

Details for Implementing Mixture Rules

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This document provides instructions on how to implement two reduced-pressure-based mixture rules (i.e., linear mixture rule in reduced pressure, LMR,R, and nonlinear mixture rule in reduced pressure, NMR,R, as presented in Table 1 and discussed in Refs. [1, 2]) for evaluating the pressure-dependent rate coefficients for reactions in gas-phase reacting flows. The accompanying Python script contains a working example, which will be used here as a demonstration. The rationale and derivations for these mixture rules were presented in [2, 3]. For context, extensive testing of the reduced-pressure-based mixture rules across highly varied prototypical reaction systems and mixture compositions [1–6] demonstrates the broadly superior accuracy of these mixture rules compared to the commonly implemented classic linear mixture rule (denoted in Table 1 as LMR,P which can result in errors of orders of magnitude [2, 3]).

The most general functional forms of mixture rules for evaluating channel-specific rate coefficients for the μ -th product channel in a mixture consisting of M inert energy-transferring colliders are presented below in Table 1. Here, T and P are the local temperature and pressure, \mathbf{X} is a vector whose elements, X_i , are local species mole fractions, and n_M is the local gas molar concentration. $|\Lambda_{0,i}^{(1)}(T)|$ and $|\Lambda_{\infty}^{(1)}(T)|$ are respectively the absolute values of the least negative chemically significant eigenvalues of the corresponding master equation in the low- and high-pressure limits. $k_{0,i}(T)$ and $k_{\infty}(T)$ are respectively the rate coefficients in the low- and high-pressure limits, and note that $k_{0,i}(T)$ and $k_{\infty}(T)$ should correspond to the total decomposition rate coefficients in each bath gas components rather than their channel-specific counterparts (as discussed in [2]).

The most general form of LMR,R presented in Table 1 is applicable to all reactions (including those proceeding through an arbitrary number of potential energy wells and to an arbitrary number of bimolecular product channels). Note the presentation of LMR,R in Table 1 differs from those presented in our previous work [1–3] since we continually increased the generality and applicability of these mixture rules to cover more types of reactions. For reactions proceeding through a single potential energy well (i.e., single-well reactions), the least negative chemically significant eigenvalues $\Lambda_i^{(1)}(T)$ are proportional to the total unimolecular decomposition rate coefficients, yielding $|\Lambda_{0,i}^{(1)}(T)| \propto k_{0,i}(T)$ and $|\Lambda_{\infty}^{(1)}(T)| \propto k_{\infty}(T)$, and hence LMR,R in Table 1 collapses to its earlier presentations for the special cases of reactions with single well [2, 4, 5] and/or single channel [1].

NMR,R, which builds on LMR,R is based on activity coefficients derived for reactions with a single potential energy well and is therefore, strictly speaking, only applicable to single-well reactions. The equivalent version of NMR,R for multi-well reactions, which requires activity coefficients from analytical solution of the corresponding master equation in the low-pressure limit, is not yet available but in the process of developing. While restricted

to single-well reactions, the form for NMR,R presented in Table 1 from [2] for single-well, multi-channel reactions in an arbitrary number of colliders collapses to its earlier representation for the special case of a single-well, single-channel reaction with two collider [1].

Table 1: Mixture rules for multi-component pressure dependence [2, 3].

LMR,P:	$k_{\mu,\text{LMR,P}}(T, P, \underline{X}) = \sum_{i=1}^M k_{\mu,i}(T, P) X_i$
LMR,R:	$k_{\mu,\text{LMR,R}}(T, P, \underline{X}) = \sum_{i=1}^M k_{\mu,p}(T, R_{\text{LMR}}) \tilde{X}_{i,\text{LMR}}$ $R_{\text{LMR}}(T, P, \underline{X}) = \frac{\sum_{i=1}^M \Lambda_{0,i}^{(1)}(T) X_i n_{\text{M}}}{ \Lambda_{\infty}^{(1)}(T) }$ $\tilde{X}_{i,\text{LMR}}(T, P, \underline{X}) = \frac{ \Lambda_{0,i}^{(1)}(T) X_i}{\sum_{n=1}^M \Lambda_{0,n}^{(1)}(T) X_n}$
NMR,R:	$k_{\mu,\text{NMR,R}}(T, P, \mathbf{X}) = \sum_{i=1}^M k_{\mu,i}(T, R_{\text{NMR}}) \tilde{X}_{i,\text{NMR}}$ $R_{\text{NMR}}(T, P, \mathbf{X}) = \frac{\sum_i f_i(T, \mathbf{X}) k_{0,i}(T) X_i n_{\text{M}}}{k_{\infty}(T)}$ $\tilde{X}_{i,\text{NMR}}(T, P, \mathbf{X}) = \frac{f_i(T, \mathbf{X}) k_{0,i}(T) X_i}{\sum_n f_n(T, \mathbf{X}) k_{0,n}(T) X_n}$

