the ‘forward’ rate coefficients and the equilibrium constant of the reaction. Occasionally, some of the elementary reactions were considered ‘irreversible’ when critically evaluated rate parameters were available for both the forward and reverse reaction steps. In our present study, the aim has been the clear separation of the effects of kinetic and thermodynamic uncertainties. Therefore, pairs of irreversible reactions were all converted into reversible ones. The Leeds mechanism containing reversible reactions only and with updated thermodynamic data is called version 1.5. The Leeds Methane Oxidation Mechanism version 1.5 is available from the Leeds mechanism web sites.<sup>11</sup> All the produced thermodynamic polynomials are available as part of the CHEMKIN input file of this mechanism.

Table 1 lists standard heats of formation for all the species present in the Leeds Methane Oxidation Mechanism. In Column 2 of Table 1 are shown the  $\Delta_f H_{298}^{\circ}$  data that have been used in our current flame simulation and uncertainty analysis study. These are our selected ‘best values’ that are recommended for use in other combustion modelling studies as well. The reference is to ref. 28, if Burcat’s original polynomial was

Table 1 Standard heats of formation for species in methane flame simulations

Species	$\Delta_f H_{298}^{\circ}$ recommended <sup>a</sup> /kJ mol <sup>-1</sup>	Uncertainty <sup>b</sup> /kJ mol <sup>-1</sup>	$\Delta_f H_{298}^{\circ}$ literature values <sup>c</sup> /kJ mol <sup>-1</sup>
CH <sub>4</sub>	-74.60 <sup>28</sup>	0.4 <sup>8</sup>	-74.4 ± 0.4, <sup>8</sup> -74.81, <sup>2,3</sup> -74.87, <sup>33</sup> -74.6 <sup>29</sup>
O <sub>2</sub>	0.00 <sup>28</sup>	0.00	0 (by definition)
CO <sub>2</sub>	-393.51 <sup>28</sup>	0.13 <sup>3</sup>	-393.59, <sup>2</sup> -393.51 ± 0.13, <sup>3</sup> -393.52, <sup>33</sup> -393.51 ± 0.13 <sup>29</sup>
H <sub>2</sub> O	-241.81 <sup>28</sup>	0.040 <sup>3</sup>	-241.88, <sup>2</sup> -241.826 ± 0.040, <sup>3</sup> -241.83, <sup>33</sup> -241.826 ± 0.04, <sup>29</sup> -241.8 <sup>46</sup>
CO	-110.52 <sup>28</sup>	0.17 <sup>3</sup>	-110.53 ± 0.1, <sup>8</sup> -110.54, <sup>2</sup> -110.53 ± 0.17, <sup>3</sup> -110.53, <sup>33</sup> -110.53 ± 0.17 <sup>29</sup>
N <sub>2</sub>	0.00 <sup>28</sup>	0	0 (by definition)
O	249.16 <sup>28</sup>	0.10 <sup>3</sup>	250.91, <sup>2</sup> 249.18 ± 0.10, <sup>3</sup> 249.17, <sup>33</sup> 249.175 ± 0.10 <sup>29</sup>
OH	37.20 <sup>38</sup>	Case a: <sup>d</sup> 2.1 <sup>3</sup> Case b: <sup>d</sup> 0.38 <sup>38</sup>	39.3 ± 1.2, <sup>8</sup> 38.91, <sup>2</sup> 39.3 ± 2.1, <sup>3</sup> 39.33 ± 0.21, <sup>9</sup> 38.99, <sup>33</sup> 39.46, <sup>36</sup> 39.29, <sup>32</sup> 39.3, <sup>36</sup> 37.20 ± 0.38, <sup>38</sup> 39.347 <sup>29</sup>
H	217.998 <sup>28</sup>	0.006 <sup>3</sup>	217.999 ± 0.006, <sup>8</sup> 217.99, <sup>2</sup> 217.998 ± 0.006, <sup>3</sup> 217.998 ± 0.004, <sup>9</sup> 218.00, <sup>33</sup> 217.998 ± 0.006 <sup>29</sup>
CHO	42.00 <sup>28</sup>	0.8 <sup>9,32</sup>	41.8 ± 4.2, <sup>2</sup> 43.1, <sup>3</sup> 41.7 ± 0.8, <sup>9</sup> 43.5, <sup>33</sup> 37.2 ± 5.0, <sup>36</sup> 42 ± 0.8, <sup>29</sup> 41.8 ± 0.8 <sup>32</sup>
CH <sub>3</sub>	146.65 <sup>37</sup>	0.4 <sup>3</sup>	145.7 ± 0.8, <sup>8</sup> 146.44 ± 0.84, <sup>2</sup> 146.4 ± 0.4, <sup>3</sup> 145.6 ± 1.3, <sup>9</sup> 145.7, <sup>33</sup> 146.8 ± 0.6, <sup>36</sup> 146.858 ± 1.0, <sup>29</sup> 146.4 ± 0.4, <sup>32</sup> 146.0, <sup>36</sup> 146.65 ± 0.29 <sup>37</sup>
H <sub>2</sub>	0.00 <sup>28</sup>	0	0 (by definition)
CH <sub>2</sub> O	-108.57 <sup>28</sup>	0.5 <sup>8</sup>	-108.6 ± 0.5, <sup>8</sup> -108.8, <sup>2</sup> -108.6, <sup>3</sup> -115.9, <sup>33</sup> -108.58, <sup>29</sup> -108.70 <sup>35</sup>
HO <sub>2</sub>	13.81 <sup>39</sup>	3.35 <sup>39</sup>	11.7 ± 2.1, <sup>2</sup> 14.6, <sup>3</sup> 2.092, <sup>33</sup> 10.5 ± 2.5, <sup>36</sup> 12.552, <sup>29</sup> 14.6, <sup>32</sup> 13.81 ± 3.35 <sup>39</sup>
CH <sub>2</sub>	390.41 <sup>28</sup>	4.0 <sup>3</sup>	389.1 ± 4.2, <sup>2</sup> 390.4 ± 4.0, <sup>3</sup> 386.4, <sup>33</sup> 390.417, <sup>29</sup> 390.5 ± 4.0, <sup>32</sup> 390.41 ± 0.84 <sup>37</sup>
CH <sub>2</sub> (S)	428.07 <sup>37</sup>	2.5 <sup>47</sup>	424.732, <sup>29</sup> 428.358 ± 4.017, <sup>32</sup> 430.1, <sup>46</sup> 428.0 ± 2.5, <sup>47</sup> 428.07 ± 0.84 <sup>37</sup>
CH	596.40 <sup>3</sup>	1.2 <sup>3</sup>	594.1, <sup>2,33</sup> 596.4 ± 1.2, <sup>3</sup> 596.47 ± 1.21, <sup>32</sup> 597.36 ± 17.5 <sup>29</sup>
CH <sub>2</sub> CO	-49.58 <sup>37</sup>	1.7 <sup>48</sup>	-46.0 ± 12.6, <sup>2</sup> -47.7 ± 1.6, <sup>3</sup> -87.24, <sup>49</sup> -47.7 ± 1.7, <sup>48</sup> -49.58 ± 0.88, <sup>37</sup> -47.698 ± 1.7 <sup>29</sup>
HCCO	177.39 <sup>28</sup>	8.8 <sup>29</sup>	175.3 ± 8.4, <sup>9</sup> 177.402 ± 8.8 <sup>29</sup>
CH <sub>2</sub> OH	-16.60 <sup>5</sup>	4.2 <sup>-9</sup>	-7.20 ± 3.21, <sup>8</sup> -17.8 ± 1.3, <sup>3</sup> -17.07 ± 3.35, <sup>32</sup> -17.8 ± 1.3, <sup>29</sup> -25.94 ± 6.28, <sup>36</sup> -15.0 ± 4.2, <sup>2</sup> -12.1 ± 4.2, <sup>9</sup> -16.6 ± 1.3 <sup>5</sup>
C <sub>2</sub> H	566.10 <sup>3</sup>	2.9 <sup>3,9,32</sup>	556 ± 8, <sup>8</sup> 564.8 ± 4.2, <sup>2</sup> 566.1 ± 2.9, <sup>3</sup> 565.3 ± 2.9, <sup>9</sup> 477.0, <sup>33</sup> 564.8 ± 4.2, <sup>36</sup> 568.522 ± 3.0, <sup>29</sup> 566.1 ± 2.9 <sup>32</sup>
C <sub>2</sub> H <sub>4</sub>	52.29 <sup>28</sup>	1.2 <sup>3</sup>	52.5 ± 0.4, <sup>8</sup> 52.09, <sup>2</sup> 52.2 ± 1.2, <sup>3</sup> 52.47, <sup>33</sup> 52.294, <sup>29</sup> 52.40 <sup>35</sup>
C <sub>2</sub> H <sub>3</sub>	299.72 <sup>28</sup>	3.4 <sup>3,32</sup>	299.0 ± 5.0, <sup>8</sup> 297.0 ± 4.2, <sup>2</sup> 300.0 ± 3.4, <sup>3</sup> 299.6 ± 3.3, <sup>9</sup> 294.6 ± 8.4, <sup>36</sup> 325.1 ± 3.4, <sup>32</sup> 299.74 ± 5.0 <sup>29</sup>
CH <sub>2</sub> HCO	10.50 <sup>3</sup>	9.2 <sup>3</sup>	10.5 ± 9.2, <sup>3,9,32</sup> 25.10 <sup>29</sup>
C <sub>2</sub> H <sub>6</sub>	-83.86 <sup>28</sup>	0.2 <sup>3</sup>	-83.8 ± 0.4, <sup>8</sup> -83.7, <sup>2</sup> -84.0 ± 0.2, <sup>3</sup> -84.00, <sup>35</sup> -83.863 <sup>29</sup>
C <sub>3</sub> H <sub>4</sub> allene (H <sub>2</sub> CCCH <sub>2</sub> )	190.91 <sup>28</sup>	8.0 <sup>c</sup>	190.92 <sup>29</sup>
H <sub>2</sub> O <sub>2</sub>	-135.88 <sup>35</sup>	0.5 <sup>c</sup>	-136.11, <sup>33</sup> -136.40, <sup>2</sup> -136.31, <sup>3</sup> -136.31, <sup>29</sup> -135.88 <sup>35</sup>
C <sub>2</sub> H <sub>2</sub>	227.39 <sup>28</sup>	1.0 <sup>3</sup>	227.4, <sup>2</sup> 228.0 ± 1.0, <sup>3</sup> 226.7, <sup>33</sup> 227.4 <sup>29</sup>
C <sub>3</sub> H <sub>6</sub>	20.41 <sup>28</sup>	0.4 <sup>3</sup>	20.0 ± 0.8, <sup>8</sup> 20.1, <sup>2</sup> 20.2 ± 0.4, <sup>3</sup> 20.413 <sup>29</sup>
C <sub>4</sub> H <sub>2</sub>	440.47 <sup>28</sup>	8.0 <sup>c</sup>	464.0, <sup>50</sup> 440.492 <sup>29</sup>
H <sub>2</sub> CCCH	339.00 <sup>8</sup>	4.0 <sup>8</sup>	339.0 ± 4.0, <sup>8</sup> 340.6 ± 8.4, <sup>32,36</sup> 346 ± 4 <sup>29</sup>
C <sub>2</sub> H <sub>5</sub>	120.90 <sup>3</sup>	1.6 <sup>3,32</sup>	119.0 ± 1.8, <sup>8</sup> 118.8 ± 2.1, <sup>2</sup> 120.9 ± 1.6, <sup>3</sup> 120.9 ± 1.7, <sup>9</sup> 108.4 ± 4.2, <sup>36</sup> 118.658 ± 2.0, <sup>29</sup> 120.9 ± 1.6 <sup>32</sup>
C	716.63 <sup>28</sup>	0.45 <sup>34</sup>	716.7, <sup>33</sup> 716.68 ± 0.45, <sup>34</sup> 715.0, <sup>2</sup> 716.67 ± 0.45 <sup>29</sup>
CH <sub>3</sub> O	17.20 <sup>3</sup>	3.8 <sup>3,9,32</sup>	17 ± 4, <sup>8</sup> 16.7 ± 4.2, <sup>2</sup> 17.6, <sup>36</sup> 17.2 ± 3.8, <sup>3,9,32</sup> 16.318 <sup>29</sup>
C <sub>3</sub> H <sub>2</sub>	591.71 <sup>28</sup>	8.0 <sup>c</sup>	476.976 <sup>29</sup>
H <sub>2</sub> CCCH <sub>2</sub>	483.72 <sup>28</sup>	8.0 <sup>c</sup>	483.751 <sup>29</sup>

