

“Understanding Collisional Energy Transfer in Multi-Component Mixtures of Combustion Systems”

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The overall conversion of fuel and oxygen to water and carbon dioxide during combustion proceeds through numerous individual reactions. A substantial fraction of these reactions are complex-forming (i.e. pressure-dependent) reactions, which depend on the collisional energy transfer characteristics of the surrounding mixture (“bath gas”). In contrast to the pure-component bath gases used in nearly all fundamental investigations, significant fractions of multiple species of disparate collisional energy transfer characteristics are present in combustion environments. Further advancements in combustion modeling capabilities for realistic mixtures require a more comprehensive understanding of the way in which multi-component bath gases affect the collisional energy transfer in complex-forming reactions.

Our master equation studies have shown failures in conventional representations of multi-component mixture effects that reach an order of magnitude. For example, Figure 1a shows deviations of the rate constant according to the conventional linear mixture rule,  $k_{LMR,P}$ , from the rate constant calculated for the mixture using the master equation,  $k$ , for a prototypical single-well, multi-channel reaction. In this reaction, unimolecular decomposition can proceed through a lower energy tight transition state to form stable products or through a higher energy loose transition state to form two radicals. The analysis was performed for a mixture of a weak collider and a strong collider. The results indicate that this deviation is strictly positive for the total decomposition rate constant (not shown) and the rate constant for the lower energy channel. However, the deviations for the higher energy channel can be positive or negative depending on the pressure. These opposite directions of the deviations for the two channels significantly impact the branching ratio between stable products or radicals, with clear implications for combustion radical chain reactions.

We have developed improved mixture rules that account for the interactions between different colliders in their contributions to the rate constant (Table 1). For example, our nonlinear mixture rule based on reduced pressure,  $k_{NMR,R}$ , yields a nearly perfect replication of the mixture rate constant calculated in master equation calculations (Figure 1b). Instead of summing the rate constants for each collider evaluated at the same pressure ( $P$ ) as in the conventional linear mixture rule, the nonlinear mixture rule involves a weighted sum of rate constants evaluated at the same reduced pressure ( $R$ ). The reduced pressure is a dimensionless parameter that compares the rate constants of the low-pressure limit, where energy transfer is infinitesimally slow, to the high-pressure limit, where the energy transfer is infinitely fast. This normalization captures the fact that rate constants evaluated at the same reduced pressure for different colliders are much closer than those evaluated at the same pressure. The weighting coefficient used for the weighted sum in the nonlinear mixture rule was derived here through analytical solutions of the master equation in the low-pressure limit.

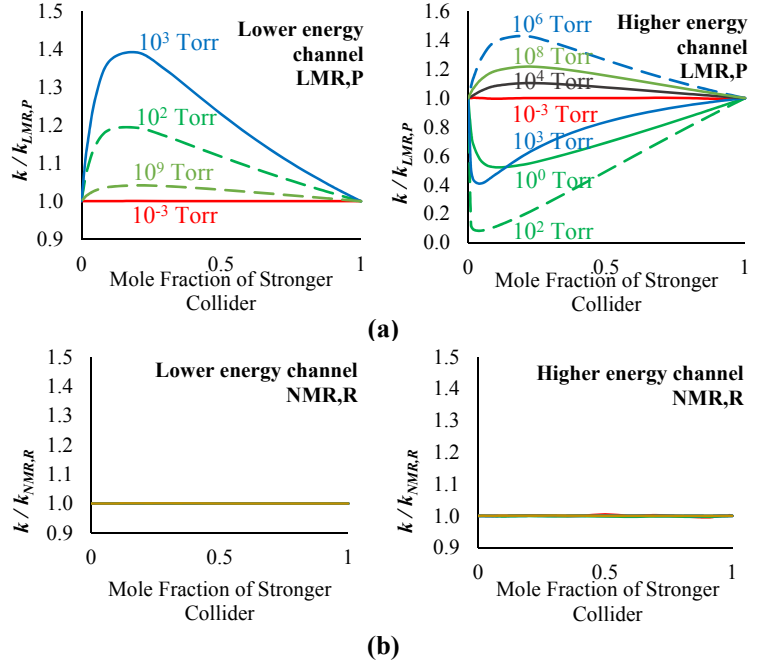


Figure 1. Deviations of the rate constant according to (a) the conventional linear mixture rule,  $k_{LMR,P}$ , and (b) our new nonlinear mixture rule,  $k_{NMR,R}$ , from the rate constant calculated for the mixture using the master equation,  $k$ , for a single-well, two-channel reaction.

Table 1. Various mixture rules for estimating rate constants in multi-component mixtures.

LMR,P:	$k_{n,LMR,P}(T, P, \underline{X}) = \sum_i k_{n,i}(T, P)X_i$
LMR,R:	$k_{n,LMR,R}(T, P, \underline{X}) = \sum_i k_{n,i}(T, R_{LMR})\tilde{X}_{n,i,LMR}$
	$R_{LMR}(T, P, \underline{X}) = \frac{\sum_i k_{0,i}(T)X_i[M]}{k_{\infty}(T)}$ $\tilde{X}_{n,i,LMR}(T, P, \underline{X}) = \frac{k_{0,n,i}(T)X_i}{\sum_j k_{0,n,j}(T)X_j}$
NMR,R:	$k_{n,NMR,R}(T, P, \underline{X}) = \sum_i k_{n,i}(T, R_{NMR})\tilde{X}_{n,i,NMR}$
	$R_{NMR}(T, P, \underline{X}) = \frac{\sum_i f_i(T, \underline{X})k_{0,i}(T)X_i[M]}{k_{\infty}(T)}$ $\tilde{X}_{n,i,NMR}(T, P, \underline{X}) = \frac{f_i(T, \underline{X})k_{0,n,i}(T)X_i}{\sum_j f_j(T, \underline{X})k_{0,n,j}(T)X_j}$

