Manual for SS-QRRK utility code

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

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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 polyrate2016-2A/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:

See also:
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. (Nonequilibrium effects can also be present in bimolecular reactions that produce two or more products, but in such cases they are expected to be much smaller, and we do not include them in those cases.)

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 (A+B → I → product or products). 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:
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:

$$k_1 = Z \exp\left(-\frac{E_0}{k_B T}\right) \quad (1)$$

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:

$$Z = \sigma \langle v_{\text{rel}} \rangle \quad (2)$$

where $\sigma$ is a velocity-independent collision cross section between A and M, and $\langle v_{\text{rel}} \rangle$ 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 $A_{\text{uni}}^\infty$.

Using the steady-state approximation for $A^*$, the unimolecular dissociation rate constant $k_{\text{uni}}$ (which is defined as $-\frac{1}{[A]} \frac{d[A]}{dt}$) is:

$$k_{\text{uni}} = \frac{k_1[M]}{1 + k_c[M]/k_2} \quad (3)$$

In the high-pressure-limit ($[M] \gg 1$),

$$k_{\text{uni}}^\infty = k_1k_2 / k_c = A_{\text{uni}}^\infty \exp\left(-\frac{E_0}{k_B T}\right) \quad (4)$$

and the unimolecular dissociation is a (pseudo-) first-order reaction; in the low-pressure-limit ($[M] \approx 0$), $k_{\text{uni}}^0 = k_1[M]$, and the dissociation reaction is of second order.
As discussed next, our approach goes beyond the original theory mentioned above. In our approach, $k_{\text{uni}}^\infty(T)$ 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 (step 2) is set equal to the temperature-dependent high-pressure-limit Arrhenius activation energy $E_a^{\text{CVT/SCT}}(T)$, which is computed as:

$$E_a = \begin{cases} \frac{E(T^4 + 2T_0T^3 - T_0^2T^2)}{(T^2 + T_0^2)^2} + nRT & \text{endothermic reaction} \\ \frac{E(T^4 + 2T_0T^3 - T_0^2T^2)}{(T^2 + T_0^2)^2} + \frac{nRT^2}{T + T_0} & \text{exothermic reaction} \end{cases}$$  

(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:

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

(6)

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

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

(7)

The value of $A_{\text{uni}}^\infty(T)$ 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:

Step 1: \( A(T) + M \xrightarrow{k_1(E; T)} k_c(T) \longrightarrow A^*(E) + M \)

Step 2: \( A^*(E) \xrightarrow{k_2(E)} P \)

Step 1 is the thermal activation step, in which the thermally equilibrated fluoroform 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

\[
k_c(T) = Z \beta_c
\]

where \( Z \) is the Lennard-Jones collision rate constant, and \( \beta_c \) 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 \( \nu \), where we express \( \nu \) in wave numbers (\( \text{cm}^{-1} \)). In practice, we set \( s \) equal to number of vibrational degree of freedom (\( 3N-6 \) for non-linear molecule), and \( \nu \) is chosen to be the reactant geometric mean frequency. The geometric mean frequency is computed as:

\[
\bar{\nu} = \left( \prod_{i=1}^{s} \nu_i \right)^{1/s}
\]

where \( \nu_i \) 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 $mhc \bar{v}$. 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

$$K_{QRRK}^{\text{QRRK}}(n, T) = \exp\left(\frac{-nhc \bar{v}}{k_B T}\right) [1 - \exp\left(\frac{-hc \bar{v}}{k_B T}\right)]^s \frac{(n + s - 1)!}{n!(s - 1)!}$$

(10)

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

$$K_{QRRK}^{\text{QRRK}}(n, T) = \frac{k_{1}^{\text{QRRK}}(E = nhc \bar{v}; T)}{k_c(T)}$$

(11)

Substituting Eq. (10) into Eq. (11) and solving for the forward rate yields $k_{1}^{\text{QRRK}}(E; T)$.