<sup>a</sup> Heats of formation recommended and used in the current study. <sup>b</sup> Estimated uncertainties of the recommended  $\Delta_f H_{298}^{\circ}$  values (see text). <sup>c</sup> Selected recent literature values; the error limits are those given in the original publications. <sup>d</sup> All calculations were carried out assuming high and low uncertainty for radical OH (see text). <sup>e</sup> Estimated uncertainty (see text).

used, but different from that if the polynomial was modified as described above. The last column of Table 1 contains a compilation of  $\Delta_f H_{298}^\circ$  data from the recent literature with reported error limits (if available).

Under the heading ‘Uncertainty’ in Table 1, estimates have been made for the accuracy of the preferred values of  $\Delta_f H_{298}^\circ$ . Many of the literature sources surveyed give error limits, but only very few of them discuss what the reported uncertainty actually means. In the reviews of thermodynamic data, error limits are quite often copied from experimental papers, where the uncertainty typically means two standard ( $2\sigma$ ) deviations. In these experimental papers, the error limits usually refer to the actual measurements (*i.e.* the precision<sup>41</sup>) only and do not reflect that other experimental determinations produced different values (*i.e.* the accuracy<sup>41</sup> of the thermodynamic data). The various sources usually suggested different error limits for the heats of formation. Therefore, our recommendations, listed in Column 3 of Table 1, are set in such a way that most of the heat of formation values of several recent reviews and articles lie within the suggested error range. In an attempt to give a better estimate for the accuracy of the heats of formation, the proposed errors are considered to correspond to one standard ( $1\sigma$ ) deviation. We note, however, that a less conservative estimation, considering the error limits to correspond to *e.g.* a 95% confidence interval, does not change qualitatively the conclusions as has been demonstrated by test calculations. The error limits are typically 0.1–0.5 kJ mol<sup>-1</sup> for molecules and small radicals and are in the range of 1.0–5.0 kJ mol<sup>-1</sup> for larger radicals. Errors as high as 8–10 kJ mol<sup>-1</sup> can be assigned to less well-known species. No uncertainty information is available from the literature for the  $\Delta_f H_{298}^\circ$  values of H<sub>2</sub>O<sub>2</sub>, C<sub>3</sub>H<sub>4</sub> (allene), C<sub>3</sub>H<sub>2</sub>, C<sub>4</sub>H<sub>2</sub>, and H<sub>2</sub>CCCCH. An estimated error of 0.5 kJ mol<sup>-1</sup> has been assigned to the heat of formation of H<sub>2</sub>O<sub>2</sub> and 8 kJ mol<sup>-1</sup> to each of the other four species.

