Brief Communication

Violation of collision limit in recently published reaction models

Dongping Chen, Kun Wang, Hai Wang

Mechanical Engineering Department, Stanford University, Stanford, CA 94305-3032, USA

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ABSTRACT

Twenty reaction models published in five consecutive issues of Combustion and Flame in 2015 and 2016 were screened for the occurrence of collision limit violations. It was found that among the 20 models tested, 15 of them contain either considerable numbers of rate coefficients that exceed their respective collision limits or reactions exceeding the collision limit in a considerable manner. In the worst case, the rate coefficient exceeds the collision limit by 73 orders of magnitude. It is proposed that computational tools should be made available for authors to conduct the same rate coefficient screening. A standard report generated by such screening tools should be submitted as a part of the supplementary material for a manuscript in which one or more reaction models are proposed; reviewers should consult the report in forming his/her opinions about the quality of the reaction model during manuscript review.

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The combustion research community has a long-standing history in using reaction mechanisms or reaction models¹ to explore the underlying physics of complex combustion phenomena [1–3]. Since the work of Hirschfelder, Curtiss, and others [4–7] in the 1950s and by Dixon-Lewis, Gardiner and others in the 1960s [8–11], and of Warnatz, Westbrook, Dryer and others into the 1980s (see, e.g., [12,13]), the use of reaction models has been instrumental in advancing our basic understanding of combustion. In the 1980s, the development of the highly-utilized Chemkin suite of package [14–17] enabled rapid advances of kinetic modeling of combustion processes.

Recent studies in chemical kinetic modeling typically employ large reaction models which in some cases can have 10⁵ reactions and 10⁴ species [18]. The growth in the size of the reaction models is unfortunately not matched by an equal magnitude of high-quality measurements or theoretical calculations of fundamental reaction rates. Today, chemical similarity or reaction class rules are often used to estimate a vast number of rate coefficients. When done carefully and properly, the resulting model can yield useful information about a combustion process, despite the fact that the model is largely empirical. When chemical similarity or reaction rules are exercised inappropriately (e.g., mismatched rate coefficients and thermochemical data), non-physical predictions can occur. Symptoms of such ill-exercised rules include a substantial number of rate coefficients exceeding the collision limit. For example, if a rate rule considers only the forward rate coefficient of an endothermic reaction, it can produce an overly large back rate coefficient if the equilibrium constant of the reaction is not properly taken into consideration.

To illustrate the problem, we sampled 20 reaction models [19–35] published in five consecutive issues of Combustion and Flame (Volume 162 Issues 11 and 12, Volume 163, Volume 164 and Volume 165) for violation of the collision limit in bimolecular reaction rate coefficients. In all cases, Chemkin compatible reaction models and their thermochemical and transport data were directly taken from the Supplementary Materials of the respective papers. For pressure-dependent reactions, only the high-pressure limit bimolecular reactions were considered. The backward reaction rate coefficient was computed via the equilibrium constant if no explicit rate expression is given. Reactions that are declared as irreversible reactions are not screened for the rate coefficients in the reverse direction.

We calculate the collision rate constant \( k_{\text{coll}} \) using

\[
k_{\text{coll}} = \frac{8\pi k_B T}{\mu} \sigma^2 \Omega^{(1,1)} N_0
\]

(1)

where \( T \) is temperature, \( k_B \) is the Boltzmann constant, \( \mu \) is reduced mass, \( \sigma \) is the collision diameter of the Lennard–Jones (LJ) 12-6 potential, \( N_0 \) is the Avogadro number, and \( \Omega^{(1,1)} \) is the reduced collision integral, which may be calculated in a parameterized form [36] as

\[
\Omega^{*} = 1.161457^{-0.14874} + 0.52487e^{-0.77327T^*} + 2.16178e^{-2.43788T^*}
\]

(2)

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¹ Corresponding author.

E-mail address: haiwang@stanford.edu (H. Wang).

¹ The use of the word “mechanism” is for historical reasons. In fact, “reaction model” is more appropriate here because a mechanism refers to how nature works whereas a model is what we use to mimic how nature works. A reaction model involves assumptions which may or may not be verified by isolated experiments.
where $T^*$ is reduced temperature ($T^* = k_b T/\varepsilon$, where $\varepsilon$ is the well depth). The collision diameter and well depth are calculated conventionally as the arithmetic and geometric means of the self-collision potential parameters, respectively. For reaction models that did not include a transport database we used the collision rate coefficient of H collision with n-dodecane at 2500 K and 2.9 × 10^{15} cm^3/mol s as an upper limit of the collision rate constant.

