Manual for SS-QRRK utility code

SS-QRRK: A Program for
System-Specific Quantum Rice-Ramsperger-Kassel Theory

SS-QRRK Version: 2019.01.10

Junwei Lucas Bao and Donald G. Truhlar

Department of Chemistry Chemical Theory Center, and Supercomputing Institute
University of Minnesota, Minneapolis, Minnesota 55455

Program version: 2019.01.10

Program version date: Jan. 10, 2019

Manual version date: Jan. 12, 2022

Table of contents

1. Introduction and recommended citations

This is a manual for the *SS-QRRK* utility code, which is included in the *Polyrate* program (in the directory `polyrate17/util/SS-QRRK/`). The *SS-QRRK* utility code is a program for calculating pressure-dependent rate constants using variational transition state theory. To execute the code, put input files with the .exe file in a working directory, and then type " ./FALLOFF.exe &".

Recommend citations (Please cite the following two papers for SS-QRRK):

 (1) "Kinetics of Hydrogen Radical Reactions with Toluene by Chemical Activation Theory Employing System-Specific Quantum RRK Theory Calibrated by Variational Transition State Theory," J. L. Bao, J. Zheng, and D. G. Truhlar, Journal of the American Chemical Society **138**, 2690-2704 (2016).   dx.doi.org/10.1021/jacs.5b11938

(2) "Predicting Pressure-Dependent Unimolecular Rate Constants Using Variational Transition State Theory with Multidimensional Tunneling Combined with System-Specific Quantum RRK Theory: A Definitive Test for Fluoroform Dissociation," J. L. Bao, X. Zhang, and D. G. Truhlar, Physical Chemistry Chemical Physics **18**, 16659-16670 (2016). dx.doi.org/10.1039/C6CP02765B

For the citation of *Polyrate* program:

(3) J. Zheng, J. L. Bao, R. Meana-Pañeda, S. Zhang, B. J. Lynch, J. C. Corchado, Y.-Y. Chuang, P. L. Fast, W.-P. Hu, Y.-P. Liu, G. C. Lynch, K. A. Nguyen, C. F. Jackels, A. Fernandez Ramos, B. A. Ellingson, V. S. Melissas, J. Villà, I. Rossi, E. L. Coitiño, J. Pu, T. V. Albu, A. Ratkiewicz, R. Steckler, B. C. Garrett, A. D. Isaacson, and D. G. Truhlar, POLYRATE–version 2017, University of Minnesota, Minneapolis, 2017

See also for applying SS-QRRK for barrierless reactions:

(4) "Barrierless association of CF_2 and dissociation of C_2F_4 by variational transition state theory and system-specific quantum Rice-Ramsperger-Kassel theory," J. L. Bao, X. Zhang, and D. G. Truhlar, Proceedings of the National Academy of Sciences, U.S.A., 113, 13606–13611 (2016).   dx.doi.org/10.1073/pnas.1616208113

2. Theoretical background of SS-QRRK

System-specific quantum RRK (SS-QRRK) theory is an efficient way to incorporate variational effects, multidimensional quantum mechanical tunneling, and multi-structural torsional anharmonicity into the calculation of pressure-dependent rate constants in the falloff region of chemical reactions. Recall that unimolecular reactions may have pressure-dependent rate constants because only in the high-pressure limit can the usual assumption of thermally equilibrated states in the reactant be justified. Furthermore, association reactions (whose reverse reactions are unimolecular) may also be pressure dependent because the newly formed states of the associated species (which can be an intermediate or a product) may redissociate before they are equilibrated.

SS-QRRK theory uses information obtained from the high-pressure-limit canonical rate constants (i.e., the thermal equilibrium rate constants) to compute the microcanonical rate constants using quantum RRK theory fitted to these high-pressure results; the resulting microcanonical rate constants are then used in the computation of the pressure-dependent rate constants. Current implementations of SS-QRRK are for three types of reactions: unimolecular reactions (both isomerization, A→P, and dissociation, A →P1 + P2), bimolecular association reactions (A+B→P), and bimolecular reaction with an associated intermediate and followed by a 2nd step reaction(s) (A+B→I→product or products). Parallel reactions could be treated for certain type of reactions (see section 4). Unimolecular reactions (both unimolecular dissociation and unimolecular isomerization) are treated using Hinshelwood-Lindemann theory; bimolecular association reactions are treated with a chemical activation mechanism.

2.1 Hinshelwood—Lindemann mechanism for unimolecular reactions

Before we proceed to consider energy-resolved rate constants, we first examine the classical Lindemann mechanism for unimolecular reaction A→ P:

$$\text{Step 1: } A + M \underset{k_c(T)}{\overset{k_1(T)}{\rightleftharpoons}} A^* + M$$

$$\text{Step 2: } A^* \xrightarrow{k_2(T)} P$$
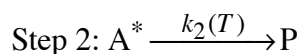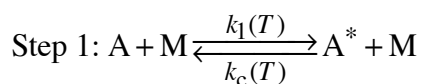
In the original Lindemann model, the rate constants are assumed to be temperature-dependent and energy-independent. The thermal activation rate constant k_1 is modeled as:

$$k_1 = Z \exp(-E_0 / k_B T) \tag{1}$$

where E_0 is called the threshold energy, k_B is Boltzmann's constant, and Z is the bimolecular collision rate constant (in units of cm^3 molecule^{-1} s^{-1}) between the reactant A and the bath gas M:

$$Z = \sigma \langle v_{rel} \rangle \tag{2}$$

where σ is a velocity-independent collision cross section between A and M, and $\langle v_{rel} \rangle$ is the average relative velocity. The rate constant k_c of the de-activation step is simply equal to Z, which assumes that every collision of the energized molecule A* with M leads to de-energization (this is called the strong-collision assumption). The dissociation rate constant k_2 is simply the high-pressure-limit Arrhenius pre-exponential factor A_{uni}^{∞}. Using the steady-state approximation for A*, the unimolecular dissociation rate constant k_{uni} (which is defined as $-\dfrac{1}{[A]}\dfrac{d[A]}{dt}$) is:

$$k_{uni} = \frac{k_1[M]}{1 + k_c[M]/k_2} \tag{3}$$

In the high-pressure-limit ([M] >> 1),

$$k_{uni}^{\infty} = k_1 k_2 / k_c = A_{uni}^{\infty} \exp(-E_0 / k_B T) \tag{4}$$

and the unimolecular dissociation is a (pseudo-) first-order reaction; in the low-pressure-limit ([M] $\approx$ 0), $k_{uni}^{0} = k_1[M]$, and the dissociation reaction is of second order.

As discussed next, our approach goes beyond the original theory mentioned above.

In our approach, $k_{uni}^{\infty}(T)$ is computed using VTST with multidimensional

tunneling; from now on, we will use canonical VTST (CVT) and small curvature

tunneling (SCT) as an example of high-pressure-limit rate constants for our description in

this manual (although in practice one may, for example, use other tunneling methods if

desired). The "threshold energy" E_0 of the unimolecular dissociation reaction in

SS-QRRK formalism is set equal to the temperature-dependent high-pressure-limit

Arrhenius activation energy $E_a^{CVT/SCT}(T)$, which is computed as:

$$
E_a = \begin{cases}
\dfrac{E(T^4 + 2T_0 T^3 - T_0^2 T^2)}{(T^2 + T_0^2)^2} + nRT & \text{endothermic reaction} \\[4mm]
\dfrac{E(T^4 + 2T_0 T^3 - T_0^2 T^2)}{(T^2 + T_0^2)^2} + \dfrac{nRT^2}{T + T_0} & \text{exothermic reaction}
\end{cases}
\tag{5}
$$

where E (kcal/mol) and T_0 (K) are fitting parameters in the following fitting formula for
fitting the computed high-pressure-limit rate constants:

$$
k = \begin{cases}
A(\dfrac{T}{300})^n \exp[-\dfrac{E(T + T_0)}{R(T^2 + T_0^2)}] & \text{endothermic reaction} \\[4mm]
A(\dfrac{T + T_0}{300})^n \exp[-\dfrac{E(T + T_0)}{R(T^2 + T_0^2)}] & \text{exothermic reaction}
\end{cases}
\tag{6}
$$

and $A_{uni}^\infty(T)$ is computed as

$$
A_{uni}^\infty(T) = k_{uni}^\infty(T) \exp[E_a^{CVT/SCT}(T)/RT]
\tag{7}
$$

The value of $A_{uni}^\infty(T)$ is now temperature-dependent and we shall call it the

frequency factor when it is used in SS-QRRK theory (see below).

The energization and dissociation rate constants are treated as energy-dependent

using SS-QRRK theory, and the collisional de-energization rate constant is computed

based on modified strong collision model, which is discussed next. In particular, we

consider the following thermal activation mechanism:

$$\text{Step 1: } A(T) + M \underset{k_c(T)}{\overset{k_1(E;T)}{\rightleftharpoons}} A^*(E) + M$$

$$\text{Step 2: } A^*(E) \xrightarrow{k_2(E)} P$$
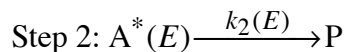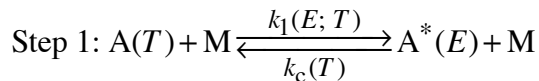
Step 1 is the thermal activation step, in which the thermally equilibrated unimolecular molecules (denoted as $A(T)$ in the mechanism to denote that species A is at temperature T) collide with bath gas M to produce the rovibrationally excited reactant $A^*(E)$ with total rovibrational energy E randomized among all modes. The rate constant of thermal activation k_1 is a function of energy E and is parametrically dependent on T. The de-activation collisional rate constant k_c is assumed to be temperature-dependent as in Lindemann–Hinshelwood theory; it is computed as

$$k_c(T) = Z\beta_c \tag{8}$$

where Z is the Lennard-Jones collision rate constant, and β_c is the collision efficiency.

To model $k_1(E; T)$ and $k_2(E)$, we use single-frequency quantum Rice-Ramsperger-Kassel theory (QRRK), in which rotation is not treated explicitly, and the molecule consists of s identical oscillators with vibrational frequency $\bar{v}$, where we express $\bar{v}$ in wave numbers (cm^{-1}). In practice, we set s equal to number of vibrational degree of freedom ($3N$-6 for non-linear molecule), and $\bar{v}$ is chosen to be the reactant geometric mean frequency. The geometric mean frequency is computed as:

$$\bar{v} = (\prod_{i=1}^{s} v_i)^{1/s} \tag{9}$$

where v_i is the vibrational frequency of normal mode i, and s is the number of vibrational degrees of freedom.