Special attention has been paid to the heat of formation of the OH radical corresponding to its great importance and because it has undergone significant revision very recently. A value of  $\Delta_f H_{298}^\circ(\text{OH}) = 39.3$  kJ mol<sup>-1</sup>, which is based on spectroscopic determinations from the late sixties, has long been generally accepted (for details see ref. 38). Recent photoionization measurements and very high-level *ab initio* calculations<sup>38</sup> have supplied, however, the significantly lower value of  $\Delta_f H_{298}^\circ(\text{OH}) = 37.2$  kJ mol<sup>-1</sup>. This latter value has been accepted in our current study. Two cases were considered concerning its uncertainty and accordingly all calculations were carried out in two versions. In case *a*, a  $1\sigma$  value of 2.1 kJ mol<sup>-1</sup> was assigned to the uncertainty in the heat of formation of OH, which reflects the scatter of data in the various sources. We expect that further investigations will decrease this uncertainty level significantly, thus we inspected also the consequence of the application of an error limit of 0.38 kJ mol<sup>-1</sup> (case *b*), which was recommended by Ruscic *et al.*<sup>38</sup>

We attempted to extend this analysis to the study of the uncertainty of  $S_{298}^\circ$  data, but very few literature sources list entropies, in particular with error limits. Because of this and since the available few entropy data are apparently in good agreement, uncertainties in entropies were neglected in the current study and those of heats of formation and reaction rate coefficients were focused on.

## Uncertainty of reaction rate coefficients

Characterization of the accuracy of a rate coefficient by a multiplying uncertainty factor has become standard practice in recent evaluations of rate parameters, like in the critical data evaluations and compilations of DeMore *et al.*,<sup>2</sup> Atkinson *et al.*,<sup>3</sup> Baulch *et al.*,<sup>4,42</sup> and Warnatz.<sup>43</sup> The uncertainty factor is designated here as  $f_j$  and has the following definition:

$$f_j = \log_{10} \left( \frac{k_j^0}{k_j^{\min}} \right) = \log_{10} \left( \frac{k_j^{\max}}{k_j^0} \right) \\ = \frac{1}{\ln 10} \ln \left( \frac{k_j^{\max}}{k_j^0} \right) \quad (4)$$

where  $k_j^0$  is the recommended value of the rate coefficient of reaction  $j$  and  $k_j^{\min}$  and  $k_j^{\max}$  are the extreme, still acceptable values. The logarithms of these extreme values are assumed to be located symmetrically around the logarithm of the recommended value. Recommendations for  $k_j^0$ , and  $k_j^{\max}$ , or related quantities are available from kinetic data evaluations. Eqn. (4) is equivalent to the statement that  $k_j^0$  is uncertain by a factor of  $10^{f_j}$ . Note that the various reviews use different designations:  $f_j = \log_{10} f$ ,  $f_j = D = \Delta \log_{10} k$ ,  $f_j = X = \Delta \log_{10} k$ , and  $f_j = \log_{10} F$  (see refs. 2, 3, 4 and 43, respectively). Rearranging eqn. (4) gives

$$\ln k_j^{\max} - \ln k_j^0 = f_j \ln 10 \quad (5)$$

Assume that  $\ln k_j$  is a stochastic variable with a symmetrical probability density function (*pdf*) and  $\ln k_j^0$  is the expected value of  $\ln k_j$ . The extreme values  $\ln k_j^{\min}$  and  $\ln k_j^{\max}$  can be considered to be different from  $\ln k_j^0$  by  $3\sigma(\ln k_j)$ . The parameter  $f_j$  was elucidated in this way by Baulch<sup>44</sup> and a similar interpretation was given by Brown *et al.*<sup>14</sup> This means that

$$3\sigma(\ln k_j) = f_j \ln 10 \quad (6)$$

and

$$\sigma^2(\ln k_j) = ((f_j \ln 10)/3)^2 \quad (7)$$

Eqn. (7) allows the approximate conversion of the uncertainty factor  $f_j$  into the variance of  $\ln k_j$ . Most rate coefficients in the Leeds Methane Oxidation Mechanism were determined by direct experimental methods essentially in isolation from other reactions. Thus, the covariance of most pairs of rate coefficients is zero and all covariances are considered zero in this study.

In evaluations of rate parameters, either a temperature independent uncertainty factor is given or the temperature dependence is characterised by notes like ‘the uncertainty is 0.1 at room temperature rising to 0.3 at flame temperature’. We assumed temperature independent uncertainties in our studies but adopted the higher factors proposed for elevated temperatures in the literature, if these were available. This has been our preference because all reactions in flame kinetics become active above 1000 K and also because we wanted to give a conservative estimation of output uncertainties. In our model, the temperature dependence of the reaction rates is described by the modified Arrhenius expression  $k_j = B_j T^{n_j} \exp(-C_j/RT)$ . Therefore, the application of a temperature independent uncertainty parameter is equivalent to assuming that only parameter  $B_j$  were uncertain, that is  $\sigma^2(\ln k_j) = \sigma^2(\ln B_j)$ .

Uncertainty factors ( $f_j$  values) have been assigned to all the 175 reversible reactions of the Leeds Methane Oxidation Mechanism. These values are listed in the comment lines of the mechanism and are also available as a computer readable data file from the Leeds mechanism web sites.<sup>11</sup>

## Calculation of the uncertainty of simulation results

Uncertain parameters used in a model give rise to simulation results that are also uncertain. Complex models tend to magnify the uncertainty of some parameters and damp the uncertainty of others. There is a wide range of methods for uncertainty analysis, which differ from each other in their applicability to different types of models, in the scope of information provided, and in the level of sophistication and compu-

tational demand. For chemical kinetic models, the most comprehensive task is the conversion of the joint probability density function (*pdf*) of parameters into the *pdf*'s of the simulation results. A more modest request is the conversion of the variance of parameters into the variance of results. It is clear that uncertainty analysis is closely related to sensitivity analysis.<sup>45,51</sup> In this paper, the term 'sensitivity analysis' is used when the effect of equal perturbation of parameters is investigated without knowing the uncertainty of parameters and the term 'uncertainty analysis' refers to the calculation of the extent of uncertainty of model output including the exploration of reasons that lead to that particular uncertainty. This is the regular usage of these terms in the chemical kinetics literature,<sup>12,52</sup> but it is different from that recommended by Saltelli *et al.* in their recent comprehensive monograph (see Chapters 1 and 2 in ref. 51). Uncertainty analysis methods include<sup>51</sup> various screening designs; Monte Carlo analysis using random, stratified-random or quasi-random points; the FAST (Fourier Amplitude Sensitivity Test) method, *etc.* These are global methods, which require a large number of model evaluations and therefore are not easily applicable for flame models with many uncertain parameters. Hence, in this paper approximate uncertainties are calculated from local sensitivities using the methods of error analysis.

### Kinetic uncertainties

Let  $Y_i$  denote the  $i$ th output of the model. For stationary, pre-mixed, 1D laminar flames,  $Y_i$  can be the laminar flame velocity; the flame temperature or the concentration of any species at any distance. The partial derivative of model output  $Y_i$  with respect to the kinetic parameter  $B_j$  of reaction  $j$  provides a linear measure of the effect of the temperature-independent perturbation of the corresponding rate coefficient. Local sensitivity coefficients,  $\partial Y_i/\partial B_j$ , are calculated by all major combustion simulation programs, including the CHEMKIN-II package.<sup>23</sup> This coefficient shows the effect of changing parameter  $B_j$  by a unit value. The semi-normalized sensitivity coefficient,  $B_j(\partial Y_i/\partial B_j) = \partial Y_i/\partial \ln B_j$ , shows the effect of a relative (*e.g.* 1%) change of the parameter  $B_j$ . Rate coefficient  $k_j$  is constant in the case of isothermal simulations and therefore  $\partial Y_i/\partial \ln k_j = \partial Y_i/\partial \ln B_j$ . This is the reason why the semi-normalized sensitivity coefficients are usually designated in chemical kinetics by  $\partial Y_i/\partial \ln k_j$  although strictly speaking it is not correct, because  $k_j$  is not a constant parameter but a function of temperature in non-isothermal simulations. In the discussions to follow, we maintain the common practice by writing  $k_j$  instead of  $B_j$  in the semi-normalized sensitivity coefficients.