For the 20 reaction models sampled, Table 1 shows the total number of bimolecular-rate coefficients, the number of these rate coefficients that exceed their respective collision limits, and the largest ratio of the rate coefficient to its collision limit. Additional test results can be found in the Supplementary Materials. The models are listed in a random order, though they are separated into two groups: Group 1 is comprised of those with transport parameters provided as a part of the model release/publication, and Group 2 contains those without transport parameters provided. The highest rate ratios are defined as:

$$k_i = \max_{T_i \leq T \leq T_{\text{max}}} \left[ k_i(T) \right]$$

where $I$ is the total number of bimolecular reaction rate coefficients, and $k_i(T)$ is the maximum of the ratio of the rate coefficient to its collision limit over a prescribed range of temperature $T_{\text{min}} \leq T \leq T_{\text{max}}$.

$$k_i^* = \max_{T_{\text{min}} \leq T \leq T_{\text{max}}} \left[ k_i(T)/k_{\text{coll},i}(T) \right]$$

Tests were also made in which the $T_{\text{min}}$ and $T_{\text{max}}$ values were taken from the applicable range of temperature in which a model was tested or applied (see Table 1). Additional tests were made with $T_{\text{max}} = 2500$ K and $T_{\text{min}} = 300, 500$ and 1000 K. The resulting temperature ranges are sometimes larger than the explicit or implied applicable temperature range of a reaction model. The tests were performed considering the fact that a user may apply the model to temperatures outside the range of applicability.

A physically sound reaction model should have no reaction with its $k_i^*$ value substantially greater than unity over the applicable temperature range of the model. As Table 1 reveals, this is not the case for most of the models tested. In our assessment, five models (1, 5, 8, 12 and 15) are acceptable as they contain no rate coefficient that exceeds the collision limit or the violations are caused by difficulties in fitting some of the rate coefficients into the modified Arrhenius equation. Four models (4, 7, 11 and 18) are found to be on the edge, and the remaining eleven models are quite unsatisfactory in two aspects: the number of rate coefficients exceeding the collision limit and the extent to which they exceed the collision limit. The number of nonphysical rate coefficients is usually not large as compared to the total number of rate coefficients, but the extent to which the rate coefficients exceed the collision limit is often disturbing. In the worst case, the ratio is of the order of 10^{73} due to mismatched thermochemical data assigned to species participating in the reaction and its rate coefficient.

The problem usually worsens toward lower temperatures because of mismatched assignments of the forward rate coefficient and species thermochemistry. The kinetic rate-thermochemistry mismatch is quite worrisome in models 2, 3, 6, 9, 10, 13, 14, 16, 17, 19 and 20. In other cases, a non-physical rate coefficient is caused by errors associated with extrapolating a rate expression to low temperatures when the rate expression was obtained in high-temperature experiments. Errors due to typos and other carelessness are also more common than expected. Obviously, it is not straightforward for a reviewer to spot the rate parameter errors during the review process, especially considering the size of many of the reaction models shown in Table 1.

Models 1, 5 and 8 have $k_i^*$ values on the order of 10^1 or 10^2. The problem is sometimes unavoidable, as it originates from difficulties in fitting rate coefficients into a modified Arrhenius expression over an extended range of temperature. The rate coefficients of many multi-channel, chemically activated reactions do not follow the Arrhenius expression. In such cases, the range of applicability of a rate expression does not extend below a cut-off temperature, and the authors usually ensure that non-physical rate values do not impact model predictions. To this end, we note that nonphysical rate coefficients do not always translate into nonphys-
ical predictions. For example, for reacting flows that are close to or governed by chemical equilibrium or chemistry is not rate limiting in an overall reactive process, nonphysical rate coefficients would not produce an appreciable effect on the prediction. Yet in this case, the range of applicability of a model containing nonphysical rate constant must be very limited. Indeed, extending the model to thermodynamic conditions beyond its intended use under any circumstances can be a source of the problem especially for reaction models that contain nonphysical rate coefficients. We note that the unwritten rule or notion that an experimental kinetic measurement must accompany itself with a detailed kinetic modeling component in order for the paper to be accepted is rather misinformed and can hinder proper interpretation of the data and gaining useful insight from the measurement.

From these results, one may conclude that around three quarters of the reaction models published recently contain non-physical rate coefficients. To help to resolve this problem, we wish to make the following specific recommendations.

1. It is crucial for reaction model developers to pay attention to collision-limit violations;
2. When submitting a manuscript for publication, authors have the responsibility to provide explanations in places when and where collision rate violations occur;
3. Computational tools, e.g., those built for Chemkin and Cantera, should be made available for authors to conduct the rate coefficient screening. A standard report generated by such screening tools can be submitted as a supplementary material for a manuscript in which one or more reaction models are proposed;
4. Reviewers should consult the report in forming his/her opinions about the quality of the reaction model during manuscript review.

Editorial policies of a similar nature exist in other fields. Examples include the demonstration of grid-independent or grid-convergent results in computational fluid dynamics, which has been implemented and utilized with success for many years.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.combustflame.2017.08.005.

References