We denote the energy of the reactant molecule as E and set E equal to $nhc\bar{v}$, where h is Planck's constant, c is the speed of light, and n is $E/hc\bar{v}$. In the QRRK model of the

microcanonical rate constant at energy E, a unimolecular reaction happens when a specific vibrational mode associated with the reaction coordinate possesses a critical energy (or threshold energy) E_0 equal to $mhc\overline{v}$. Note that n and m are not usually integers.

First consider $k_1(E;T)$. The equilibrium constant for step 1 is the fraction of the molecules with n quanta of excitation, which is

$$K^{\mathrm{QRRK}}(n,T) = \exp(\frac{-nhc\overline{v}}{k_{\mathrm{B}}T})[1 - \exp(\frac{-hc\overline{v}}{k_{\mathrm{B}}T})]^s \frac{(n+s-1)!}{n!(s-1)!} \tag{10}$$

The equilibrium constant equals the ratio of forward to reverse rates:

$$K^{\mathrm{QRRK}}(n,T) = k_1^{\mathrm{QRRK}}(E = nhc\overline{v};T)/k_c(T) \tag{11}$$

Substituting Eq. (10) into Eq. (11) and solving for the forward rate yields $k_1^{\mathrm{QRRK}}(E;T)$.

Next consider the QRRK rate constant $k_2(E)$; this is equal to the frequency factor times the fraction of molecules with at least m quanta in one chosen mode, and for a quantum mechanical oscillator with s identical frequencies $\overline{v}$ and temperature T, this is given by

$$k_2^{\mathrm{QRRK}}(E = nhc\overline{v}) = A^{\mathrm{QRRK}} \frac{n!(n-m+s-1)!}{(n-m)!(n+s-1)!} \tag{12}$$

In SS-QRRK, we set the frequency factor A^{QRRK} equal to $A_{\mathrm{uni}}^{\infty}(T)$ given by Eq. (7), and we set the threshold energy equal to the high-pressure local Arrhenius activation energy given by Eq. (5), which yields

$$m = E_{\mathrm{a}}^{\mathrm{CVT/SCT}}(T)/hc\overline{v} \tag{13}$$

The analog of Eq. (3) is

$$k_{\text{uni}}(T,p) = \sum_{n=m}^{+\infty} \frac{k_1^{\text{QRRK}}(E = nhc\overline{v};T)[M]}{1 + \dfrac{k_c(T)[M]}{k_2^{\text{QRRK}}(E = nhc\overline{v})}} \tag{14}$$

where $k_c(T)$ is obtained by Eq. (8), $k_1^{\text{QRRK}}(E;T)$ is obtained by Eqs. (10) and (11),

and $k_2^{\text{QRRK}}(E)$ is from Eq (12).

Now, it can be shown why we choose the frequency factor and threshold energy by

Eqs. (7) and (5). In the high-pressure-limit, Eq. (14) reduces to:

$$k_{\text{uni}}(T,p) = \sum_{n=m}^{+\infty} \frac{k_1(E = nhc\overline{v};T)k_2(E = nhc\overline{v})}{k_c(T)} \tag{15}$$

and, by carrying out the summations, Eq. (4) is obtained. The high-pressure-limit

canonical rate constants computed by SS-QRRK theory are therefore same as the ones

determined by CVT/SCT theory. Therefore our SS-QRRK microcanonical rate constant

formalism can build in variational effects, multidimensional tunneling based on the

directly calculated potential energy surface along the tunneling path, and vibrational and

torsional anharmonicity with no additional computational cost.

2.2 Chemical activation mechanism for bimolecular association

The chemical activation mechanism for a bimolecular reaction with an associated
intermediate is:

$$A + B \underset{k_{-1}(E)}{\overset{k_1(T)}{\rightleftharpoons}} \quad AB^* \quad \xrightarrow{k_2(E)} P$$
$$\downarrow k_c[M] \tag{Type 1}$$
$$AB$$
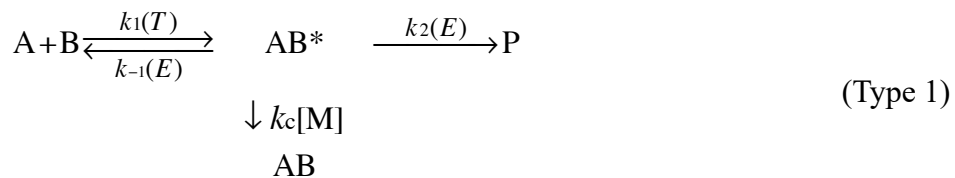
and the chemical activation mechanism for a for bimolecular association reaction is:

$$A+B \underset{k_{-1}(E)}{\overset{k_1(T)}{\rightleftharpoons}} AB* \xrightarrow{k_c[M]} AB \qquad \text{(Type 2)}$$

where A and B are reactants, AB* is the ro-vibrationally excited unimolecular state, AB is the stabilized unimolecular state (i.e., AB is the intermediate in a type-1 reaction, and it is the product of a type-2 reaction), and P is the product in a type-1 reaction.