The variance of model output  $Y_i$  can be calculated from the variance of the parameters using the rule of propagation of errors.<sup>41</sup> Assuming zero covariance for all pairs of parameters, one obtains the following expressions:

$$\sigma_{Kj}^2(Y_i) = \left( \frac{\partial Y_i}{\partial \ln k_j} \right)^2 \sigma^2(\ln k_j) \quad (8)$$

$$\sigma_K^2(Y_i) = \sum_j \sigma_{Kj}^2(Y_i) \quad (9)$$

$$S_{K\%ij} = \frac{\sigma_{Kj}^2(Y_i)}{\sigma_K^2(Y_i)} \times 100 \quad (10)$$

In these equations the subscript K refers to kinetic uncertainty,  $\sigma^2(\ln k_j)$  is the variance of the logarithm of rate coefficient  $k_j$  due to experimental uncertainty and  $(\partial Y_i/\partial \ln k_j)^2$  is the square of the semi-normalized sensitivity coefficient. Partial variance  $\sigma_{Kj}^2(Y_i)$  is the contribution of the uncertainty of rate coefficient of reaction  $j$  to the variance of model output  $Y_i$  that we call the 'partial kinetic uncertainty contribution'. If the model were linear, then  $\sigma_K^2(Y_i)$ , the 'kinetic uncertainty contribution'

would be the exact variance of  $Y_i$  due to the uncertainty of kinetic parameters. In case of non-linear models, the error introduced by this linear approximation is small if the local sensitivity coefficients,  $\partial Y_i/\partial \ln k_j$ , are small.  $S_{K\%ij}$  indicates the percentage contribution of  $\sigma_{Kj}^2(Y_i)$  to  $\sigma_K^2(Y_i)$ . The related quantity,  $S_{Kij} = \sigma_{Kj}^2(Y_i)/\sigma_K^2(Y_i)$ , is a linear approximation to the 'first order sensitivity index' of the variance-based uncertainty analysis methods (see Chapter 8 in ref. 51). This measure is also called 'partial variance' in the FAST method.<sup>52,53</sup>

Estimation of the uncertainty of model output from local sensitivities of dynamic models was first discussed by Atherton *et al.*<sup>54</sup> In the chemical kinetics literature, it seems to have appeared first in ref. 45. The method as outlined above has been encoded in the KINALC program package<sup>55</sup> for the calculation of the uncertainty of combustion simulation results from local sensitivities.

In combustion kinetics, Warnatz introduced the following uncertainty measure, which he called the 'sensitivity-uncertainty index':<sup>12</sup>

$$C_j(Y_i) = \left| \frac{\partial Y_i}{\partial \ln k_j} f_j \right| \quad (11)$$

Combining this expression with eqns. (6) and (8) gives:

$$C_j(Y_i) = \left| \frac{3}{\ln 10} \frac{\partial Y_i}{\partial \ln k_j} \sigma(\ln k_j) \right| \approx 1.30 \sqrt{\sigma_{Kj}^2(Y_i)} \quad (12)$$

That is, the Warnatz's indices provide essentially the same magnitude and order of importance of uncertainties as the square root of the partial kinetic uncertainty contributions defined in this work. The sum of Warnatz's indices has no physical meaning, however, unlike the sum of the partial contributions.

Among the few kinetic uncertainty analyses reported in the combustion literature, that by Brown and co-workers<sup>14</sup> applies a methodology most similar to ours. Their uncertainty analysis has also been based on local sensitivities and conventional error analysis, but there are also significant differences. First, the only model result considered by Brown *et al.* was the flame velocity. Second, non-normalized sensitivity coefficients were used in their study and accordingly, the stochastic variable was the kinetic parameter  $B_j$  and not its logarithm. Thus, the originally symmetrical uncertainty limits in  $\log_{10} B_j$  (taken from Baulch *et al.*<sup>42</sup>) became asymmetrical in  $B_j$ . For example,  $\log_{10} B_j = 10 \pm 0.3$  became<sup>14</sup>  $B_j = (1.0_{-0.5}^{+1.0}) \times 10^{10}$ . To overcome this difficulty, the geometric mean of the two uncertainty limits was used by the authors, that is,  $B_j = 1.0 \pm 0.71 \times 10^{10}$  was assumed in the above example. We believe that this is an inappropriate treatment of the problem and argue that the analysis should be carried out using stochastic variables having symmetrical *pdf*'s as described above.

### Thermodynamic and overall uncertainties

The uncertainty of the output of chemical kinetic models that originates from the errors of thermodynamic parameters can be calculated similarly to the effect of the errors of kinetic parameters. Assume that  $\Delta_f H_{298}^\circ$  is a stochastic variable with a symmetrical *pdf* and that the value used in the model is the expected value of this variable for each species. Also assume that the heats of formation data are uncorrelated. With these premises, the following equations can be derived for the calculation of the variance of model output  $Y_i$ :

$$\sigma_{Tj}^2(Y_i) = \left( \frac{\partial Y_i}{\partial \Delta_f H_{298}^\circ(j)} \right)^2 \sigma^2(\Delta_f H_{298}^\circ(j)) \quad (13)$$

$$\sigma_T^2(Y_i) = \sum_j \sigma_{Tj}^2(Y_i) \quad (14)$$

$$S_{\Gamma\%ij} = \frac{\sigma_{Tj}^2(Y_i)}{\sigma_T^2(Y_i)} \times 100 \quad (15)$$

where subscript T refers to thermodynamic uncertainty,  $\partial Y_i / \partial \Delta_f H_{298}^{\circ}(j)$  is a local heat of formation sensitivity coefficient, which is a linear estimation of the effect of changing the heat of formation,  $\sigma_T^2(Y_i)$  is the variance of model output  $Y_i$  due to the uncertainties of the heats of formation of all species, named here as the ‘thermodynamic uncertainty contribution’, and  $\sigma_{Tj}^2(Y_i)$  is the contribution of the uncertainty of the heat of formation of species  $j$  to the variance of model output  $Y_i$  that we call the ‘partial thermodynamic uncertainty contribution’.  $S_{\Gamma\%ij}$  indicates the percentage contribution of  $\sigma_{Tj}^2(Y_i)$  to  $\sigma_T^2(Y_i)$ .

Rate coefficients of the reactions for methane combustion are usually not used for the derivation of thermodynamic data and therefore the rate coefficients and the heat of formation data used in our mechanism can be considered uncorrelated. Consequently, the overall uncertainty (variance) of a model output,  $\sigma^2(Y_i)$  is the sum of the kinetic uncertainty contribution and the thermodynamic uncertainty contribution:

$$\sigma^2(Y_i) = \sigma_K^2(Y_i) + \sigma_T^2(Y_i) \quad (16)$$

The square root of the overall variance,  $\sigma(Y_i)$ , is understood as overall standard deviation of model output  $Y_i$ .

