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ON THE RATIONAL INTERPRETATION OF DATA ON LAMINAR FLAME SPEEDS AND IGNITION DELAY TIMES

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This article examines a seemingly trivial issue, namely, the apparently large scatter found for the laminar flame speeds of fuel-rich mixtures as compared to those of lean mixtures. Using the hydrogen/air flame speed at atmospheric pressure as an example, it is demonstrated that this perceptive notion is based on rather uninformed data presentation. It is shown that the cause for the notion has little to do with the data itself, but it is the result that the flame speed data are customarily plotted against the equivalence ratio, which by its asymmetric definition, compresses the data for lean mixtures and expands the data for rich ones. When plotting the flame speed against the symmetrized equivalence ratio defined as $\bar{\phi} \equiv \phi/(1+\phi)$, it can be readily shown that the flame speed data have, in fact, similar uncertainties across the entire range of stoichiometric mixtures tested thus far. A statistical analysis of an extensive set of flame speed data further illustrates the above point, namely, a nearly invariant confidence interval across the same range of stoichiometry. The aforementioned result, coupled with a similar statistical analysis performed for a representative set of shock-tube ignition delay time, highlights the importance of the systematic treatment of the uncertainty in these global, yet fundamental combustion property measurements in aiding reaction model development and testing. For this purpose, an impact factor is proposed for combustion experiments, by combining the sensitivity of the response to rate parameters with the inherent uncertainty of the experiment. It is demonstrated that with the exception of some extreme cases, the impact factors of the flame speed and shock tube ignition delay data are quite close to each other, making both indispensable for model testing. Overall the study illustrates that as a quantitative science, fundamental combustion property measurements must consider inherent experimental uncertainty and require a careful analysis of the uncertainty in order to yield useful results.

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INTRODUCTION

During the past decade or so, there has been increasing interest in the use of experimentally determined laminar flame speed, s_u°, and the ignition delay, τ_{ign}, in the development and test of reaction models for fuel oxidation. Consequently, the demand on the fidelity and accuracy of the data on these global combustion properties has also become more stringent. Among the many fuel/oxidizer mixtures studied, perhaps the hydrogen/oxygen system has commanded the most interest because the system is the essential building block for the oxidation mechanisms of practically all hydrocarbon fuels. Figure 1 summarizes recent experimental data on the s_u° of hydrogen/air mixtures as a function of the equivalence ratio, ϕ, at atmospheric pressure (Aung et al., 1997; Hu et al., 2009; Huang et al., 2006; Kwon and Faeth, 2001; Lamoureux et al., 2003; Tang et al., 2008; Taylor, 1991; Tse et al., 2000; Vagelopoulos et al., 1994); the computed results using the recent kinetic model of Burke et al. (2012) are also included to illustrate typical discrepancies between data and predictions based on a given model. The uncertainty in the s_u° data is represented by scatter in the data values shown, which reflects differences across facilities, methods, and data analysis.

There are two prominent features of Figure 1 showing that, while the scatter in the experimental data seems to be rather tight for the lean mixtures ($\phi < 1$), it starts to increase beyond $\phi \approx 1.0$, and that the scatter is rather large around and beyond the range of the maximum flame speed at $\phi \approx 1.8$. This observation has generated considerable discussion at recent conferences, leading to the suggestion of some inherent differences in lean and rich hydrogen oxidation. The purpose of the present note is to demonstrate that the observed difference is a consequence of how the data are presented, and as such the concern that the scatter in the fuel-rich data is larger than lean data is unwarranted. The demonstration will be further supplemented by a similar consideration of the data on the ignition delays of homogeneous mixtures.