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 $\bar{v}$ and temperature $T$, this is given by

$$k_{2}^{\text{QRRK}}(E = nhc \bar{v}) = A_{QRRK}^{\text{QRRK}} \frac{n!(n - m + s - 1)!}{(n - m)!(n + s - 1)!}$$

(12)

In SS-QRRK, we set the frequency factor $A_{QRRK}^{\text{QRRK}}$ equal to $A_{unii}^{\text{QRRK}}(T)$ 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

$$m = \frac{E_{a}^{\text{CVT/SCT}}(T)}{hc \bar{v}}$$

(13)
The analog of Eq. (3) is

\[ k_{\text{uni}}(T, p) = \sum_{n=m}^{+\infty} \frac{k_{1}^{\text{QRRK}}(E = n\hbar c\bar{\nu}; T)[M]}{1 + \frac{k_{c}(T)[M]}{k_{2}^{\text{QRRK}}(E = n\hbar c\bar{\nu})}} \]  

(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:

\[ k_{\text{uni}}(T, p) = \sum_{n=m}^{+\infty} \frac{k_{1}(E = n\hbar c\bar{\nu}; T)k_{2}(E = n\hbar c\bar{\nu})}{k_{c}(T)} \]  

(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 approximately the same computational effort that CVT/SCT allows one to include them efficiently in the high-pressure limit.

### 2.2 Chemical activation mechanism for bimolecular association

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

\[ A + B \xrightarrow{k_{1}(T)} AB \xrightarrow{k_{-1}(E)} \quad \xrightarrow{k_{2}(E)} P \]

\[ \downarrow k_{c}[M] \]

\[ \text{AB} \]  

(Type 1)
and the chemical activation mechanism for a bimolecular association reaction is:

\[ A + B \xrightarrow[k_{-1}(T)]{k_1(T)} \text{AB}^* \xrightarrow[k_c][\text{M}]{k_c[M]} \text{AB} \] (Type 2)

where A and B are reactants, \( \text{AB}^* \) 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 yields

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

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

for reaction type 1 and

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

for reactions type 2, where \( f(E) \) is the fraction of energized species (\( \text{AB}^* \)) at energy \( E \), which is given by

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

where

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

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 ($h\nu$). 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:

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

(21)

where $\langle \Delta E \rangle$ 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 $\langle \Delta E \rangle_{\text{down}}$ 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. Chem. Phys. 1977, 66, 4745). For moderate–sized molecules, $F_E$ is nearly unity (Troe, 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:

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

(22)

or it can be computed using the Whiten-Rabinovitch approximation (J. Troe, J. Phys. Chem., 1979, 83, 114).

The collision efficiency can also be estimated as:

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

(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 \( k_{\text{LJ}} \) is the product of the hard-sphere collision rate constant \( k_{\text{HS}} \) 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

\[
k_c = \beta c \Omega^*_{2,2} k_{\text{HS}}
\]

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 \( \Omega^*_{2,2} \):

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

(25)

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

The hard–sphere collision rate constant \( k_{\text{HS}} \) is computed as:

\[
k_{\text{HS}} = \pi \left( \frac{d_A + d_M}{2} \right)^2 \sqrt{\frac{8k_B T}{\pi \mu}}
\]

(26)

where the vdW diameters \( d_A \) and \( d_M \) are computed from the Lennard-Jones parameters \( \sigma_{A-A} \) and \( \sigma_{M-M} \) using the relation \( d = 2^{1/6} \sigma \), and \( \mu \) 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):

\[
k = \begin{cases} 
  A \left( \frac{T}{300} \right)^n \exp \left[ - \frac{E(T + T_0)}{R(T^2 + T_0^2)} \right] & \text{endothermic reaction} \\
  A \left( \frac{T + T_0}{300} \right)^n \exp \left[ - \frac{E(T + T_0)}{R(T^2 + T_0^2)} \right] & \text{exothermic reaction}
\end{cases}
\]  

(27)

where \( A \) (for unimolecular reaction, its unit is \( s^{-1} \); and for bimolecular reaction, its unit is \( \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \)), \( n \) (unitless), \( E \) (unit: kcal/mol) and \( T_0 \) (unit: K) are fitting parameters. The ideal gas constant \( R \) is in the unit of kcal \( \text{mol}^{-1} \text{ K}^{-1} \) with value 0.00198588. Then, the temperature-dependent Arrhenius activation energies can be computed from the local slopes of Arrhenius plots, which yields:

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

(28)

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

\[
A^\infty(T) = k^\infty(T) \exp \left[ \frac{E_a(T)}{RT} \right]
\]  

(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

The input template for unimolecular reaction (A → P) is:

```plaintext
#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
6.69850E+11 25.7
7.699440E+11 25.9
```
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 $\Delta E$. 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 $\Delta E$ parameter: $<\Delta E>_{all}$ (i.e. average energy transferred during both activation and deactivation collisions), $<\Delta E>_{down}$ (i.e., average energy transferred only for deactivation collisions). 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 $<\Delta E>_{all}$).
- **FE**: The $F_E$ parameter for the activated unimolecular states. If user specify a positive number, then it means that the value specified by the user
specified is directly used as $F_E$; if a value of -1 is specified, it means that $F_E$ will be computed based on Whitten-Rabinovitch approximation (with an additional input file: vibinfo.inp). 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 $\sigma$ (unit: Å), $\varepsilon$ (unit: Kelvin, i.e., $\varepsilon/k_B$), molar mass (unit: gram per mole).

