

Two Dimensional Master Equation: Steady-State Solution (TS)

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“TS is a chemical kinetic program that solves a two-dimensional master-equation for chemically activated gas-phase reactions in parallel using the Steady-State approach. It is developed, implemented, and maintained by T. L. Nguyen and J. F. Stanton, version Feb.-27-2020”.

Abstract:

In the field of chemical kinetics, the solution of a two-dimensional master equation that depends explicitly on both total internal energy (E) and total angular momentum (J) is a challenging problem. In this work, a weak-E/**fixed-J** collisional model (i.e. weak-collisional internal energy relaxation/free-collisional angular momentum relaxation) is used along with the steady-state approach to solve the resulting (simplified) two-dimensional (E,J)-grained master equation for chemically activated reaction systems. The corresponding solutions give thermal rate constants and product branching ratios as functions of both temperature and pressure. The TS program can be used to predict and analyze experimental chemical kinetics results.

If this work is used, please consider citing the following references:

- 1) J. R. Barker et al. Ann Arbor, Michigan, USA (<http://aoss.engin.umich.edu/multiwell/>), **2020**.
- 2) T. L. Nguyen and J. F. Stanton, A Steady-State Approximation to the Two-Dimensional Master Equation for Chemical Kinetics Calculations, *J. Phys. Chem. A* **119**, 7627-7636 (2015).
- 3) T. L. Nguyen, H. Lee, D. A. Matthews, M. C. McCarthy and J. F. Stanton, Stabilization of the Simplest Criegee Intermediate from the Reaction between Ozone and Ethylene: A High-Level Quantum Chemical and Kinetic Analysis of Ozonolysis, *J. Phys. Chem. A* **119**, 5524-5533 (2015).

Any problems in the use of the TS program:

Please do not hesitate to contact us. We have greatly appreciated any reports of possible errors.

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Thank you and good luck!

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FEATURES

TS program can be used to compute the following properties:

- ✓ Steady-state solutions (i.e. thermal rate constants, $k(T,P)$ and product yields, $\gamma(T,P)$) for two-dimensional master equation.
- ✓ Microvariational transition state theory, vRRKM.
- ✓ 1D-asymmetric Eckart tunneling transmission probability, $P_{1D-E}(E)$.
- ✓ 1D-WKB tunneling transmission probability, $P_{1D-WKB}(E)$.
- ✓ Sums and densities of states for harmonic oscillators.

QUICK START with TS

If users can provide *relative energies of stationary points* on potential energy surface (PES) and *rovibrational parameters* (e.g. harmonic vibrational frequencies and rotational constants), TS program can be used to obtain thermal rate constants and product branching ratios as functions of both pressure and temperature (assuming harmonic oscillators and rigid rotors). Two examples, one is for OH + CO reaction and the other is for O₃ + C₂H₄ reaction, are provided for convenience. Users can also include asymmetric Eckart or WKB tunneling models to study of tunneling effects. In addition, the treatment of microvariational RRKM is also implemented. This vRRKM may be useful for a loose transition structure or for a dissociation channel without a tight transition state (e.g. HC(O)OH \rightleftharpoons HCO + OH).

A) INTRODUCTION

Chemical reactions occurring in combustion, atmospheric environments, and space are complicated processes, which often proceed through multiple intermediates (also called wells) to produce various products. In these systems, there can be considerable competition between unimolecular reactions (i.e. dissociation/isomerization) and collisional energy transfer processes of vibrationally excited intermediates; thermal reaction rate constants and product yields can depend strongly on both temperature and pressure.¹⁻⁶ To deal with this issue, one can construct and then solve an energy-grained master equation.¹⁻¹¹ Apart from two extreme conditions (i.e. at the high- and low-pressure limits where analytical solutions of the master-equation can be obtained),^{9,12-14} one must solve an energy-grained master equation numerically.¹⁻¹¹ The solutions (phenomenological (thermal) rate constants and product yields) can vary with both temperature and pressure; and they are frequently calculated within the steady-state approach. In addition, solutions that can vary as a function of reaction time under non-equilibrium conditions (e.g. time evolution for concentrations of intermediates) can also be computed. There are at least two techniques that are commonly used to solve the master equation, including stochastic simulation and deterministic methods.¹⁰ Each method has its own advantages and drawbacks. The advantages of the steady-state approach (which belongs to the deterministic method) used here include a rapid solution of the equation