Subscripts μ and i refer to the μ -th channel and the i -th mixture component, respectively. Activity coefficients, $f_i(T, \mathbf{X})$, in NMR,R are calculated using Algorithm 3 below.

A pseudo-code for implementing LMR,R is presented in Algorithm 1. The basic idea is to map the pressure-dependent rate coefficients of the μ -th channel for each collider, $k_{\mu,i}(T, P)$, to the same reduced pressure, R_{LMR} , and apply a linear sum of the mapped rate coefficients, $k_{\mu,i}(T, R_{\text{LMR}})$, weighted by their fractional contributions to the reduced pressure, $\tilde{X}_{i,\text{LMR}}$. In practice, $|\Lambda_{0,i}(T)|$ and $|\Lambda_{\infty}(T)|$, or $k_{0,i}(T)$ and $k_{\infty}(T)$ for single-well reactions, can be provided in the form of separate Arrhenius expressions for each collider, or in the form of an Arrhenius expression for a reference collider accompanied by a set of third-body efficiencies for other colliders. $k_{\mu,i}(T, P)$ can take the analytical forms of such as PLOG expressions or Chebyshev polynomials for each collider, or simply take a list of rate coefficients evaluated at different pressures (as implemented in the example Python script). Note that many terms in Algorithm 1 cancel out in the evaluation process if the ideal gas law, $n_{\text{M}}(T, P) = P/(R_u T)$, is used to evaluate the local molar concentration (as what is assumed in the example Python script), yielding a simplified Algorithm 2 for implementation, which does not require specifying $|\Lambda_{\infty}(T)|$ or $k_{\infty}(T)$ for implementation. Ideally, every species in the reacting flow should be treated as a separate collider and hence has its own distinct low-pressure-limit $|\Lambda_{0,i}(T)|$. However, this might not be feasible in practice. In the cases where a “default” collider is used to represent species without explicitly specified third-body efficiencies or pressure-dependent rate coefficients, the effective mole fraction for this “default” collider should be the sum of mole fractions of all species it represents.

Algorithm 1: Pseudo-code for LMR,R Implementation.

Input: $T, P, \mathbf{X}, |\Lambda_\infty^{(1)}(T)|$, for $i = 1, \dots, M$, $|\Lambda_{0,i}^{(1)}(T)|$ and $k_{\mu,i}(T, P)$

Output: $k_{\mu,\text{LMR,R}}(T, P, \mathbf{X})$

· Calculate the local molar concentration $n_M(T, P)$;

· Evaluate the reduced pressure $R_{\text{LMR}}(T, P, \mathbf{X}) = \frac{\sum_{n=1}^M |\Lambda_{0,n}^{(1)}(T)| X_n n_M}{|\Lambda_\infty^{(1)}(T)|}$;

· **for** $i = 1, \dots, M$ **do**

(i) Search for the absolute pressure P_i that gives R_{LMR} , i.e.,

$$\text{Find } P_i \quad \text{s.t.} \quad \frac{|\Lambda_{0,i}^{(1)}(T)| n_M(T, P_i)}{|\Lambda_\infty^{(1)}(T)|} = R_{\text{LMR}}$$

(ii) Map channel-specific rate coefficients to the reduced pressure,

$$k_{\mu,i}(T, R_{\text{LMR}}) = k_{\mu,i}(T, P_i)$$

(iii) Calculate the fractional contributions to the reduced pressure,

$$\tilde{X}_{i,\text{LMR}}(T, P, \mathbf{X}) = \frac{|\Lambda_{0,i}^{(1)}(T)| X_i}{\sum_n |\Lambda_{0,n}^{(1)}(T)| X_n}$$

end

· Evaluate the mixture rules, $k_{\mu,\text{LMR,R}}(T, P, \mathbf{X}) = \sum_{i=1}^M k_{\mu,i}(T, R_{\text{LMR}}) \tilde{X}_{i,\text{LMR}}$.

