Tutorial for TUMME 2023

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Outline

- Introduction
- Installation
- How to run
- Input file
- Output files
- Others
- Example
Introduction

What is TUMME?

- TUMME (Tsinghua University Minnesota Master Equation solver) is a computer program for setting up and solving one-dimensional energy-dependent master equations for gas-phase chemical kinetics.
- TUMME can solve for the phenomenological rate constants and the time evolution of energy-bin populations for a gas-phase reaction network involving single or multiple intermediate energy-wells in a (P, T) ensemble.

What can TUMME do?

- Construct the transition matrix of a master equation with discrete energy bins
- Calculate rate constants for collisional energy transfer
- Calculate microcanonical reaction rates including anharmonicity, recrossing, and tunneling
- Calculate phenomenological rate constants for a complicated reaction map
- Calculate the time evolution of energy populations
- Characterize the pressure and temperature dependences of chemical kinetics
Basic assumptions of TUMME

- **Markov random process**
  The transition process depends on the current state and has no historical memory.

- **RRKM assumption**
  The intramolecular vibrational relaxation (IVR) is faster than reaction.

- **Bimolecular reagents equilibrated**
  Bimolecular pairs are always in thermal equilibrium.

- **Pressure, temperature, and concentrations**
  - a) Constant pressure, constant temperature
  - b) Bath gas is ideal gas
  - c) Bath gas concentration $>>$ reactant and product concentrations

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**Diagram**

- Energy $E$
- Reaction progress $s$
- Master equation sketch

- $k_{13}(E)$
- $k_{35}(E)$
- $P_3(E'|E)$
- $P_3(E|E')$
Features of TUMME

- Microcanonical flux coefficients by multistructural variational transition state theory (MS-VTST) with multidimensional tunneling (ZCT, SCT, LCT, or μOMT)
- Inverse-Laplace transform for microcanonical rate flux coefficients
- “Exponential-down” collision relaxation mode with energy-dependent $\Delta E_d$
- Phenomenological rate constants from chemically significant eigenmodes
- Pseudo-first order treatment when bimolecular reactions involved
- MPI and MP parallelism of computer code
- Double/quadruple/octuple precision for floating-point arithmetic
- Interfaces available for Polyrate, MSTor, and Gaussian
Installation command:

```
[user@~] tar -Jxvf TUMME2023.xz
[user@~] cd TUMME2023/
[user@~/TUMME2023] ./configure
```

- TUMME is written using Python3.
- To run basic TUMME, Anaconda should be installed.
- To use high-precision libraries, you need the configure file to compile.
- To use MPI, you need to install `mpi4py` module according to this webpage:
  

Details in the file configure
Run command:

```bash
[<user@~>/TUMME2023] tumme param.in
```

- The script will run different commands according to the keyword `#PARALLEL` defined in the input file.
- The name of the input file can be any file name.

Details in the file `tumme`
Structure of the standard input file “param.in”

- Parallelism keywords
- Parameter section
- Reaction section
- Species section
Input file – 2

Interface to external files

Species properties can be read from Polyrate file, Gaussian file, and Species-section, and the priority is

*Polyrate file > Gaussian file > Species section*
Output files

- *.rate
  Temperature-and-pressure-dependent rate constants and high-pressure limits.

- *.out
  Properties of species and reactions and parameters while solving master equation.

- File printing microcanonical flux coefficients
- File printing partition functions
- File printing collisional energy transfer functions
- File printing time evolution of energetic-bin populations
- File printing CSE eigenvalues
- File printing CSE eigenvectors

  CSE ≡ chemically significant eigenmodes
About energy

- Distinguish concepts of \( dE \), \( ESOT \), \( EMAX \), and \( EEOT \).
- Ensure \( ESOT > dE \) and \( EMAX > EEOT \).
- The depth of an isomer well may be truncated due to the numerical method of normalization.
- If some energies of species are read from \( E0 \) or \( EELE \) and others from \( G09file \), one should ensure they have consistent zeros of energy.
- At low temperatures, when molecules mainly populate low energy levels, one should decrease the value of \( ESOT \).
- At high temperatures, when molecules populate high energy levels, one should increase the value of \( ESOT \).
### About symmetry number