In order to compare the kinetic and thermodynamic uncertainties and for the sake of a uniform treatment of the results we define the following parameter vector:  $\mathbf{p} = \{\ln k_1, \ln k_2, \dots, \ln k_m, \Delta_f H_{298}^{\circ}(1), \Delta_f H_{298}^{\circ}(2), \dots, \Delta_f H_{298}^{\circ}(n)\}$ , which includes the logarithm of the rate coefficients of the  $m$  elementary reactions and the heats of formation of  $n$  species taking part in the methane oxidation mechanism. Let us now define  $\sigma_j^2(Y_i)$  as the uncertainty contribution of parameter  $p_j$  (which is either partial kinetic or partial thermodynamic uncertainty contribution). Then,  $S_{\%ij}$  provides the percentage share of  $\sigma_j^2(Y_i)$  to the overall variance  $\sigma^2(Y_i)$ :

$$S_{\%ij} = \frac{\sigma_j^2(Y_i)}{\sigma^2(Y_i)} \times 100 \quad (17)$$

Values  $\sigma_j^2(Y_i)$  or  $S_{\%ij}$  can be used to create a joint rank order of uncertainty contributions of kinetic and thermodynamic parameters.

Bromly *et al.*<sup>13</sup> have carried out a joint kinetic and thermodynamic uncertainty analysis on a special system, the NO-sensitised low temperature oxidation of methane. They defined kinetic ( $i_{i,j}$ ) and thermodynamic ( $i_{i,j}^H$ ) ‘impact factors’ in the following way:

$$i_{i,j} = \left| \frac{\partial \ln Y_i}{\partial \ln k_j} f_j \right| \approx 1.30 \sqrt{\sigma_{Kj}^2(\ln Y_i)} \quad (18)$$

$$i_{i,j}^H = \left| \frac{\partial \ln Y_i}{\partial \Delta_f H_{298}^{\circ}(j)} \sigma(\Delta_f H_{298}^{\circ}(j)) \right| = \sqrt{\sigma_{Tj}^2(\ln Y_i)} \quad (19)$$

These impact factors are reproduced here using the notations of this paper and are related to the partial uncertainty contributions defined above. These equations show that the impact factors of Bromly *et al.*<sup>13</sup> are practically identical to the square root of the contribution of a parameter to the variance of the logarithm of the model output. This approach is equally effective in setting a hierarchical order of the kinetic and thermodynamic sources that contribute to the uncertainty of model results. However, the sum of these ‘impact factors’ do not provide the total uncertainty of a model result.

All sensitivities and uncertainties discussed so far refer to model output values, like calculated concentrations. However, in chemical kinetic simulations not only the calculated concentrations carry important information, but also the locations of the concentration peaks. These locations can be deduced from the concentration-distance curves, but their sensitivity is not

calculated by the simulation codes. However, following the reasoning of ref. 56 (p. 446), the required sensitivities can be calculated from the derivative of the sensitivity and concentration curves with respect to the spatial variable at location of the peak. Assume that the concentration of species  $i$  has maximum at location  $x^*$ . Eqns. (20) and (21) provide the kinetic and thermodynamic sensitivities, respectively, for the location of the maximum.

$$\frac{\partial x^*}{\partial \ln k_j} = - \frac{\frac{\partial^2 c_i(x^*)}{\partial x \partial \ln k_j}}{\frac{\partial^2 c_i(x^*)}{\partial x^2}} \quad (20)$$

$$\frac{\partial x^*}{\partial \Delta_f H_{298}^{\circ}(j)} = - \frac{\frac{\partial^2 c_i(x^*)}{\partial x \partial \Delta_f H_{298}^{\circ}(j)}}{\frac{\partial^2 c_i(x^*)}{\partial x^2}} \quad (21)$$

These derived local sensitivities can be used to calculate the kinetic and thermodynamic uncertainties of the location of maximal concentrations in laminar flames.

## Discussion of methane flame uncertainty analysis results

Premixed adiabatic laminar one-dimensional methane-air flames were simulated using the Leeds Methane Oxidation Mechanism<sup>11</sup> version 1.5. The cold boundary conditions were  $p = 1$  atm and  $T = 298$  K and included lean ( $\varphi = 0.62$ ), stoichiometric ( $\varphi = 1.00$ ) and rich ( $\varphi = 1.20$ ) fuel-to-air ratios. The simulations were carried out with the PREMIX code<sup>57</sup> of the CHEMKIN-II collection of programs.<sup>23</sup> PREMIX can calculate normalized local reaction sensitivities,  $\partial \ln Y_i / \partial \ln k_j$ , and normalized heat of formation sensitivities. More precisely, instead of heat of formation sensitivities, PREMIX calculates  $(a_{6,j} / Y_i) (\partial Y_i / \partial a_{6,j})$  coefficients, where parameter  $a_{6,j}$  has been defined in eqn. (2). This coefficient can easily be transformed to  $\partial Y_i / \partial \Delta_f H_{298}^{\circ}(j)$ , which is needed for eqn. (13).

Heat of formation sensitivities and rate coefficient sensitivities for the following model outputs were determined: laminar flame velocity,  $v_L$ , maximum adiabatic flame temperature,  $T_{\max}$ , and maximum concentration  $[H]_{\max}$ ,  $[O]_{\max}$ ,  $[OH]_{\max}$ ,  $[CH]_{\max}$  and  $[CH_2]_{\max}$ . The calculation of the exact values of these quantities is important in several applications of flame simulations.<sup>1</sup> Laminar flame velocity is a generally applicable quantity for the description of the speed of combustion. The reproduction of experimental flame velocity is considered to be a measure of the quality of chemical kinetic mechanisms, but its role in combustion modelling is often exaggerated (see below). The most effective chain carrier in hydrocarbon combustion systems is the H-atom; therefore the exact calculation of its concentration is of high importance. Exact calculation of flame temperature is also important, because the conversion rate of fuels in flames depends strongly on temperature and because a possible aim of combustion calculations is the determination of heat release. Another usual aim of combustion simulations is the calculation of NO production. NO generation is determined by the local temperature and the concentration of radicals O and OH *via* the extended Zeldovich mechanism. In the Fenimore mechanism of NO generation and at reburn conditions, the NO production is controlled to a great extent by the concentration of radicals CH and CH<sub>2</sub>.

Sensitivity coefficients obtained in methane flame simulations were converted into uncertainty information as described in the previous sections. All of the overall standard deviations obtained are presented in Table 2. The computed flame velocity has  $\sigma(v_L)$  values of 2.5 cm s<sup>-1</sup>, 4.6 cm s<sup>-1</sup> and 5.5 cm s<sup>-1</sup> at lean, stoichiometric and rich conditions, respectively.

**Table 2** Overall standard deviations for laminar flame velocity, top flame temperature and maximum concentration of radicals H, O, OH, CH and CH<sub>2</sub> as a percentage of the mean value,  $100 \times \sigma(Y_i)/Y_i$ , obtained from methane flame simulation/uncertainty analysis studies

$Y_i$	$100 \times \sigma(Y_i)/Y_i$					
	$\phi = 0.62^a$		$\phi = 1.00^a$		$\phi = 1.20^a$	
	case $a^b$ (%)	case $b^c$ (%)	case $a^b$ (%)	case $b^c$ (%)	case $a^b$ (%)	case $b^c$ (%)
$v_L$	17.82	17.82	12.08	12.08	20.15	20.15
$T_{\max}$	0.16	0.09	0.10	0.09	0.05	0.05
$[H]_{\max}$	2.67	1.17	2.20	1.87	6.48	5.46
$[O]_{\max}$	0.96	0.91	3.44	1.48	13.29	9.55
$[OH]_{\max}$	17.14	3.13	11.73	2.15	8.99	4.08
$[CH]_{\max}$	67.52	61.50	24.58	21.26	19.33	18.62
$[CH_2]_{\max}$	167.22	165.02	25.99	25.29	24.61	24.61

<sup>a</sup> Fuel-to-air ratio. <sup>b</sup> Obtained with  $\Delta_f H_{298}^\circ(\text{OH}) = 37.2 \pm 2.1 \text{ kJ mol}^{-1}$  (see text). <sup>c</sup> Obtained with  $\Delta_f H_{298}^\circ(\text{OH}) = 37.2 \pm 0.38 \text{ kJ mol}^{-1}$  (see text).