LAMINAR FLAME SPEED

The traditional plot of $s_u^\circ(\phi)$, while providing direct quantitative information on the physical input and response parameters as shown in Figure 1, is not an appropriate measure to indicate the physical influence of either the relative fuel/air concentrations or the sensitivity of the flame response to fuel/air stoichiometry. The definition of ϕ is unevenly skewed, being bounded by a finite span between (0, 1) for lean mixtures and a semi-infinite span between $(1, \infty)$ for rich mixtures. Consequently, variations of the response parameters exhibit steeper slopes on the lean side than the rich side. This asymmetry then translates to the spatial spreads in ϕ, as well as the apparent magnification of uncertainty associated with it in plots of the flame responses, including s_u°, showing greater spread for $\phi > 1$ as compared to $\phi < 1$ mixtures.

A rational measure of the influence of lean-vs.-rich mixtures should be the normalized and symmetrized equivalence ratio, $\bar{\phi}$, that may be defined as $\bar{\phi} \equiv \phi/(1 + \phi)$. Clearly, $\bar{\phi}$ varies within the same spread in intervals, (0, 0.5) and (0.5, 1) for the lean and rich mixtures, respectively (Law, 2006). Figure 2 shows the variation of s_u° with $\bar{\phi}$ for the data

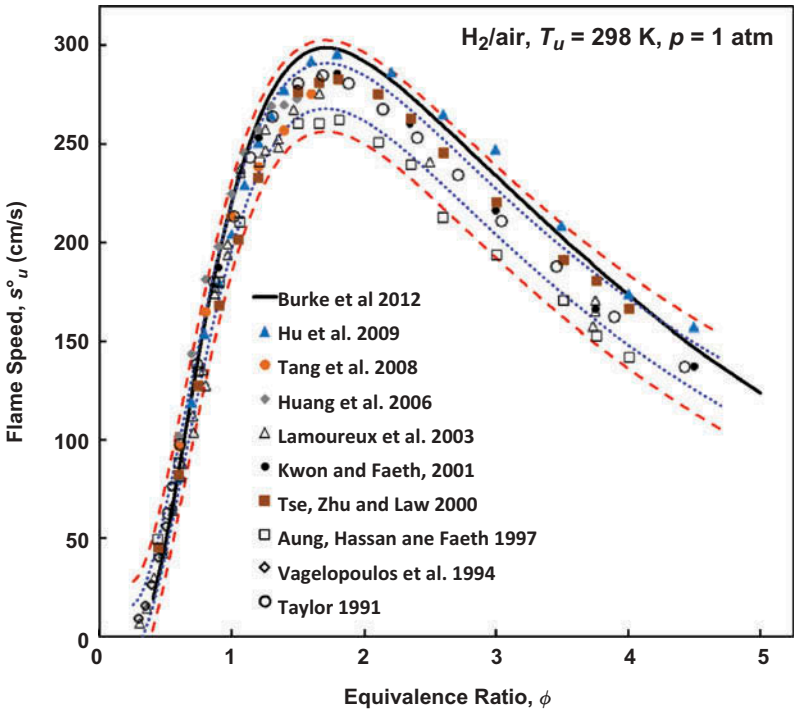

Figure 1 Experimentally determined (symbols) and computationally predicted (solid line) S_u° for hydrogen/air mixtures at 1 atm pressure and 298 K unburned temperature as a function of the equivalence ratio, ϕ. The dotted and dashed lines represent the 1σ (68.3%) and 2σ (95.5%) confidence intervals of the data, respectively.

shown in Figure 1. It is seen that the data scatter is now about equal on both sides of the stoichiometry. Furthermore, the plot reveals yet another apparent observation of the $s_u^\circ(\bar{\phi})$ plot. Namely, the scatter in s_u° appears to be the largest around the range of its maximum values, $0.55 < \bar{\phi} < 0.65$, which approximately corresponds to $1.2 < \phi < 1.8$. This observation is again inappropriate when we analyze the data scatter statistically.