Applying the steady-state approximation to the chemical activation mechanism chemical activation mechanism yields

$$k_{\text{stab}} = \frac{d[AB]}{[A][B]dt} = k_1^{\text{MS-CVT/SCT}} \sum_{E_0}^{+\infty} \frac{k_c[M] f(E)}{k_c[M] + k_{-1}^{\text{QRRK}}(E) + k_2^{\text{QRRK}}(E)} \qquad (16)$$

$$k_P = \frac{d[P]}{[A][B]dt} = k_1^{\text{MS-CVT/SCT}} \sum_{E_0}^{+\infty} \frac{k_2^{\text{QRRK}}(E) f(E)}{k_c[M] + k_{-1}^{\text{QRRK}}(E) + k_2^{\text{QRRK}}(E)} \qquad (17)$$

for reaction type 1 and

$$k_{\text{stab}} = \frac{d[AB]}{[A][B]dt} = k_1^{\text{MS-CVT/SCT}} \sum_{E_0}^{+\infty} \frac{k_c[M] f(E)}{k_c[M] + k_{-1}^{\text{QRRK}}(E)} \qquad (18)$$

for reactions type 2, where $f(E)$ is the fraction of energized species (AB*) at energy E, which is given by

$$f(E) = \frac{k_{-1}^{\text{QRRK}}(E) K(E)}{\sum_{E_0}^{+\infty} k_{-1}^{\text{QRRK}}(E) K(E)} \qquad (19)$$

where

$$K(E) = \exp(\frac{-nhv}{k_B T})[1 - \exp(\frac{-hv}{k_B T})]^s \frac{(n+s-1)!}{n!(s-1)!} \qquad (20)$$

In eqs (16), (17), and (18), [M] is the concentration of the bath gas, which is calculated using the ideal gas law, $[M] = p/RT$, E_0 is the threshold energy, which is computed using Eq. (5), and $k^{\text{QRRK}}(E)$ denotes a quantum RRK theory energy-resolved rate constant, which is computed using Eq. (12) with the corresponding A factor and threshold energy.

The summations in eqs (16), (18), and (19) are evaluated with a step size of one quantum ($h\bar{v}$). The quantity $n!$ is computed using a gamma function or Stirling's approximation.

2.3 Energy transfer parameters

The collision efficiency is computed by solving the following equation:

$$\frac{\beta_c}{1-\beta_c^{1/2}} = \frac{|\langle \Delta E \rangle|}{F_E k_B T} \tag{21}$$

where $\langle \Delta E \rangle$ (sometimes is also denoted as $\langle \Delta E \rangle_{all}$, which is itself a negative number) is the average vibrational energy transferred during both energization and de–energization processes (note that $|\langle \Delta E \rangle|$ is smaller than the often encountered $\langle \Delta E \rangle_{down}$ parameter that is the average energy transferred in collisions in which the vibrational energy goes down); and F_E is the thermal fraction of unimolecular states above the threshold energy and is defined in Troe's work (Troe, J. *J. Chem. Phys.* 1977, 66, 4745). For moderate–sized molecules, F_E is nearly unity (Troe, J. *J. Phys. Chem.* 1979, 83, 114).

The temperature dependence of F_E can be treated with Troe's method when it is needed: F_E can be computed using Troe's definition:

$$F_E = \frac{\int_{E_0}^{+\infty} \rho(E)e^{-E/k_B T}\, dE}{k_B T \rho(E_0)e^{-E_0/k_B T}} \tag{22}$$

or it can be computed using the Whiten-Rabinovitch approximation (J. Troe, *J. Phys. Chem.*, 1979, 83, 114). Alternatively, it could be computed by using density of states come from multistructural coupled-torsional potential anharmonicity partition functions (MS-T); and this requires the usage of the MSTor program (which is a separate program that is freely downloadable from our group).

The collision efficiency can also be estimated as:

$$\beta_c = \left(\frac{\langle \Delta E \rangle_{\text{down}}}{\langle \Delta E \rangle_{\text{down}} + F_E k_B T} \right)^2 \tag{23}$$

where $\langle \Delta E \rangle_{\text{down}}$ is the averaged energy transferred for *only* the de-activation process, by which we mean for only collisions in which the vibrational energy goes down.

The Lennard-Jones collision rate constant k_{LJ} is the product of the hard-sphere collision rate constant k_{HS} and the dimensionless reduced collision integral $\Omega^*_{2,2}$, which is defined by Hirschfelder et al (Hirschfelder, J. O.; Curtiss, C. F.; Bird, R. B. In Molecular Theory of Gases and Liquids; Wiley and Sons: London, 1967.). Therefore

$$k_c = \beta_c \Omega^*_{2,2} k_{HS} \tag{24}$$

The values of the reduced collision integral can be evaluated by numerical integration and have been fitted by other workers with various simple algebraic expressions. Usually, we choose Troe's fitting expression (Troe, J. *J. Chem. Phys.* 1977, 66, 4745; Troe, J. *J. Chem. Phys.* 1977, 66, 4758) for computing $\Omega^*_{2,2}$:

$$\Omega^*_{2,2} = \begin{cases} [0.697 + 0.5185 \log_{10}(\frac{k_B T}{\varepsilon_{\text{A-M}}})]^{-1} & \frac{k_B T}{\varepsilon_{\text{A-M}}} \in [3,300] \\[2ex] [0.636 + 0.567 \log_{10}(\frac{k_B T}{\varepsilon_{\text{A-M}}})]^{-1} & \frac{k_B T}{\varepsilon_{\text{A-M}}} \notin [3,300] \end{cases} \tag{25}$$

where $\varepsilon_{\text{A-M}}$ is the Lennard-Jones interaction parameter between molecule A and M and is computed as the geometric average of $\varepsilon_{\text{A-A}}$ and $\varepsilon_{\text{M-M}}$.