These are 17.8%, 12.1%, and 20.2%, of the respective mean values. Our findings are in accordance with the uncertainty analysis results of Brown *et al.*<sup>14</sup> These authors have found that the ratio of the overall standard deviation and the mean value of laminar flame velocity for a stationary laminar hydrogen-air flame varies between 8% and 10% (20 to 30 cm s<sup>-1</sup>) in the fuel-to-air ratio range of  $\phi = 0.7$ –2.0. Brown *et al.* have also carried out preliminary calculations for a methane-air flame using an earlier version of the Leeds Methane Oxidation Mechanism and found the uncertainty to be 12%–13%. Combustion mechanisms are usually required to reproduce the experimental flame velocity within  $\pm 1 \text{ cm s}^{-1}$ . The above results show, however, that this is not a realistic demand because the current magnitudes of errors of rate parameters induce an uncertainty of  $\pm 2$ –5 cm s<sup>-1</sup> for methane-air and  $\pm 20$ –30 cm s<sup>-1</sup> for hydrogen-air flames. The excellent concurrence of simulated flame velocity with experiment is essentially a result of fortuitous agreement or ‘fine-tuning’ (simultaneous adjustment of several rate coefficients in the reaction mechanism).

The top flame temperature has an uncertainty of 2.3 K (0.10%) at stoichiometric and 1–2 K (0.05–0.16%) at rich and lean conditions assuming large error limits for the heat of formation of OH radical (case *a*). The uncertainty of temperature is even lower (0.05%–0.09%), if a lower uncertainty for  $\Delta_f H_{298}^\circ(\text{OH})$  is assumed (case *b*). The very low uncertainty of the calculated temperature is reassuring since temperature is a very important control variable in combustion systems.

It is seen in Table 2 that the overall standard deviations for the maximum concentration of radicals H and O are relatively small (1–3%) at lean and stoichiometric conditions, but become larger (6–13%) at rich conditions. Uncertainty of  $[OH]_{\max}$  is higher (9–17%) and it decreases with increasing fuel-to-air ratio. The uncertainty of the maximum concentration of radicals H, O, and OH is much smaller if the error of the heat of formation value of OH is assumed to be small (case *b*); the most significant is the improvement for  $[OH]_{\max}$ . The calculated  $[CH]_{\max}$  and  $[CH_2]_{\max}$  have high uncertainties at all conditions.

Fig. 1 shows the share of the kinetic and thermodynamic uncertainty contributions to the total variance of model output  $Y_i$ , expressed as  $\sigma_K^2(Y_i)/\sigma^2(Y_i) \times 100$  and  $\sigma_T^2(Y_i)/\sigma^2(Y_i) \times 100$ . It is clearly seen in Fig. 1 that the uncertainty of laminar flame velocity is fully of kinetic origin. Similarly, the uncertainties of the maximum concentration of radicals CH and CH<sub>2</sub> mostly originate from kinetic sources. In their study, Brown *et al.*<sup>14</sup> examined only the kinetic sources of the uncertainty of flame velocity. Our results demonstrate that it was a good approximation by the authors since all uncertainty in the calculated flame velocity comes from the rate parameters applied. As can be expected, the maximum temperature is fully controlled by the thermodynamic data and the errors of rate parameters

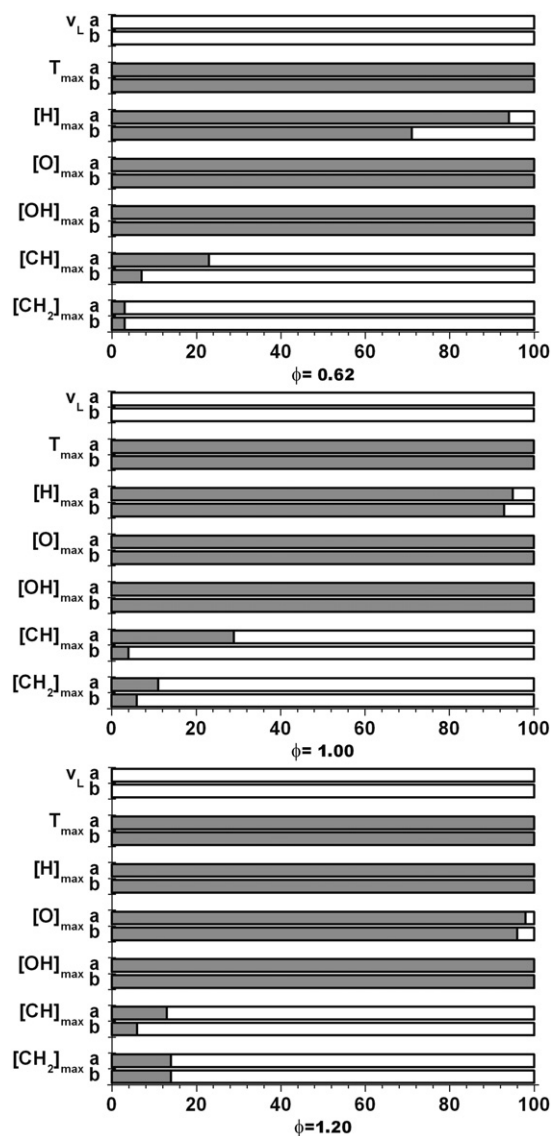
have no perceptible effect on this model output. It was unexpected, however, that the uncertainty of the maximum concentration of radicals H, O and OH are also fully or mainly of thermodynamic origin. The general conclusions are independent of the fuel-to-air ratios and the assumed uncertainty for  $\Delta_f H_{298}^\circ(\text{OH})$ .

As far as we know, this is the first comparison of kinetic and thermodynamic uncertainties for methane flame simulation results. The only similar calculations were carried out by Bromly *et al.*<sup>13</sup> Bromly and co-workers performed a combined experimental and modelling study on the NO-sensitised oxidation of methane in a plug-flow reactor between 773 and 973 K. The measured concentration profiles of CH<sub>4</sub>, CO, CO<sub>2</sub>, NO and NO<sub>2</sub> were described by a detailed chemical mechanism. This was the basis of the kinetic and thermodynamic uncertainty analyses, for which the authors used the ‘impact factors’ defined by eqns. (18) and (19). The chemistry of the low temperature NO-sensitised oxidation of methane in a plug-flow reactor is vastly different from that of the premixed methane flame, therefore the results are not directly comparable. It is interesting to note, however, that Bromly *et al.*<sup>13</sup> have found the thermodynamic uncertainty to exert greater influence on the calculated concentration of products compared to kinetic uncertainty.

Fig. 2 shows the partial kinetic and partial thermodynamic uncertainty contributions expressed as the percentage of total variances, *i.e.*,  $S^2_{0ij}$  (see eqn. (17)), at the three fuel-to-air ratios and two cases for each of the seven model results investigated. Uncertainty of the calculated flame velocity is caused by errors of the rate coefficients of the reactions  $\text{O}_2 + \text{H} = \text{OH} + \text{O}$ ,  $\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$ ,  $\text{O}_2 + \text{H} + \text{M} = \text{HO}_2 + \text{M}$  and  $\text{H} + \text{CH}_3(+\text{M}) = \text{CH}_4(+\text{M})$ . The effect of the last reaction becomes important at stoichiometric and rich conditions. Heat of formation errors do not play a role in affecting the uncertainty of flame velocity.