We present below the results of a statistical analysis of the H_2/air flame speed data using standard rational function analysis and nonlinea least squares procedure, in which every data value was treated with equal weights. $s_u^\circ(\phi)$, is modeled as a rational function of the form $s_{u,calc}^\circ(\phi) = p(\phi)/Q(\phi)$, where P and Q are polynomials: $P(\phi) = \sum_{i=0}^{n_p} P_{i-1}\phi^{i-1}$ and $Q(\phi) = 1 + \sum_{i=1}^{n_q} q_i\phi^i$, p_i and q_i are the associated coefficients, and n_p and n_q are the orders of the polynomials. The values of n_p and n_q may be determined through a convergence test on the fit and confidence intervals. For the current data set, we found $n_p = n_q = 3$. A c confidence interval of the size $2\delta(c)$ may be calculated using:

$$\delta(c) = t(c, n_{df}) \left\{ \left(\frac{\sum_{j=1}^{n} \left(s_{u,expt,j}^\circ - s_{u,cale,j}^\circ \right)^2}{n_{df}} \right) \left[1 + \frac{1}{n} + \frac{(\phi - \phi_{mean})^2}{\sum_{j=1}^{n} (\phi - \phi_{mean})^2} \right] \right\}^{1/2}$$

where $t(c, n_{df})$ is the t-value of Student's t-distribution, n is the number of data points, $n_{df} = n - (n_p + n_q)$ is the degree of freedom, j represents the jth data point ($j = 1, \ldots, n$),

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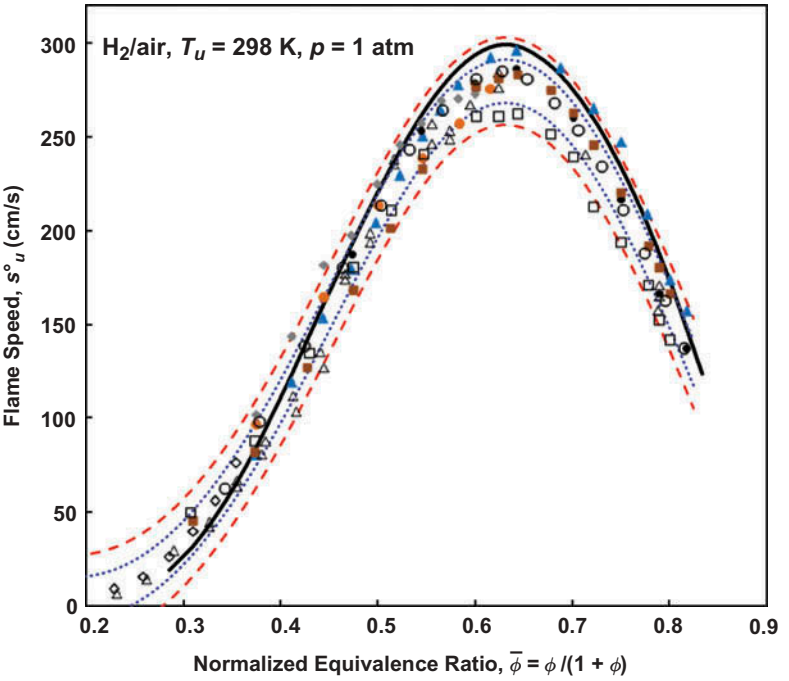

Figure 2 Variation of experimental (symbols) and computed (solid line) s_u° with the normalized equivalence ratio, $\bar{\phi}$. The legend is the same as that of Figure 1. The dotted and dashed lines represent the 1σ (68.3%) and 2σ (95.5%) confidence intervals of the data, respectively.

and $\phi_{mean} = \left(\sum_{j=1}^{n} \phi_j\right) \Big/ n$. The 1σ (68.3%) and 2σ (95.5%) confidence interval bands calculated above are shown in Figures 1 and 2. It is seen that the uncertainty of the data measured by the confidence interval is nearly independent of ϕ and is equal to approximately 23 cm/s for 1σ. The above analysis can be performed also by using $\bar{\phi}$ as the independent variable. The result is found to be identical to the $s_u^\circ(\phi)$ analysis just discussed, as expected.