<table>
<thead>
<tr>
<th>Need to define <strong>Rotsigma</strong> when</th>
<th>Not need to define <strong>Rotsigma</strong> when</th>
</tr>
</thead>
<tbody>
<tr>
<td>Read properties from <em>Polyrate</em></td>
<td>Read density of state from <em>MSTor</em></td>
</tr>
<tr>
<td>Read properties from <strong>Species</strong> section</td>
<td>Read properties from <em>Gaussian</em></td>
</tr>
</tbody>
</table>

### About frequency scaling factor

<table>
<thead>
<tr>
<th>Need to define <strong>Freqscale</strong> when</th>
<th>Not need to define <strong>Freqscale</strong> when</th>
</tr>
</thead>
<tbody>
<tr>
<td>Read properties from <em>Gaussian</em></td>
<td>Read density of state from <em>MSTor</em></td>
</tr>
<tr>
<td>Read properties from <strong>Species</strong> section</td>
<td>Read properties from <em>Polyrate</em></td>
</tr>
</tbody>
</table>

\(^a\) If, as usual, the frequency scaling has been done in *MSTor* and *Polyrate*.
1,2-H-shift isomerization of isobutyl

This is an example for the simplest isomerization reaction. In this example, TST(RRKM) is used with the single-structure-rigid-rotor-harmonic-oscillator approximation. The rate constant and time-evolution of species concentrations are extracted from the master equation

\[
\frac{dy}{dt} = -Wy
\]

where \(y\) is a vector containing the population of \(R\) and \(P_b\), and \(W\) is the transition matrix.

**(Input):** the standard input file

**(Output):** rate constants and the time evolution of concentrations.

\[(\text{CH}_3)_2\text{CHCH}_2\cdot \leftrightarrow (\text{CH}_3)_3\text{CH}\cdot\]

Example 1 (cont.)

Standard input file

Parallelism block

Global parameter block

Collision section

Relaxation section

Species block

Well/isomer

Geometry

Frequency

Energy

Temperature

Pressure

Species where zero of energy is placed

Time-evolution

Reaction block

Define the reactant, transition state, and product
Example 1 (cont.)

- Standard output file

Global parameters

Isomer properties

Energies

Elementary reactions

Parameters for each $(T, p)$ condition.
Example 1 (cont.)

- Rate constants output file

Phenomenological rate constants

“Merge” happened

The time-evolution of isomers
C-C and C-H $\beta$-scission of isobutyl

This is an example of competing unimolecular reactions. In this example, TST(RRKM) is used with the single-structure-rigid-rotor-harmonic-oscillator approximation. Rate constants are extracted from the master equation

$$\frac{d\mathbf{y}}{dt} = -\mathbf{Wy} + \mathbf{Bs} \quad (2)$$

based on CSE theory, where $\mathbf{y}$ is a vector containing the population of R. For the time evolution, TUMME neglect the $\mathbf{Bs}$ term of eq (2) and uses the following homogeneous master equation:

$$\frac{d\mathbf{y}}{dt} = -\mathbf{Wy} \quad (3)$$

**Input:** the standard input file
**Output:** rate constants and the time-evolution of concentrations.

Standard input file

Parallelism block

Parameter block

Collision section

Relaxation section

Temperature

Pressure

Species where zero of energy is placed

Precision of the transition matrix

Reaction block

Define the reactant, transition state and product
Example 2 (cont.)