Brown *et al.*<sup>14</sup> found that errors of the rate coefficients of reactions  $\text{O}_2 + \text{H} = \text{OH} + \text{O}$  and  $\text{O}_2 + \text{H} + \text{M} = \text{HO}_2 + \text{M}$  cause high uncertainty to the velocity of hydrogen-air flame. Warnatz<sup>12</sup> has demonstrated that the calculated velocity of a propane-air flame is uncertain mainly due to errors of the rate coefficients of the reactions  $\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$ ,  $\text{O}_2 + \text{H} = \text{OH} + \text{O}$  and  $\text{O}_2 + \text{H} + \text{M} = \text{HO}_2 + \text{M}$ . Thus, it can be concluded that the very same reactions cause the most uncertainty to the calculated velocity of hydrogen-, methane-, and propane-air flames. The reason is that mainly these reactions control the level of the radical pool in the combustion of all hydrogen containing fuels.

In freely propagating flames, the reference point of the coordinate system is at fixed temperature, which in our case is at 400 K. It is expected intuitively that if a parameter perturbation moves the peaks of radical concentrations closer to this point, it also increases the velocity of the flame. Using eqns.



**Fig. 1** Kinetic (white bars) and thermodynamic (grey bars) uncertainty contributions expressed as the percentage of the total variances of methane flame simulation outputs. Plotted are  $(\sigma_K^2(Y_i)/\sigma^2(Y_i)) \times 100$  and  $(\sigma_T^2(Y_i)/\sigma^2(Y_i)) \times 100$  at lean, stoichiometric and rich conditions. Lines 'a' and 'b' correspond to computational results obtained with assumed OH heat of formation uncertainties ( $1\sigma$ ) of  $\pm 2.1$  and  $\pm 0.38$   $\text{kJ mol}^{-1}$ , respectively.

(20) and (21), the sensitivities of the location of the concentration peaks were calculated and then these were converted into thermodynamic and kinetic uncertainties. The largest relative uncertainties ( $S\%_{ij}$ ) were practically identical for all radicals (H, O, OH, CH,  $\text{CH}_2$ ) and were identical to the flame velocity uncertainties. This shows an internal consistency of the results, because these similar uncertainties were calculated from very different sensitivity data.

The uncertainty of the calculated maximum flame temperature is relatively low (see the second row in Fig. 2). It mainly originates from the error of the heat of formation of OH in lean methane-air flames. At stoichiometric and rich conditions the uncertainty of  $T_{\text{max}}$  is determined by errors of  $\Delta_f H_{298}^\circ(\text{CH}_2\text{HCO})$  and  $\Delta_f H_{298}^\circ(\text{CH}_4)$ . The influence of the error of the heat of formation of the vinyloxy radical on the uncertainty of the calculated adiabatic top temperature in methane flame modelling is noteworthy, and calls for a more accurate determination of this thermodynamic quantity. Errors of rate coefficients cause negligible effect on  $T_{\text{max}}$ . The uncertainties of the maximum concentration of H, O and OH are mainly determined by errors of  $\Delta_f H_{298}^\circ(\text{OH})$ ,  $\Delta_f H_{298}^\circ(\text{O})$  and

$\Delta_f H_{298}^\circ(\text{CH}_2(\text{S}))$  in lean and stoichiometric flames and also by errors of  $\Delta_f H_{298}^\circ(\text{CH}_2\text{OH})$  and  $\Delta_f H_{298}^\circ(\text{HCCO})$  in rich flames. Uncertainty of the calculated concentration of CH is controlled by the errors of some kinetic parameters and the heat of formation of OH. At lean conditions, errors in the rate coefficients of the reactions  $\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$ ,  $\text{O}_2 + \text{H} = \text{OH} + \text{O}$ ,  $\text{O}_2 + \text{H} + \text{M} = \text{HO}_2 + \text{M}$  and  $\text{HCO} + \text{M} = \text{H} + \text{CO} + \text{M}$  have a high influence, while at stoichiometric and rich conditions, reactions  $\text{C}_2\text{H}_2 + \text{OH} = \text{C}_2\text{H} + \text{H}_2\text{O}$ ,  $\text{C}_2\text{H}_2 + \text{CH} = \text{C}_2\text{H} + \text{CH}_2$  and  $\text{H} + \text{CH}_2 = \text{CH} + \text{H}_2$  take over. The influence of the heat of formation of OH diminishes if it is assumed to be more accurate (case b). The uncertainty of  $[\text{CH}_2]_{\text{max}}$  (last row in Fig. 2) is determined by errors of the rate coefficients of the following reactions at lean conditions:  $\text{O}_2 + \text{H} = \text{OH} + \text{O}$ ,  $\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$ ,  $\text{O}_2 + \text{H} + \text{M} = \text{HO}_2 + \text{M}$  and  $\text{HCO} + \text{M} = \text{H} + \text{CO} + \text{M}$ . At rich and stoichiometric conditions, errors of  $k(\text{CH}_3 + \text{OH} = \text{CH}_2(\text{S}) + \text{H}_2\text{O})$  and  $\Delta_f H_{298}^\circ(\text{CH}_2)$  also play a role in determining the uncertainty of the calculated maximum concentration of  $\text{CH}_2$ .

## Summary

A method has been developed to estimate the uncertainties of combustion modelling results from the uncertainties of the input rate coefficients and heats of formation. Application for a premixed laminar methane flame was presented. The method employs: (i) the determination of the local kinetic and thermodynamic sensitivity coefficients, (ii) assignment of error limits to the input kinetic and thermodynamic parameters and (iii) the combination of sensitivity coefficients and parameter errors to obtain uncertainty parameters for selected model outputs by the application of error analysis.

The following easily applicable equations and uncertainty parameters have been derived to characterise uncertainty of simulation results:

$$\sigma^2(Y_i) = \sigma_K^2(Y_i) + \sigma_T^2(Y_i) = \sum_j \sigma_{K_j}^2(Y_i) + \sum_j \sigma_{T_j}^2(Y_i)$$

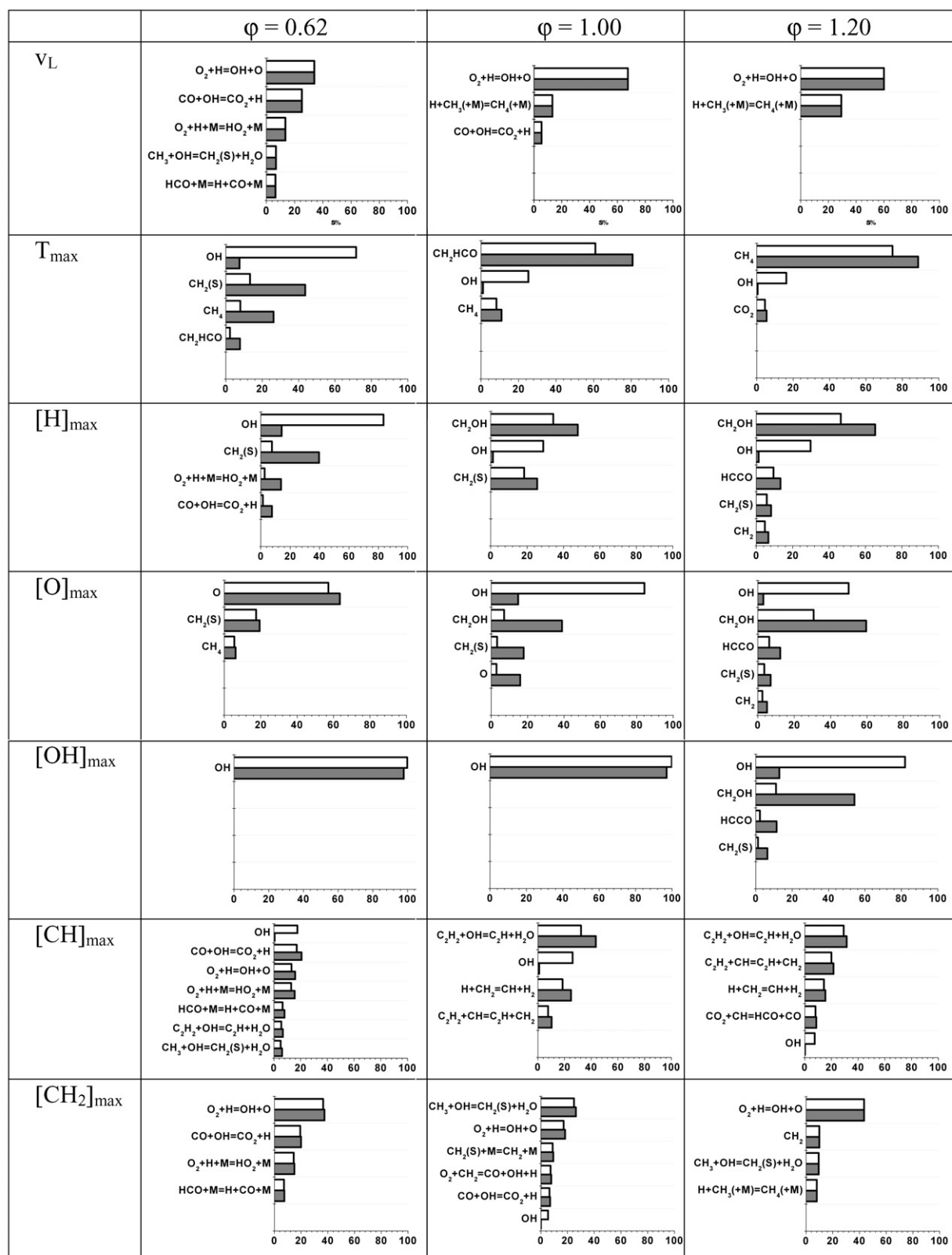
$$\sigma_{K_j}^2(Y_i) = (\partial Y_i / \partial \ln k_j)^2 \sigma^2(\ln k_j)$$