**paramBath**
Lennard-Johns parameters for bath gas.

**Method**
For unimolecular dissociation or isomerization reaction, the keyword “HLQRRK” must be specified.

**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 $A \rightarrow P$. 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.
4.2 Bimolecular association

The input template for bimolecular association reaction \((A + B \rightarrow P)\) 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.
rxn1AEa
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”.


<table>
<thead>
<tr>
<th><strong>rxn1</strong></th>
<th><strong>rate</strong></th>
<th>User specified high-pressure-limit rate constant for the forward bimolecular association reaction ( (A + B \rightarrow P) ).</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>rxnneg1AEa</strong></td>
<td></td>
<td>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 ( \dot{E}a ) in right column; this information should be consistent with the order of the temperatures that one has specified under <strong>TrxnList</strong></td>
</tr>
<tr>
<td><strong>paramPstar</strong></td>
<td></td>
<td>Lennard-Johns parameters for the unimolecular product ( P ), in the order of ( \sigma ) (unit: Å), ( \varepsilon ) (unit: Kelvin, i.e., ( \varepsilon/k_B )), molar mass (unit: gram per mole).</td>
</tr>
<tr>
<td><strong>sPstar</strong></td>
<td></td>
<td>The number of vibrational degree of freedom for ( P ).</td>
</tr>
<tr>
<td><strong>GeoMeFreq</strong></td>
<td></td>
<td>The geometric mean frequency (in the unit of cm(^{-1})) of unimolecular product ( P ).</td>
</tr>
</tbody>
</table>
4.3 Bimolecular reaction with an intermediate

4.3.1

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

```plaintext
#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
rnx1   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.)

<table>
<thead>
<tr>
<th>Rxn2</th>
<th>YES</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For bimolecular reactions with a stable intermediate, the “Rxn2” must be set to be “YES” to indicate the existence of a second-step reaction.

<table>
<thead>
<tr>
<th>rxn2AEa</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>rxnneg1AEa</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

To specify \( A \) factor and activation energy for high-pressure-limit reaction \( AB \rightarrow A + B \)

<table>
<thead>
<tr>
<th>rxn1</th>
<th>rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

User specified high-pressure-limit rate constant for the forward bimolecular association reaction \( (A + B \rightarrow AB) \).

<table>
<thead>
<tr>
<th>GeoMeFreq</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The geometric mean frequency (in the unit of \( \text{cm}^{-1} \)) of unimolecular intermediate \( AB \).

<table>
<thead>
<tr>
<th>paramAB</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Lennard-Johns parameters for the unimolecular intermediate \( AB \), in the order of \( \sigma \) (unit: Å), \( \varepsilon \) (unit: Kelvin, i.e., \( \varepsilon/k_B \)), molar mass (unit: gram per mole).

<table>
<thead>
<tr>
<th>sABstar</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The number of vibrational degree of freedom for \( AB \).

4.3.2.

For reaction type:

\[
A + B \rightarrow AB \rightarrow P1 \\
A + B \rightarrow AB \rightarrow P2 \\
A + B \rightarrow AB \rightarrow P3
\]

i.e., a bimolecular reaction with a stable intermediate, and followed by second step.
consists of multiple parallel reactions (in this example, we have 3 parallel reactions in the second step), the following input can be used:

```plaintext
#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
```
The key point in the input file here is that “Rxn2 3” means there are 3 parallel reactions in the second step, and their $A$ and $E_a$ parameters are specified respectively after the specification of “rxn1AEa”. Also, please notice that “Rxn2 1” is equivalent to “Rxn2 YES”, and “Rxn2 0” is equivalent to “Rxn2 NO” in the previous sections.
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) 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 Polyrate2016-2A/util/SS-QRRK/testrun/ and the corresponding output files are in Polyrate2016-2A/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.