The hard–sphere collision rate constant k_{HS} is computed as:

$$k_{HS} = \pi (\frac{d_A + d_M}{2})^2 \sqrt{\frac{8 k_B T}{\pi \mu}} \tag{26}$$

where the vdW diameters d_A and d_M are computed from the Lennard-Jones parameters

$\sigma_{\text{A-A}}$ and $\sigma_{\text{M-M}}$ using the relation $d = 2^{1/6}\sigma$, and μ is the reduced mass of A and M.

3. Fitting high-pressure-limit rate constants

Before carrying out the SS-QRRK calculations, the user should use *Polyrate* to compute the high-pressure-limit rate constants and possibly to perform multi-structural torsional anharmonicity corrections using MSTor code. For transition states without conformational complexity one can use the original VTST, and for transition states with conformational complexity one can use multi-path or multi-structural VTST; in either case one can include multidimensional quantum mechanical tunneling. After computing the high-pressure-limit rate constants, the user should use the following equation to fit the rate constants (different formula should be applied for endothermic and exothermic reactions):

$$k = \begin{cases} A(\dfrac{T}{300})^n \exp[-\dfrac{E(T+T_0)}{R(T^2+T_0^2)}] & \text{endothermic reaction} \\[3mm] A(\dfrac{T+T_0}{300})^n \exp[-\dfrac{E(T+T_0)}{R(T^2+T_0^2)}] & \text{exothermic reaction} \end{cases} \tag{27}$$

where A (for unimolecular reaction, its unit is s^{-1}; and for bimolecular reaction, its unit is cm^3 molecule^{-1} s^{-1}), n (unitless), E (unit: kcal/mol) and T_0 (unit: K) are fitting parameters. The ideal gas constant R is in the unit of kcal mol^{-1} K^{-1} with value 0.0019872. Then, the temperature-dependent Arrhenius activation energies can be computed from the local slopes of Arrhenius plots, which yields:

$$E_a = \begin{cases} \dfrac{E(T^4+2T_0T^3-T_0^2T^2)}{(T^2+T_0^2)^2} + nRT & \text{endothermic reaction} \\[3mm] \dfrac{E(T^4+2T_0T^3-T_0^2T^2)}{(T^2+T_0^2)^2} + \dfrac{nRT^2}{T+T_0} & \text{exothermic reaction} \end{cases} \tag{28}$$

Finally, the local Arrhenius frequency factor A, which is also temperature-dependent, can be computed as:

$$A^\infty(T) = k^\infty(T)\exp[E_a(T)/RT] \tag{29}$$

4. Description of input

The input of the SS-QRRK code is template-based; users should use the template that corresponds to their type of calculation and then change the values accordingly. Next we shall discuss the input templates for SS-QRRK calculations and the meanings of the keywords. Some common keywords are only explained once (in section 4.1).

4.1 Unimolecular reaction

4.1.1. Single Unimolecular reaction

The input template for unimolecular reaction (A → P1 + P2) is:

```
-------------------------------------------------------------------------------------------------------
#BasicInfo
numbTrxn 10
Trxnlist
298.
300.
400.
500.
600.
700.
800.
900.
1000.
1500.
numbP  11
unitP lg10bar
Plist
3.
2.75
2.5
2.25
2.
1.75
1.5
1.25
1.
0.75
-1.75
#Collision
ColliIntg    Troe
avgEtrans   740. cal*mol-1   0.  all
FE          1.15
paramA       5.8  254.0  120.0
paramBath    3.4  120.0  39.948
#FalloffMethod
Method  HLQRRK
rxn1    AEa
9.405083E+10    24.3
1.006091E+11    24.4
4.716439E+11    25.4
```

```
6.669850E+11    25.7
7.699440E+11    25.9
8.789665E+11    26.1
1.013173E+12    26.2
1.167539E+12    26.5
1.361410E+12    26.7
2.658167E+12    28.5
sAstar       30.
GeoMeFreq    580.880669720707
MaxE         8000.
#END
```

Meanings of keywords:

numbTrxn   number of temperatures

Trxnlist   list of temperatures. This should be consistent with number of temperatures.

numbP   number of pressures

unitP   unit of the input pressures. Available options are: torr, bar, atm, Pa, kPa, lg10atm, lg10bar, lg10torr

Plist   List of pressures; this should be consistent with number of pressures that user input

ColliIntg   The form of the collision integral one uses. Available options are: Troe, Reid

avgEtrans   Average energy transferred parameter ΔE. Available units are: cm**-1, kcal*mol-1, cal*mol-1. The temperature dependence can be incorporated by using: $\Delta E(T) = \Delta E(T/300)^n$. There are two types of ΔE parameter: $<\Delta E>_{all}$ (i.e. average energy transferred during both activation and deactivation collisions, which is specified by keyword "all"), $<\Delta E>_{down}$ (i.e., the average energy transferred only for deactivation collisions, which is specified by keyword "down"). For example, "avgEtrans 740. cal*mol−1 0. all" means we are using $|<\Delta E>_{all}| = 740$ cal/mol, and the temperature-dependence coefficient $n = 0$ (i.e., we do not consider T-dependence of $<\Delta E>_{all}$).