The nearly constant confidence intervals then bring us to the second point on the $s_u^\circ(\phi)$ plot, namely, while the absolute uncertainty of the data are equal, the relative uncertainty is not. To illustrate this point, we plot the experimental-to-computational deviation in Figure 3, which for consistent referencing is defined as the ratio of the experimental $s_{u,expt}^\circ$ to the numerically computed one, $s_{u,expt}^\circ$ using the kinetic model of Burke et al. (2012) and updated transport coefficient library of Middha and Wang (2005). The results demonstrate the following. First, the scatter is actually the smallest around the regime of the maximum S_u° because of the correspondingly larger *absolute* values, and is progressively amplified as the mixture becomes leaner or richer. This observation again highlights the perceptive deficiency and the need for proper scaling and statistical analysis. Fundamentally, it is reasonable to expect that data of extremely off-stoichiometric, weakly burning flames exhibit greater uncertainty as compared to those of the near-stoichiometric flames, as suggested in Ji et al. (2010). Flame stability, Lewis number, and differential diffusion effects, as well as reactant concentration uncertainties can all attribute to the uncertainty in the S_u° determination. In particular, a recent study (Wu et al., 2014) has identified substantial uncertainty for lean H_2/air flames, in that the data values can differ by as much as 60% due to the

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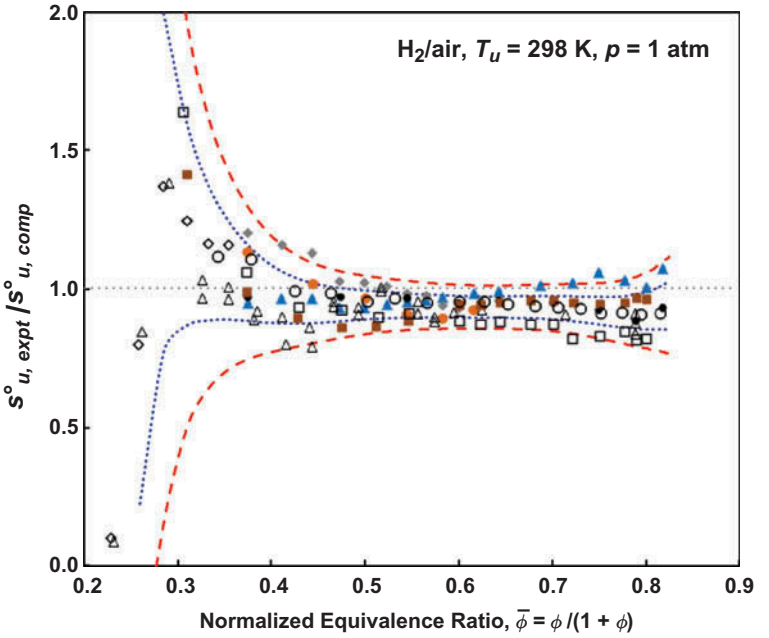

Figure 3 The experimental-to-computed ratio $s^{\circ}_{u,expt}/s^{\circ}_{u,comp}$ as a function of the normalized equivalence ratio, $\bar{\phi}$. The legend is the same as that of Figure 1. The dotted and dashed lines represent the 1σ (68.3%) and 2σ (95.5%) confidence intervals of the data, respectively.

extrapolation procedure employed to eliminate stretch effects. Such discrepancies are perhaps inherent and unavoidable in such measurements, and could reduce the value of the data in testing flame reaction kinetics that emerge as important at low flame temperatures (Law and Egolfopoulos, 1992).

IGNITION DELAYS

A similar concern with data presentation and interpretation is the ignition delay time, τ_{ign}, which is another global combustion property frequently used in testing kinetic models. Figure 4 shows a customary plot of this property, with τ_{ign} in the logarithmic scale versus the inverse temperature. Because of the lack of overlapping measurement, we use here the experimental data $\tau_{ign,expt}$ taken from a single group (Pang et al., 2009) as an example. The corresponding simulated data were obtained by the CHEMSHOCK code (Li et al., 2008) using the reaction model of Burke et al. (2012). The simulation superimposes the relevant gas dynamics (expansion and compression processes) by utilizing the pressure trace acquired from the actual experiments, and as such is probably the closest simulation at present. The calculation procedure is discussed in Li et al. (2008). The plot shows largely close agreement throughout, except for a couple of data points below 1000 K; noting in passing the significantly enlarged uncertainty of the ignition delay data as compared to that of the flame speed, owing to the nature of the shock tube experiments, which are sensitive to non-ideal effects in shock tube operations. A similar statistical analysis on $\ln(\tau_{ign,expt})$ shows that the 1σ and 2σ confidence intervals range from 18% to 22%