Algorithm 2: Simplified Pseudo-code for LMR,R Using the Ideal Gas Law.

Input: T, P, \mathbf{X} , for $i = 1, \dots, M$, $|\Lambda_{0,i}^{(1)}(T)|$ and $k_{\mu,i}(T, P)$

Output: $k_{\mu,\text{LMR,R}}(T, P, \mathbf{X})$

· **for** $i = 1, \dots, M$ **do**

(i) Calculate the absolute pressure P_i that gives R_{LMR} via

$$P_i = P \frac{\sum_{n=1}^M |\Lambda_{0,n}^{(1)}(T)| X_n}{|\Lambda_{0,i}^{(1)}(T)|}$$

(ii) Map channel-specific rate coefficients to the reduced pressure,

$$k_{\mu,i}(T, R_{\text{LMR}}) = k_{\mu,i}(T, P_i)$$

(iii) Calculate the fractional contributions to the reduced pressure,

$$\tilde{X}_{i,\text{LMR}}(T, P, \mathbf{X}) = \frac{|\Lambda_{0,i}^{(1)}(T)| X_i}{\sum_n |\Lambda_{0,i}^{(1)}(T)| X_n}$$

end

· Evaluate the mixture rules, $k_{\mu,\text{LMR,R}}(T, P, \mathbf{X}) = \sum_{i=1}^M k_{\mu,i}(T, R_{\text{LMR}}) \tilde{X}_{i,\text{LMR}}$.

To implement NMR,R, in addition to the input required by LMR,R in Algorithm 1-2, activity coefficients for each collider at considered condition, $f_i(T, \mathbf{X})$ for $i = 1, \dots, M$, also need to be specified. NMR,R (cf. Table 1) differs from LMR,R in its additional incorporation of activity coefficients for each component, $f_i(T, \mathbf{X})$, which account for nonlinearities in the low- pressure limit [2]. A detailed derivation of $f_i(T, \mathbf{X})$ and the procedures to solve for it for each component in a single-well, multi-channel system are available in [2]. Algorithm 3 below summarizes the corresponding procedures. Here, $Z_i(T)$ is the collision frequency of the i -th component, $\langle \Delta E \rangle_{d,i}(T)$ is the averaged amount of energy transferred per downward collision, and F_E is a reaction-specific quantity describing the energy dependence of the density of states of the complex near the lowest decomposition threshold [2]. For a single-well, multi-channel reaction, F_E can be evaluated using Eq. (1) below.

$$F_E = \frac{\int_{E_{01}^\dagger}^{\infty} \rho(E) \exp(-E/k_B T) dE}{\rho(E_{01}^\dagger) \exp(-E_{01}^\dagger/k_B T) k_B T} \quad (1)$$

where $\rho(E)$ is the density of states of the complex at energy level E , k_B is the Boltzmann constant, and E_{01}^\dagger is the lowest decomposition threshold for the complex.

Once $f_i(T, \mathbf{X})$'s are determined for each component, it is straightforward to implement NMR,R following Algorithm 4 or Algorithm 5 if the ideal gas law is assumed.

Algorithm 3: Pseudo-code for Solving Activity Coefficients [2].

Input: T , \mathbf{X} , for $i = 1, \dots, M$, $Z_i(T)$, $\langle \Delta E \rangle_{d,i}(T)$, and F_E

Output: $f_i(T, \mathbf{X})$

· **for** $i = 1, \dots, M$ **do**

(i) Calculate the averaged amount of energy transferred per upward collision via

$$\langle \Delta E \rangle_{u,i}(T) = \frac{\langle \Delta E \rangle_{d,i} F_E k_B T}{\langle \Delta E \rangle_{d,i} + F_E k_B T}$$

where k_B is the Boltzmann constant;

(ii) Calculate the collision-frequency-weighted mole fraction,

$$\hat{X}_i(T, \mathbf{X}) = \frac{Z_i X_i}{\sum_{n=1}^M Z_n X_n}$$

end

· Solve for the M roots for which $D_i > 0$ via

$$\sum_{i=1}^M \frac{\hat{X}_i D_i}{\langle \Delta E \rangle_{d,i} + \langle \Delta E \rangle_{u,i}} \left(\frac{\langle \Delta E \rangle_{d,i}}{\langle \Delta E \rangle_{d,i} + D_i} - \frac{\langle \Delta E \rangle_{u,i}}{\langle \Delta E \rangle_{u,i} - D_i} \right) - 1 = 0$$