Our master equation studies have also indicated similar improvements of reduced-pressure based mixture rules compared to the conventional linear mixture rule for multi-well reactions. For example, Figures 2a and 2b compare the performance of the conventional linear mixture rule (LMR,P) and our linear reduced-pressure-based mixture rule (LMR,R) for a prototypical multi-well system, where isomerization between the two wells can proceed through a lower energy tight transition state and decomposition from one well to bimolecular products can proceed through a higher energy tight transition state. Similar to the single-well reaction above, the maximum deviations for this multi-well reaction occur at mole fractions where the contributions from each mixture component are comparable. Whereas the conventional linear mixture rule yields deviations of  $\sim 50\%$ , our new reduced-pressure-based mixture rule reproduces master equation calculations within  $\sim 5\%$ .

We have also quantified the importance of the abovementioned mixture effects in simulations of combustion phenomena. Our combustion simulations have indicated that consideration of multi-component effects on complex-forming reactions can have important implications for predicting a variety of combustion properties, including ignition delay times and flame speeds.

Another quintessential feature of multi-component combustion mixtures is the large fraction of reactive collision partners, which can induce bimolecular reactions on timescales that compete with energy transfer. This can result in non-Boltzmann kinetic sequences in combustion mixtures where the energy from exothermic reactions is insufficiently randomized via collisional energy transfer prior to further reactions.

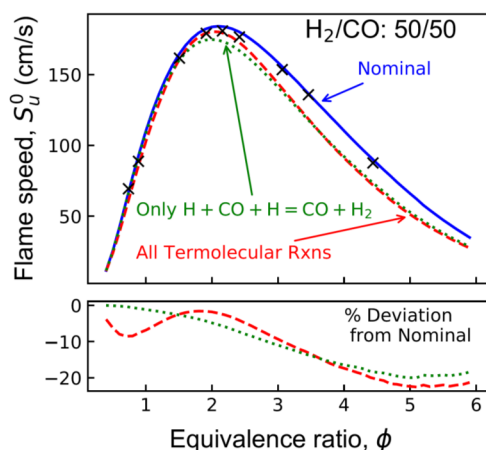


Figure 3. Model predictions of flame speeds using a kinetic model excluding chemically termolecular reactions (nominal) and including chemically termolecular reactions (as indicated).

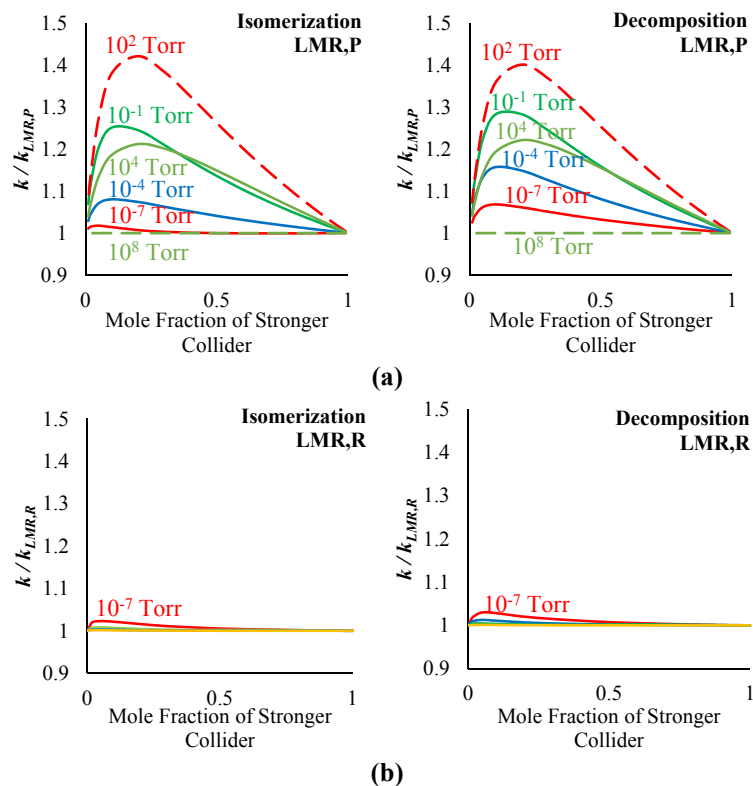


Figure 2. Deviations of the rate constant according to (a) the conventional linear mixture rule,  $k_{LMR,P}$ , and (b) our new linear mixture rule,  $k_{LMR,R}$ , from the rate constant calculated for the mixture using the master equation,  $k$ , for a two-well, one-decomposition-channel reaction.

Phenomenologically, these non-Boltzmann kinetic sequences give rise to chemically termolecular reactions in which three reactants participate in bond breaking and formation. We have identified several potential chemically termolecular reactions with important implications for combustion predictions, including for predictions of flame speeds as shown in Figure 3.

This Doctoral New Investigator grant from the ACS-PRF was my first research grant to be awarded. It therefore has had a significant impact on my early career by helping me establish my research program at Columbia and advance computational methodologies for future investigations. This grant has contributed to the education and career development of the graduate students involved in this project. The results we have generated during this project have been presented at numerous national and international conferences and have led to two archival journal publications in press and more manuscripts currently in preparation.