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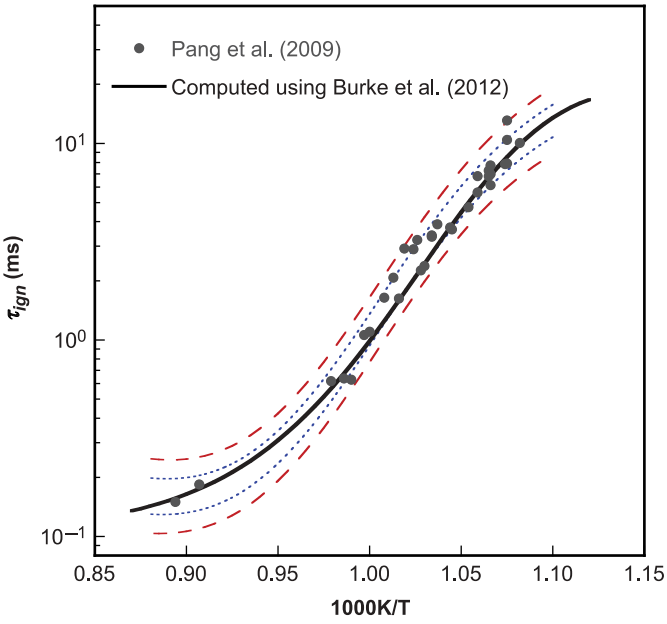

Figure 4 Ignition delay times determined by Pang et al. (2009) for a 4% H_2/2% O_2/94% Ar mixture at an average pressure of 3.5 atm (symbols) and computed using an isochoric-isoenergetic assumption with the reaction model of Burke et al. (2012). The CHEMSHOCK simulation results (solid line) are taken from Pang et al. (2009) wherein a modified version of GRI Mech 3.0 was used. The dotted and dashed lines represent the 1σ and 2σ confidence intervals of the data, respectively.

and 38% to 45% of the $\ln(\tau_{ign,expt})$ values, respectively, across the range of 1000 K/T considered. The confidence interval values translate into respective 1σ and 2σ uncertainty multiplication/division factors of approximately 1.2 and 1.5 in τ_{ign}. It is then clear that experimental-vs.-computed deviations can exceed 50% for individual data points, as shown in Figure 5, where the experimental data are plotted using $\tau_{ign,comp}$ as the reference.

SENSITIVITY ANALYSIS

Recognizing the inherent experimental uncertainties that are present in both laminar flame and shock tube experiments, repercussions of the data scatter can be assessed by evaluating the sensitivity of model prediction to kinetics. Figure 6 shows a typical set of the logarithmic sensitivity coefficients of S_u° and τ_{ign} with respect to the rate constants of the dominant reactions. The sensitivity coefficients of τ_{ign} are local and were computed numerically using a perturbation factor below which truncation error becomes notable. It is seen that although the uncertainties of the τ_{ign} data notably exceed those of S_u°, the sensitivity of τ_{ign} to the rate coefficients of the major chain branching ($H + O_2 \rightarrow OH + O$) and termination ($H + O_2 + M \rightarrow HO_2 + M$) reactions are also substantially larger than that of the flame speeds. Consequently, an impact factor of a specific experiment may be defined with proper normalization, as the ratio of the sensitivity coefficient and the confidence interval of the data. For example, the impact factor of a particular flame speed data point j with respect to a particular rate coefficient i may be expressed by:

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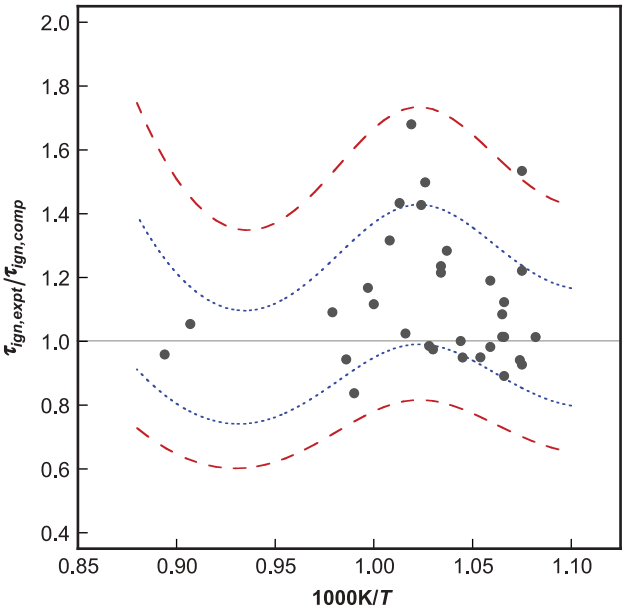

Figure 5 The experimental-to-computed ratio $\tau_{ign,expt}/\tau_{\tau ign,comp}$ for the ignition delay data of Pang et al. (2009) (4% H_2/2% O_2/94% Ar mixture at an average pressure of 3.5 atm). The legend is the same as that of Figure 1. The dotted and dashed lines represent the 1σ and 2σ confidence intervals of the data, respectively.

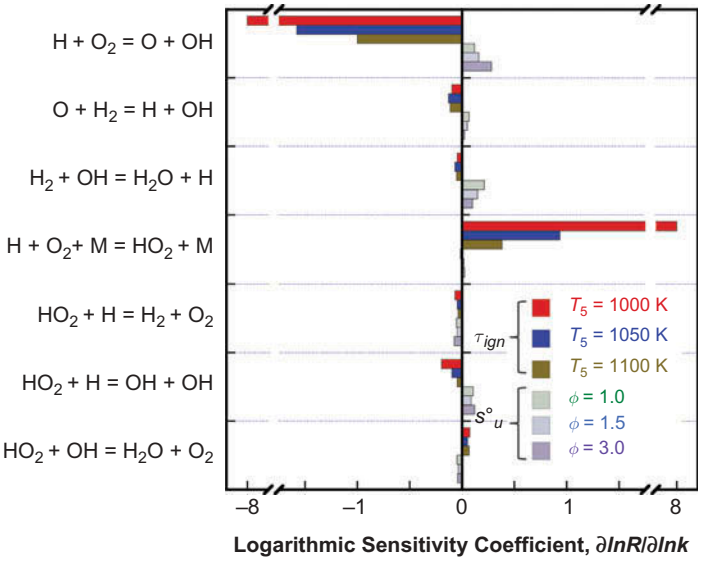

Figure 6 Logarithmic sensitivity coefficients of $R = \tau_{ign}$ computed for a 4% H_2/2% O_2/94% Ar mixture at an average pressure of 3.5 atm at representative temperatures (upper three) and of $R = S_u^\circ$ computed for H_2/air mixtures at 1 atm pressure and 298 K unburned-gas temperature at represented ϕ values (lower three).

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$$I_{S^{\circ}_{u,j},i} = \left(\frac{\partial \ln s^{\circ}_{u,j}}{\partial \ln k_i}\right) \frac{\langle s^{\circ}_{u,expt,j}\rangle}{\delta(95.5\%)}$$

where $\langle s^{\circ}_{u,expt,j}\rangle$ is the average experimental value under that condition and $\delta(95.5\%)$ is one-half of the 2σ confidence interval of the data. Obviously, a large $\delta(95.5\%)$ value or uncertainty would diminish the impact of the data. For ignition delay times, the impact factor may be defined similarly as:

$$I_{\tau_{ign,i},j} = \left(\frac{\partial \ln \tau_{ign,j}}{\partial \ln k_j}\right) \frac{1}{\delta(95.5\%)}$$

where the sensitivity coefficients are nearly the same with/without imposing the experimental pressure. Figure 7 lists the representative I values for the ignition delay times and laminar flame speeds examined in the current study. It is seen that other than the magnified impact of the ignition delay time at $T_5 = 1000$ K on the main chain branching and termination reactions discussed above, the ignition delay times under other conditions and the laminar flame speed data have comparable impact factors to the rate coefficients of the dominant reactions. This is true despite the fact that the sensitivity coefficients of shock-tube ignition delay to the rate parameters are generally larger than those of the flame speed. The larger scatter in the ignition delay time, however, diminishes the degree to an extent to which the data can be used to constrain the model. Finally, we note that the impact factor introduced here is similar, in essence, to the concept of information content that may be determined through a combination of response surface technique and control theory (Frenklach et al. 2004).

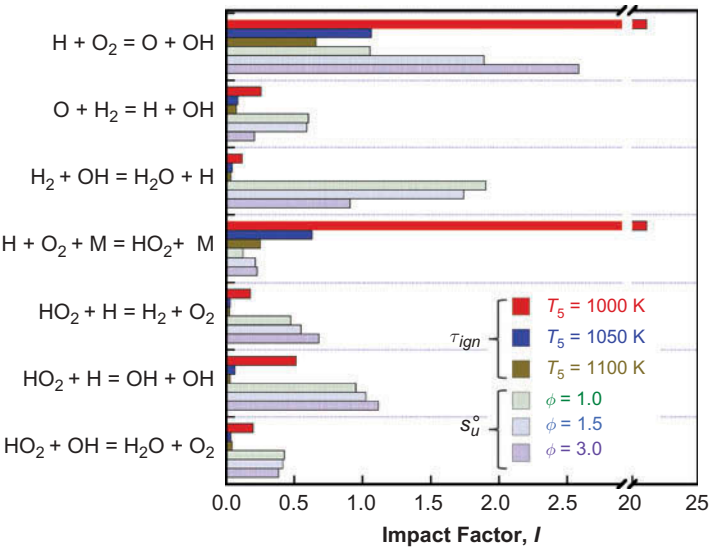

Figure 7 Impact factors for representative ignition delay times (4% H_2/2% O_2/94% Ar mixture at an average pressure of 3.5 atm) and laminar flame speed of H_2/air mixtures at 1 atm pressure and 298 K unburned-gas temperature.

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SUMMARY

It is demonstrated that the apparently large scatter of the H_2/air laminar flame speed data for fuel-rich mixtures is a mere consequence of the specific form in which the data are presented. When the equivalence ratio and the laminar flame speed are appropriately normalized and scaled respectively, or when the available data are subject to a careful statistical analysis, the uncertainty assumes similar magnitude for both lean and rich mixtures. It is also clear that for a given set of data the perceptive notions of even experts can be misled when interpreting the dataset without subjecting such data to a rigorous statistical analysis or proper normalization procedure. A similar statistical analysis was made for the ignition delay times measured in shock tubes for a representative $H_2/O_2/Ar$ mixture. The results show that, although the ignition delay data are often associated with significantly larger scatter than the laminar flame speed, the impact of such data must be viewed in light of the often tremendously larger sensitivities of such response to the rate parameters. An impact factor is proposed that combines the sensitivity coefficients with the confidence interval of the data in a joint consideration. Comparing the two sets of global combustion data considered here, the impact factors of the laminar flame speed are comparable to the shock tube ignition delay time in all but one case, in which the ignition response becomes ultra-sensitive to the ratio of the main chain branching and termination rate parameters. In conclusion, we note that the study reported herein illustrates the point that as a quantitative science, fundamental combustion property measurements must consider inherent experimental uncertainty and a careful analysis of the uncertainty in order to yield informative results.