$$\sigma_{T_j}^2(Y_i) = (\partial Y_i / \partial \Delta_f H_{298}^\circ(j))^2 \sigma^2(\Delta_f H_{298}^\circ(j))$$

In the expressions above  $Y_i$  designates the simulation output (e.g., calculated laminar flame velocity, flame temperature, concentration etc.);  $\sigma^2(Y_i)$  is the overall uncertainty (variance),  $\sigma_K^2(Y_i)$  and  $\sigma_T^2(Y_i)$  designate the kinetic (rate coefficient) uncertainty contribution and thermodynamic (heat of formation) uncertainty contribution, respectively. The partial uncertainty contributions,  $\sigma_{K_j}^2(Y_i)$  and  $\sigma_{T_j}^2(Y_i)$  are suitable to determine an order of importance of input parameters in affecting the uncertainty of the model output. The sensitivity coefficients,  $(\partial Y_i / \partial \ln k_j)^2$  and  $(\partial Y_i / \partial \Delta_f H_{298}^\circ(j))^2$ , can be calculated using combustion simulation programs. The rate coefficient uncertainty factor,  $f_j$ , and heat of formation variance,  $\sigma^2(\Delta_f H_{298}^\circ(j))$  are either available from critical data evaluations or should be estimated. Variance of rate coefficients can be calculated from the uncertainty factor  $f_j$ :  $\sigma^2(\ln k_j) = (f_j \ln 10)/3)^2$ .

Uncertainty analyses as described above were employed on the Leeds Methane Oxidation Mechanism.<sup>10</sup> The thermodynamic data in the mechanism were revised and recommended heats of formation with error limits were assigned to all species. Error limits ( $f_j$  factors) were also assigned to the rate coefficients of all reactions. Uncertainty parameters for flame velocity, maximum flame temperature and maximum concentration of radicals H, O, OH, CH and  $\text{CH}_2$  were calculated for laminar, premixed, flat, atmospheric pressure methane-air flames at lean, stoichiometric and rich conditions.





**Fig. 2** Percentage shares ( $S\%_{ij}$ ) of the uncertainty of heat of formation and rate coefficient data to the total uncertainty of the calculated laminar flame velocity, maximum temperature and maximum concentration of radicals H, O, OH, CH and  $CH_2$  in methane flame simulations. Only shares larger than 5% are shown. The upper (white) bars refer to case *a*, ( $\sigma(\Delta_f H_{298}^{\circ}(\text{OH})) = 2.1 \text{ kJ mol}^{-1}$ ), and the lower (grey) bars refer to case *b*, ( $\sigma(\Delta_f H_{298}^{\circ}(\text{OH})) = 0.38 \text{ kJ mol}^{-1}$ ). On the vertical axes, the elementary reactions and chemical formulas refer to rate coefficients and heats of formation, respectively.

The uncertainty analyses have shown the calculated top flame temperature to be accurate within a few tenths of a percent; the uncertainty of  $[H]_{max}$  and  $[O]_{max}$  is also small. However, the calculated overall uncertainty for flame velocity and the maximum concentration of OH, CH and  $CH_2$  is fairly large

at all conditions. The overall uncertainty of  $T_{max}$ ,  $[H]_{max}$ ,  $[O]_{max}$  and  $[OH]_{max}$  originates mainly from errors of input thermodynamic data. The laminar flame velocity and maximum concentration of CH and  $CH_2$  radicals are uncertain primarily because of the errors of rate coefficients.

The Leeds Methane Oxidation Mechanism contains 175 reactions and 36 species. However, errors of the heats of formation of only a few species cause uncertainty to the model results. These species are OH, CH<sub>2</sub>(S), CH<sub>2</sub>, CH<sub>2</sub>OH, HCCO and CH<sub>2</sub>HCO. For the  $\Delta_f H_{298}^\circ$  values of these radicals, we have assigned the standard deviations of 2.1, 2.5, 4.0, 4.2, 8.8 and 9.2 kJ mol<sup>-1</sup>, respectively. These error limits are among the higher ones, although some of the other heats of formation have larger uncertainty in the mechanism. The species listed above are primary candidates for studies to determine thermodynamic properties more accurately. Similarly, there are very few reactions that cause uncertainty to simulation results. These reactions are O<sub>2</sub> + H = OH + O, O<sub>2</sub> + H + M = HO<sub>2</sub> + M, CO + OH = CO<sub>2</sub> + H, H + CH<sub>3</sub>(+M) = CH<sub>4</sub>(+M), +M, and CH<sub>3</sub> + OH = CH<sub>2</sub>(S) + H<sub>2</sub>O, moreover the acetylene reactions C<sub>2</sub>H<sub>2</sub> + OH = C<sub>2</sub>H + H<sub>2</sub>O and C<sub>2</sub>H<sub>2</sub> + CH = C<sub>2</sub>H + CH<sub>2</sub>. The first three reactions are among the most frequently studied ones in gas kinetics and, accordingly, their rate coefficients have relatively small uncertainty factors ( $f_j \approx 0.3$ ). Nevertheless, the results obtained here indicate that the rate coefficients of these reactions are not yet known with high enough accuracy for exact methane flame modelling. Rate coefficients of the acetylene reactions have much higher uncertainty ( $f_j = 1.0$ ). However, there are several other reaction steps in the methane oxidation mechanism which, although have similarly large uncertainty factors, cause little or entire negligible impact on the uncertainty of modelling results.

Our general conclusion is that uncertainty analysis information should always be supplied with chemical kinetic modelling results. When tests of chemical kinetic models against bulk experimental data are published, the experimental data are usually plotted with *error bars*, while the simulation results are designated by single lines, suggesting that these are error-free quantities. If uncertainty margins of the simulation results were also calculated and plotted, a more realistic comparison of experiments and modelling could be obtained. The overall standard deviations, attached to the model output, would indicate which results are well supported by the model and which ones are merely nominal values that happened to result from the selected set of input parameters.

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