Please note that there are multiple approaches for approximating the collision efficiency based on the input energy-transfer parameter. The default is to use eq. 196 (with $|<\Delta E>_{all}|$ as input) or eq. 198 (with $<\Delta E>_{down}$ as input) in *Chem. Soc. Rev.*, 2017, 46, 7548-7596. Other variations are also available: (1) "`avgEtrans  500. cm**-1  0. down GLT`" calls for the Gilbert-Luther-Troe correction (*Ber. Bunsenges. Phys. Chem.* 1983, 87, 169–177); (2) "`avgEtrans 740. cal*mol-1  0.  all CD`" calls for the Carstensen–Dean correction (H. H. Carstensen, and A. M. Dean, in *Comprehensive Chemical Kinetics*, Volume 42, 101–184.).

FE	The F_E parameter for the activated unimolecular states. If the user specifies a positive number, then it means that the value specified by the user is directly used as F_E; if a value of -1 (negative one) is specified, then it means that F_E will be computed based on Whitten-Rabinovitch approximation (with an additional input file: vibinfo.inp) with Troe's approximated formula; if a value of -2 is specified, then it means that F_E will be computed based on Whitten-Rabinovitch approximation (with an additional input file: vibinfo.inp) with numerical integration (Please refer to and cite: Junwei Lucas Bao, Donald G Truhlar, "Effect of energy dependence of the density of states on pressure-dependent rate constants", *Physical Chemistry Chemical Physics*, 20, 30475–30479 (2018)). Please refer to section 4.4 for more information about the additional input files.
paramA	Lennard-Johns parameters for reactant A, in the order of σ (unit: Å), ε (unit: Kelvin, i.e., ε/k_B), molar mass (unit: gram per mole).
paramBath	Lennard-Johns parameters for bath gas.
Method	For unimolecular dissociation or isomerization reaction, the keyword

`rxn1 AEa`	To specify the *A* factor (temperature-dependent local frequency factor, which is determined by eq. (29)) and activation energy (determined by eq. (28), in the unit of kcal/mol) for the high-pressure-limit unimolecular reaction A → P. Under this keyword, the user should specify *A* in left column and *E*a in right column; this information should be consistent with the order of the temperatures that one has specified under `Trxnlist`
`sAstar`	number of vibrational degree freedom of A
`GeoMeFreq`	The geometric mean frequency (in the unit of cm^{-1}) of unimolecular reactant A. The geometric mean frequency is computed as eq. (9).
`MaxE`	The summation upper limit for quantum RRK theory (unit: kcal/mol); this value should be set to be high enough so that the summation is converged. A value of 8000 is recommended.

A single isomerization reaction: A → P

For a single isomerization reaction, a modified `HLQRRK` version is available, and we encourage the user to use this version for treating single **isomerization** reaction (especially when the isomerization is endothermic). Note that this is ONLY for a single isomerization reaction, and it is NOT applicable for unimolecular dissociation reactions (i.e., when one has more than one products.). The modification is based on the work reported in *Trans. Faraday Soc.* 1968, 64, 94, and the corresponding SS-QRRK version for the current implementation is reported in *Journal of the American Chemical Society*, 2018, 140, 17556; this modification is based on single independent reaction assumption.

The format of the input file is very similar to the one shown above:

```
#FalloffMethod
Method  HLQRRK
modified  1
rxn1    AEa
9.405083E+10    24.3
1.006091E+11    24.4
4.716439E+11    25.4
6.669850E+11    25.7
7.699440E+11    25.9
8.789665E+11    26.1
1.013173E+12    26.2
1.167539E+12    26.5
```

```
1.361410E+12    26.7
2.658167E+12    28.5
RxnDE      1.5
sAstar       30.
GeoMeFreq    580.880669720707
MaxE        8000.
#END
```

The user only need to add two additional lines: (1) **modified 1**; (2) "**RxnDE 1.5**", which indicates that the forward isomerization reaction is endothermic, and the reaction enthalpy at 0 K (i.e., the zero-point-energy included reaction energy) is 1.5 kcal/mol for the example isomerization reaction shown here.

 The user can also use this modification for multiple parallel **isomerization** reactions (i.e., PHLQRRK), although in this case, our implementation is based on a direct modification which uses the 2nd term in the denominator in equation 176 in *Chemical Society Reviews* **46**, 7548-7596 (2017) as a leading correction. This approach merely serves as an approximation for the cases with multiple parallel reactions, and it is only an estimation for the effect of the existence of multiple parallel reactions.