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REFERENCES

Aung, K.T., Hassan, M.I., and Faeth, G.M. 1997. Flame stretch interactions of laminar premixed hydrogen/air flames at normal temperature and pressure. *Combust. Flame*, **109**, 1–24.

Burke, M.P., Chaos, M., Ju, Y., Dryer, F.L., and Klippenstein, S.J. 2012. Comprehensive H_2/O_2 kinetic model for high-pressure combustion. *Int. J. Chem. Kinet*., **44**, 444–474.

Frenklach, M., Packard, A., Seiler, P., Feeley, R. 2004. Collaborative data processing in developing predictive models of complex reaction systems. *Int. J. Chem. Kinet*., **36**, 57–66.

Huang, Z., Zhang,Y., Zeng, K., Liu, B., Wang, Q., and Jiang, D. 2006. Measurements of laminar burning velocities for natural gas–hydrogen–air mixtures. *Combust. Flame*, **146**, 302–311.

Hu, E., Huang, Z., He, J., Jin, C., and Zheng, J. 2009. Experimental and numerical study on laminar burning characteristics of premixed methane–hydrogen–air flames. *Int. J. Hydrogen Energy*, **34**, 4876–4888.

Ji, C., Dames, E., Wang, Y.L., Wang, H., and Egolfopoulos, F.N. 2010. Propagation and extinction of premixed C_5–C_{12} *n*-alkane flames. *Combust. Flame*, **157**, 277–287.

Kwon, O.C., and Faeth, G.M. 2001. Flame/stretch interactions of premixed hydrogen-fueled flames: Measurements and predictions. *Combust. Flame*, **124**, 590–610.

Lamoureux, N., Djebaïli-Chaumeix, N., and Paillard, C.E. 2003. Laminar flame velocity determination for H_2–air–He–CO_2 mixtures using the spherical bomb method. *Exp. Therm. Fluid Sci*., **27**, 385–393.

Law, C.K. 2006. *Combustion Physics*, Cambridge University Press, New York.

Law, C.K., and Egolfopoulos, F.N. 1992. A unified chain-thermal theory of fundamental flammability limits. *Proc. Combust. Inst*., **24**, 137–144.

Li, H., Owens, Z., Davidson, D.F., and Hanson, R.K. 2008. A simple reactive gas dynamic model for the computation of gas temperature and species concentrations behind reflected shock waves. *Int. J. Chem. Kinet*., **40**, 189–198.

Middha, P., and Wang, H. 2005. First-principle calculation for the high-temperature diffusion coefficients of small pairs: The H-Ar case. *Combust. Theor. Model*., **9**, 353–363.

Pang, G.A., Davidson, D.F., and Hanson, R.K. 2009. Experimental study and modeling of shock tube ignition delay times for hydrogen–oxygen–argon mixtures at low temperatures. *Proc. Combust. Inst*., **32**, 181–188.

Tang, C., Huang, Z., Jin, C., He, J., Wang, J., Wang, X., and Miao, H. 2008. Laminar burning velocities and combustion characteristics of propane–hydrogen–air premixed flames. *Int. J. Hydrogen Energy*, **33**, 4906–4914.

Taylor, S.C. 1991. Burning velocity and the influence of flame stretch. PhD thesis. University of Leeds, Leeds, UK.

Tse, S.D., Zhu, D.L., and Law, C.K. 2000. Morphology and burning rates of expanding spherical flames in H_2/O_2/inert mixtures up to 60 atmospheres. *Proc. Combust. Inst*., **28**, 1793–1800.

Vagelopoulos, C.M., Egolfopoulos, F.N. and Law, C.K. 1994. Further considerations on the determination of laminar flame speeds with the counterflow twin-flame technique. *Proc. Combust. Inst*., **25**, 1341–1347.

Wu, F.J., Liang, W.K., Chen, Z., Ju, Y. and Law, C.K. 2014. Uncertainty in the stretch extrapolation of laminar flame speed from expanding spherical flames. *Proc. Combust. Inst*., **35**. In press. DOI: 10.1016/j.proci.2014.05.065.

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