### Standard input file

**Species block**

<table>
<thead>
<tr>
<th>Name R</th>
<th>Geometry[A]</th>
<th>C</th>
<th>0.0000000</th>
<th>0.06835100</th>
<th>-0.36837900</th>
</tr>
</thead>
<tbody>
<tr>
<td>...</td>
<td>End_Geometry</td>
<td>Frequency[c-m-1]</td>
<td>76.5658</td>
<td>150.8529</td>
<td>176.9492</td>
</tr>
<tr>
<td>...</td>
<td>End_Frequency</td>
<td>EERK[ev]</td>
<td>2.937584765</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Wells / isomers**

**Transition states**

<table>
<thead>
<tr>
<th>Name Rs</th>
<th>Geometry[A]</th>
<th>C</th>
<th>-0.00000000</th>
<th>0.10845050</th>
<th>0.01394900</th>
</tr>
</thead>
<tbody>
<tr>
<td>...</td>
<td>End_Geometry</td>
<td>Frequency[c-m-1]</td>
<td>83.0861</td>
<td>115.2996</td>
<td></td>
</tr>
<tr>
<td>...</td>
<td>End_Frequency</td>
<td>EERK[ev]</td>
<td>4.51441416</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Bimolecular pairs**

<table>
<thead>
<tr>
<th>Name Pa</th>
<th>Sp2Mol</th>
<th>The first molecular fragment species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geometry[A]</td>
<td>C</td>
<td>0.0000000</td>
</tr>
<tr>
<td>... End_Geometry</td>
<td>Frequency[c-m-1]</td>
<td>920.0904</td>
</tr>
<tr>
<td>... End_Frequency</td>
<td>EERK[ev]</td>
<td>0.0</td>
</tr>
<tr>
<td>... End_Elelevel</td>
<td>Rotsigma</td>
<td>6</td>
</tr>
</tbody>
</table>

**The second molecular fragment species**

<table>
<thead>
<tr>
<th>Name Pa</th>
<th>Sp2Mol</th>
<th>The first molecular fragment species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geometry[A]</td>
<td>C</td>
<td>-1.26496100</td>
</tr>
<tr>
<td>... End_Geometry</td>
<td>Frequency[c-m-1]</td>
<td>80.80033</td>
</tr>
<tr>
<td>... End_Frequency</td>
<td>EERK[kcal/mol]</td>
<td>0.0</td>
</tr>
</tbody>
</table>

**The atomic fragment species**

<table>
<thead>
<tr>
<th>Name Pc</th>
<th>Sp2Mol</th>
<th>The first molecular fragment species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geometry[A]</td>
<td>C</td>
<td>0.0000000</td>
</tr>
<tr>
<td>... End_Geometry</td>
<td>Frequency[c-m-1]</td>
<td>29.8139</td>
</tr>
<tr>
<td>... End_Frequency</td>
<td>EERK[kcal/mol]</td>
<td>0.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Name Sp2Atom</th>
<th>13_r</th>
<th>Sp2Mol</th>
<th>The first molecular fragment species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symbol</td>
<td>H</td>
<td>EERK[kcal/mol]</td>
<td>0.0</td>
</tr>
<tr>
<td>End_Sp2Atom</td>
<td>EERK[ev]</td>
<td>4.452257969</td>
<td></td>
</tr>
</tbody>
</table>

End_Bim
Example 2 (cont.)

- **Standard output file**

  - **Global parameters**
  - **Isomer properties**
  - **Elementary reactions**

  Parameters for each \((T, p)\) condition.

  

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (K)</td>
<td>7.000E+02</td>
</tr>
<tr>
<td>Pressure (Torr)</td>
<td>1.000E-10</td>
</tr>
<tr>
<td>Energy step (cm(^{-1}))</td>
<td>4.86525E+01</td>
</tr>
<tr>
<td>Energy reference (cm(^{-1}))</td>
<td>2.73888E+04</td>
</tr>
</tbody>
</table>

  [RELAXATION INFO]
  - **Name:** R
  - **Size:** 560
  - **bmax [a.u.]:** 17.007535
  - **Z[1/s]:** 3.117643E-03
  - **Truncated well E0 [cm\(^{-1}\)]:** 112.075
  - **True well E0 [cm\(^{-1}\)]:** 0.000

  [END OF INFO]

  [ME INFO]
  - **Size:** 560
  - **Min CSE eigenvalue [1/s]:** 7.194008E-07
  - **Max CSE eigenvalue [1/s]:** 7.194008E-07
  - **Min IERE eigenvalue [1/s]:** 1.458961E-05
  - **Max IERE eigenvalue [1/s]:** 3.15746E+10

  [EPICS]
  - **CSE No.:** 1
  - **R:** 9.61931E-01

  [Kappa]
  - **Bin Name:** Pa
  - **Pc:** R

  [Binding]
  - **R well corresponds to eigen mode 1**

  [END OF INFO]
Example 2 (cont.)