4.1.2 Unimolecular reaction with parallel reaction channels

 For the following thermal activation unimolecular reaction with multiple parallel

reaction channels:

$$A \begin{matrix} \rightarrow P1 \\ \rightarrow P2 \\ \rightarrow \cdots \\ \rightarrow PN \end{matrix}$$

 We give an example input file in below, for a unimolecular reaction with 3 parallel

reaction channels:

```
#BasicInfo
numbTrxn 10
Trxnlist
298.
300.
400.
500.
600.
700.
800.
900.
1000.
1500.
numbP  2
unitP lg10bar
Plist
3.
-1.
#Collision
ColliIntg   Troe
avgEtrans 740. cal*mol-1   0. all
FE     -1
paramA  5.8 254.0 120.0
paramBath   3.4 120.0 39.948
```

```
#FalloffMethod
Method  PHLQRRK   3
rxn1    AEa       1
4.702541500E+10         24.3
5.030455000E+10         24.4
2.358219500E+11         25.4
3.334925000E+11         25.7
3.849720000E+11         25.9
4.394832500E+11         26.1
5.065865000E+11         26.2
5.837695000E+11         26.5
6.807050000E+11         26.7
1.329083500E+12         28.5
rxn1    AEa       2
4.702541500E+10         24.3
5.030455000E+10         24.4
2.358219500E+11         25.4
3.334925000E+11         25.7
3.849720000E+11         25.9
4.394832500E+11         26.1
5.065865000E+11         26.2
5.837695000E+11         26.5
6.807050000E+11         26.7
1.329083500E+12         28.5
rxn1    AEa       3
4.702541500E+10         24.3
5.030455000E+10         24.4
2.358219500E+11         25.4
3.334925000E+11         25.7
3.849720000E+11         25.9
4.394832500E+11         26.1
5.065865000E+11         26.2
5.837695000E+11         26.5
6.807050000E+11         26.7
1.329083500E+12         28.5
sAstar      30.
GeoMeFreq   580.880669720707
MaxE        4000.
#END
```

The key point in this input is that: (1) for a thermal activation unimolecular reaction with parallel channels, "Method PHLQRRK   3" is required, in which "PHLQRRK" means we are applying Hinshelwood—Lindemann SS-QRRK theory for parallel reactions ("P" stands for parallel), and "3" means there are 3 parallel reaction channels (and the user should specify a number N if there are N parallel reactions instead of 3 parallel reactions that are used here as an example); (2) for each parallel reaction, the A and E_a should be specified under the section "rxn1   AEa   I", where "I" represents the information for the I-th parallel reaction.

4.2 Bimolecular association

The input template for bimolecular association reaction (A + B → P) is as follows:

```
#BasicInfo
numbTrxn 3
Trxnlist
    298.15
    300.
    400.
numbP  4
unitP lg10atm
Plist
3.
-0.5
-0.75
-3.
#Collision
ColliIntg    Troe
avgEtrans 92 cm**-1  0. all
FE      1.15
paramPstar   6.00  410.0  93.0
paramBath    2.93  38.0  2.0
#FalloffMethod
Method  QRRK
Rxn2   NO
rxn1     rate
2.7165E-14
2.8101E-14
1.3146E-13
#QRRKData
sPstar       42.
GeoMeFreq    1085.669208
MaxE         8000.
rxnneg1AEa
1.5444E+13           29.78
1.5961E+13           29.8
2.9953E+13           30.25
#END
```

In section 4.1, we have already covered most common keywords. Here, we only explain new keywords:

Method	For bimolecular reactions, the keyword "QRRK" must be specified in order to do SS-QRRK calculation. (Do not be confused with the "HLQRRK" keyword, which is specifically used for unimolecular reaction with Hinshelwood-Lindemann theory.)
Rxn2 NO	For bimolecular association reaction, which does not involve a stable intermediate, the option for "Rxn2" must be "NO".

rxn1	rate	User specified high-pressure-limit rate constant for the forward bimolecular association reaction (A + B $\rightarrow$ P).
rxnneg1AEa		To specify the *A* factor (temperature-dependent local frequency factor, which is determined by eq. (29)) and activation energy (determined by eq. (28), in the unit of kcal/mol) for the high-pressure-limit unimolecular reaction P $\rightarrow$ A + B (i.e., the reverse reaction of bimolecular association). Under this keyword, the user should specify *A* in left column and *E*a in right column; this information should be consistent with the order of the temperatures that one has specified under Trxnlist
paramPstar		Lennard-Johns parameters for the unimolecular product P, in the order of σ (unit: Å), ε (unit: Kelvin, i.e., ε/k_B), molar mass (unit: gram per mole).
sPstar		The number of vibrational degree of freedom for P.
GeoMeFreq		The geometric mean frequency (in the unit of cm^{-1}) of unimolecular product P.

4.3 Bimolecular reaction with an intermediate

4.3.1

The input template for bimolecular reaction with a stable intermediate (A + B $\rightarrow$ AB $\rightarrow$ P) is:

```
#BasicInfo
numbTrxn 3
Trxnlist
    298.15
    300.
    400.
numbP  3
unitP lg10atm
Plist
0.25
0.
-0.25
#Collision
ColliIntg    Troe
avgEtrans 92 cm**-1 0. all
FE      1.15
paramAB   6.00  410.0  93.0
paramBath   2.93  38.0  2.0
#FalloffMethod
Method  QRRK
Rxn2    YES
rxn1     rate
2.1632E-16
2.2860E-16
2.4896E-15
#QRRKData
sABstar        42.
GeoMeFreq    1092.49876
MaxE       8000.
rxnneg1AEa
1.7242E+12           26.55
1.9273E+12           26.61
4.3192E+13           28.62
rxn2AEa
2.0228d+12           23.12
2.2603d+12           23.18
3.4447d+13           24.95
#END
```

In section 4.1 and 4.2, we have already covered most common keywords. Here, we only explain new keywords:

| Method | For bimolecular reactions with a stable intermediate, the keyword "QRRK" must be specified in order to do SS-QRRK calculation. (Do not be confused with the "HLQRRK" keyword, which is specifically |

used for unimolecular reaction.)