· Substitute the solved D_i into the linear system of equations to solve for C_i via

$$\sum_{i=1}^M \frac{C_i D_i}{\langle \Delta E \rangle_{u,n} - D_i} + 1 = 0$$

where $n = 1, \dots, M$;

· **for** $i = 1, \dots, M$ **do**

Calculate the activity coefficient, f_i , via

$$f_i(T, \mathbf{X}) = \frac{\langle \Delta E \rangle_{d,i} + F_E k_B T}{\langle \Delta E \rangle_{d,i} + \langle \Delta E \rangle_{u,i}} \left(1 - \sum_{n=1}^M \frac{C_n D_n}{\langle \Delta E \rangle_{d,i} + D_n} \right)$$

end

Algorithm 4: Pseudo-code for NMR,R Implementation.

Input: $T, P, \mathbf{X}, k_\infty(T)$, for $i = 1, \dots, M$, $k_{0,i}(T)$, $f_i(T, \mathbf{X})$, and $k_{\mu,i}(T, P)$

Output: $k_{\mu,\text{NMR},\text{R}}(T, P, \mathbf{X})$

· Calculate the local molar concentration $n_{\text{M}}(T, P)$;

· Evaluate the reduced pressure $R_{\text{NMR}}(T, P, \mathbf{X}) = \frac{\sum_{n=1}^M f_n(T, \mathbf{X}) k_{0,n}(T) X_n n_{\text{M}}}{k_\infty(T)}$;

· **for** $i = 1, \dots, M$ **do**

(i) Search for the absolute pressure P_i that gives R_{LMR} , i.e.,

$$\text{Find } P_i \quad \text{s.t.} \quad \frac{k_{0,i}(T) n_{\text{M}}(T, P_i)}{k_\infty(T)} = R_{\text{NMR}}$$

(ii) Map channel-specific rate coefficients to the reduced pressure,

$$k_{\mu,i}(T, R_{\text{NMR}}) = k_{\mu,i}(T, P_i)$$

(iii) Calculate the fractional contributions to the reduced pressure,

$$\tilde{X}_{i,\text{NMR}}(T, P, \mathbf{X}) = \frac{f_i(T, \mathbf{X}) k_{0,i}(T) X_i}{\sum_n f_n(T, \mathbf{X}) k_{0,n}(T) X_n}$$

end

· Evaluate the mixture rules, $k_{\mu,\text{NMR},\text{R}}(T, P, \mathbf{X}) = \sum_{i=1}^M k_{\mu,i}(T, R_{\text{NMR}}) \tilde{X}_{i,\text{NMR}}$.

Algorithm 5: Simplified Pseudo-code for NMR,R Using the Ideal Gas Law.

Input: T, P, \mathbf{X} , for $i = 1, \dots, M$, $k_{0,i}(T)$, $f_i(T, \mathbf{X})$, and $k_{\mu,i}(T, P)$

Output: $k_{\mu,\text{NMR},\text{R}}(T, P, \mathbf{X})$

· **for** $i = 1, \dots, M$ **do**

(i) Calculate the absolute pressure P_i that gives R_{NMR} via

$$P_i = P \frac{\sum_{n=1}^M f_n(T, \mathbf{X}) k_{0,n}(T) X_n}{k_{0,i}(T)}$$

(ii) Map channel-specific rate coefficients to the reduced pressure,

$$k_{\mu,i}(T, R_{\text{NMR}}) = k_{\mu,i}(T, P_i)$$

(iii) Calculate the fractional contributions to the reduced pressure,

$$\tilde{X}_{i,\text{NMR}}(T, P, \mathbf{X}) = \frac{f_i(T, \mathbf{X}) k_{0,i}(T) X_i}{\sum_n f_n(T, \mathbf{X}) k_{0,n}(T) X_n}$$

end

· Evaluate the mixture rules, $k_{\mu,\text{NMR},\text{R}}(T, P, \mathbf{X}) = \sum_{i=1}^M k_{\mu,i}(T, R_{\text{NMR}}) \tilde{X}_{i,\text{NMR}}$.

References

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