- Rate constants output file

Phenomenological rate constants

Falloff curves
Example 3

Hydrogen Abstraction from HCHO by OH (TST)

This is an example of a bimolecular reaction. This example uses TST(RRKM) theory with the single-structure-rigid-rotor-harmonic-oscillator is used for reaction 2, and the reaction 1 is estimated by the inverse-Laplacian transform to the hard-sphere model. Based on the CSE theory, the rate constant is extracted from

\[
\frac{dy}{dt} = -Wy + Bn_{HCHO}n_{OH}
\]

(4)

where the \( n_{HCHO}n_{OH} \) is left unknown. For time-evolution calculations, the reaction is assumed to be pseudo-first order, and eq. (4) is converted to homogeneous form by appending the \( n_{HCHO} \) concentration to the population vector \( y \) to get vector \( y^* \),

\[
\frac{dy^*}{dt} = -W^*y^*
\]

(5)

**Input:** the standard input file, *Polyrate* file for the reaction 2.

**Output:** rate constants and the time-evolution of concentrations.

Example 3 (cont.)

### Global parameters block

- **Collision**
  - `TUMME`: Tsinghua University Minnesota Master Equation solver
  - Standard input file
  - Global parameters block
  - Relaxation
  - Barriered elementary reaction, read from Polyrate file
  - Barrierless elementary reaction, ILT + hard-sphere

### Reactions block

- **Species block**
  - Bimolecular pair(s) with pseudo-first order assumption

5/19/2023
The time-evolution of \( n_{\text{OH}} \) (solid lines) and \( n_{\text{RC}} \) (dash-dot lines). The initial condition is set as \( n_{\text{OH}}(t)=0=10^{-7} \) mol/L, \( n_{\text{RC}}(t)=0 \) and \( n_{\text{HCHO}} \) is assumed to be constant at \( 10^{-5} \) mol/L.
Example 4

Hydrogen Abstraction from HCHO by OH (MS-VTST/SCT)

This is an example of a bimolecular reaction. In this example, MS-CVT/SCT is used for reaction 2, and rate constants for reaction 1 are estimated by an inverse Laplace transform applied to the hard-sphere model. The rate constant is extracted from eq. (4) based on CSE theory, and the time evolution is estimated from eq. (5).

**Input:** the standard input file, Polyrate file for reaction 2, MStor files for RC and TS

**Output:** rate constants and the time-evolution of concentrations.

\[
\text{HCHO} + \text{OH} \rightarrow \text{HCHO} \cdot \cdot \cdot \text{HO} \rightarrow \text{HCO} + \text{H}_2\text{O}
\]

Example 4 (cont.)

Standard input file

Global parameters block
- Collision
- Relaxation

Reactions block
- Bariered elementary reaction, read from Polyrate file
- Barrierless elementary reaction, ILT + hard-sphere

Species block
- Bimolecular pair(s) with pseudo-first order assumption
The time evolution of \( n_{OH}(t) \) (solid lines) and \( n_{RC}(t) \) (dash-dot lines) are assumed to be constant at 10^(-7) mol/L. The initial condition is set as \( n_{OH}(t=0)=10^{-7} \) mol/L; \( n_{RC}(t=0) \) and \( n_{HCHO} \) are assumed to be constant at 10^(-5) mol/L.
Example 4 (cont.)

Comparison with example 3

Time-evolution of the example 3 (TST)

Time-evolution of the example 4 (VTST)
Thank you for your interest in TUMME.

You are invited to provide feedback to: xuxuefei@tsinghua.edu.cn and truhlar@umn.edu

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