Rxn2 YES	For bimolecular reactions with a stable intermediate, the "Rxn2" must be set to be "YES" to indicate the existence of a second-step reaction.
rxn2AEa	To specify the A factor (temperature-dependent local frequency factor, which is determined by eq. (29)) and activation energy (determined by eq. (28), in the unit of kcal/mol) for the high-pressure-limit unimolecular reaction AB $\rightarrow$ P (i.e., the second-step reaction). Under this keyword, the user should specify A in left column and Ea in right column; this information should be consistent with the order of the temperatures that one has specified under Trxnlist
rxnneg1AEa	To specify A factor and activation energy for high-pressure-limit reaction AB $\rightarrow$ A + B
rxn1 rate	User specified high-pressure-limit rate constant for the forward bimolecular association reaction (A + B $\rightarrow$ AB).
GeoMeFreq	The geometric mean frequency (in the unit of cm^{-1}) of unimolecular intermediate AB.
paramAB	Lennard-Johns parameters for the unimolecular intermediate AB, in the order of σ (unit: Å), ε (unit: Kelvin, i.e., ε/k_B), molar mass (unit: gram per mole).
sABstar	The number of vibrational degree of freedom for AB.

4.3.2.

For a chemical activation mechanism that belongs to the following type:

$$A + B \longrightarrow AB \begin{array}{l} \rightarrow P1 \\ \rightarrow P2 \\ \rightarrow \cdots \\ \rightarrow PN \end{array}$$
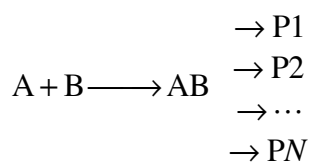
i.e., a bimolecular reaction with a stable intermediate being formed, and then followed by the second step consists of multiple parallel reactions (in the following example input, we have 3 parallel reactions in the second step; there is no limit in the number of parallel reactions that one can specify for the 2nd step), the following input can be used:

```
#BasicInfo
numbTrxn 3
Trxnlist
    298.15
    300.
    400.
numbP  5
unitP lg10atm
Plist
3.
0.25
0.
-0.25
-3.
#Collision
ColliIntg    Troe
avgEtrans 92 cm**-1 0. all
FE      1.15
paramAB   6.00  410.0  93.0
paramBath    2.93  38.0  2.0
#FalloffMethod
Method  QRRK
Rxn2  3
rxn1     rate
2.1632E-16
2.2860E-16
2.4896E-15
#QRRKData
sABstar        42.
GeoMeFreq    1092.49876
MaxE        8000.
rxnneg1AEa
1.7242E+12             26.55
1.9273E+12             26.61
4.3192E+13             28.62
rxn2AEa   1
1.0114d+12            23.12
1.13015d+12           23.18
1.72235d+13           24.95
rxn2AEa   2
0.5057d+12           23.12
0.565075d+12          23.18
0.861175+13          24.95
rxn2AEa   3
5.057d+11            21.12
```

```
5.65075d+11                 21.18
8.61175+12                  22.95
#END
```

The key point in this input file is that, "Rxn2   3" means there are 3 parallel reactions in the second step, and their A and E_a parameters are specified respectively under the sections "rxn2AEa   1", "rxn2AEa   2", and "rxn2AEa   3", which are located after finishing specifying the information for the reverse reaction (from AB back to A + B) under the "rxnneg1AEa" section. Also, please notice that "Rxn2   1" is equivalent to "Rxn2   YES", and "Rxn2   0" is equivalent to "Rxn2   NO" in the previous section 4.2 and 4.3.

4.4 Other input files

When the "FE" option is specified as "-1", the F_E factor is computed using the Whitten-Rabinovitch approximation. This is the most convenient option for computing F_E. When the F_E factor is computed by the Whitten-Rabinovitch approximation, vibinfo.inp is needed as additional input file.

In vibinfo.inp, the vibrational zero-point energy (in kcal/mol, for the unimolecular species that is at the stationary point) is specified on the first line, followed by the vibrational frequencies (in cm^{-1}).

```
 39.76669  / ZPE in kcal/mol
 67.6166
 74.9266
 81.1074
 95.0748
114.2145
125.9215
321.9349
399.5684
410.5671
417.2896
438.9300
466.7933
543.3220
615.2602
665.2141
674.6209
860.1783
886.6351
926.5675
933.1321
934.0968
937.4362
1909.0212
2053.4916
2114.4137
2134.0820
2148.7552
2153.5027
2153.8935
2159.6340
```

5. Test runs

We have included five test runs in `Polyrate17/util/SS-QRRK/testrun/` and the corresponding output files are in `Polyrate17/util/SS-QRRK/testo/`

Test run1: Unimolecular reaction, with user specified F_E=1.15

Test run2: Unimolecular reaction, with F_E being computed by Whiten-Rabinovitch

Test run3: Bimolecular reaction with an intermediate

Test run4: Unimolecular reaction, with F_E being computed from density of states

Test run5: Bimolecular association reaction

Test run6: Bimolecular reaction with an intermediate, and followed by the second step with 3 parallel reactions.

Test run7: Unimolecular reaction with 3 parallel reaction channels.