that is independent of pressure (unlike the stochastic approach); and that it is well-suited to complicated reaction mechanisms. However, the steady-state method cannot provide chemical kinetics properties that vary as a function of reaction time. Such time-dependent properties can only be computed using either stochastic simulation method or the eigenvalue-eigenvector (matrix) technique.¹⁰ There are a number of chemical kinetics software programs available, including MULTIWELL¹⁵ and USESAM¹⁶ software packages that use (exact) stochastic simulation methods; matrix techniques have been applied in MESMER,¹⁷ VARIFLEX,¹⁸ UNIMOL,¹⁹ CHEMRATE,²⁰ and other programs. All these packages have been designed to work with a one-dimensional energy-grained master equation (1DME), in which only the internal energy (E) is considered. The roles of angular momentum are either ignored or just partly included. However, the effects of angular momentum²¹⁻²⁶ (e.g. centrifugal effects) are found to play an important role in some reactions where there are significant changes of rotational constants amongst the transition states and intermediates along the reaction path. Therefore, such effects should sometimes (or often) be taken into account in computing microcanonical rate constants. Various approximate models have been suggested to capture these effects.²⁷⁻²⁹ The most common assumes that the stationary points on potential energy surface are described by a symmetric top in which the rotations are completely separable from the vibrations and may

be treated approximately as either active or inactive (i.e. adiabatic) motions or used in a hybrid model that is a mixture of the two.²⁷⁻²⁹

In 1996, Jeffrey et al.³⁰ were the first to report full iterative solutions of the two-dimensional master equation for thermal unimolecular reactions using the Nesbet algorithm.³¹ In the same year, Robertson et al.³² reformulated the 2DME problem in terms of a simplified diffusion equation and solved it using inverse iteration. One year later, Venkatesh et al.³³ carried out a full theoretical analysis of the two-dimensional master equation formulation of the problem of intermolecular energy transfer in the context of multiple-well, multiple-channel chemically activated reactions. In 1999, the same group³⁴ applied efficient numerical methods to analyze the internal structure of the master equation kernel (that describes intramolecular and intermolecular energy transfer in multiple-well, multiple-channel systems) to the chemically activated reaction $\text{C}_2\text{H}_5 + \text{O}_2$. They suggested the use of a Krylov-subspace method to determine the uppermost portions of the internal spectrum of the master equation kernel. In 2002, Miller and Klippenstein³⁵ reported solution of a two-dimensional master equation for thermal dissociation of methane in the low-pressure limit. In addition, these authors also suggested three different collisional models to reduce the two-dimensional problem to one dimension using a technique of Smith and Gilbert.^{21,22} Note that in the current version of the Multiwell software suite,¹⁵ Marcus's approach¹⁵ that reduced the two-dimensional to a one-dimension problem by

invoking “*centrifugal corrections*” has been fairly widely used. This approach is exact at the high-pressure limit, but only approximate at lower pressures. For reviews of master equation methods, the interested reader is referred to the literature.¹⁻¹¹

In this work, we use the matrix technique to solve a **fixed-J** 2D master-equation in parallel, simplified by assuming the steady-state approach.

B) INPUT/OUTPUT (I/O) DATA

I. INPUT DATA

Input data are required in **TS** program include:

- 1) Relative energies of stationary points (i.e. minima and transition states), which play important roles in chemical kinetics, on vibrationally adiabatic potential energy surface (VA-PES).
- 2) All external files that contain either rovibrational parameters (such as harmonic vibrational frequencies and three rotational constants) or sums and densities of states as a function of (vibrational) energy for all stationary points. If users can provide sums and densities of states in an external file, we would recommend users use the MULTIWELL software program¹⁵ to generate these files using DENSUM, BDENS, and/or SCTST modules; the MULTIWELL is user-friendly and well documented.¹⁵ These external files have the “*relatively same*” formats as those of “densum.out”, “bdens.out”, or “sctst.out” printed out from the MULTIWELL.

- 3) All external files that comprise three rotational constants (in cm^{-1}) for all stationary points.
- 4) By default, an initial energy distribution function $F(E,J)$ will be generated in **TS** program, but $F(E,J)$ may be provided via an external file (that must be named “**FE.EXTERNAL**”) by users.
- 5) Users need to modify an external *C-shell* file named “**run0.dummy**” to set up a current-directory, working-directory, temporary-directory, and path appropriately.
- 6) A list of grid points for angular momentum number (from 0 to a maximum value) is defined in an external *C-shell* file named “**run_J.sh**”. Depending on reaction conditions, users may need to modify this file as well.
- 7) A list of pressures (in Torr) is given in an external *C-shell* file named “**run_P.sh**”. **TS** program will compute thermal rate constants at each set of T, P and J (i.e. $k(T,P,J)$), one at a time and one by one. A provided *C-shell* file (named “**run_collect.sh**”) will then be used to collect all values of $k(T,P,J)$ in order to compute thermal rate constants $k(T,P)$ or product yields $Y(T,P)$ as a function of pressure (in Torr) at a pre-selected temperature (in K) for each product channel.
- 8) Finally, users need to create a main input file named “**TS.INP**”, which includes all information (from STEP 1 to STEP 5 as mentioned above) such as energies, reaction mechanism, rotational constants, and others.

“TS.INP” is organized as follows, taking $\text{OH} + \text{CO} \rightarrow \text{H} + \text{CO}_2$ reaction as an example (also see Figure 1).

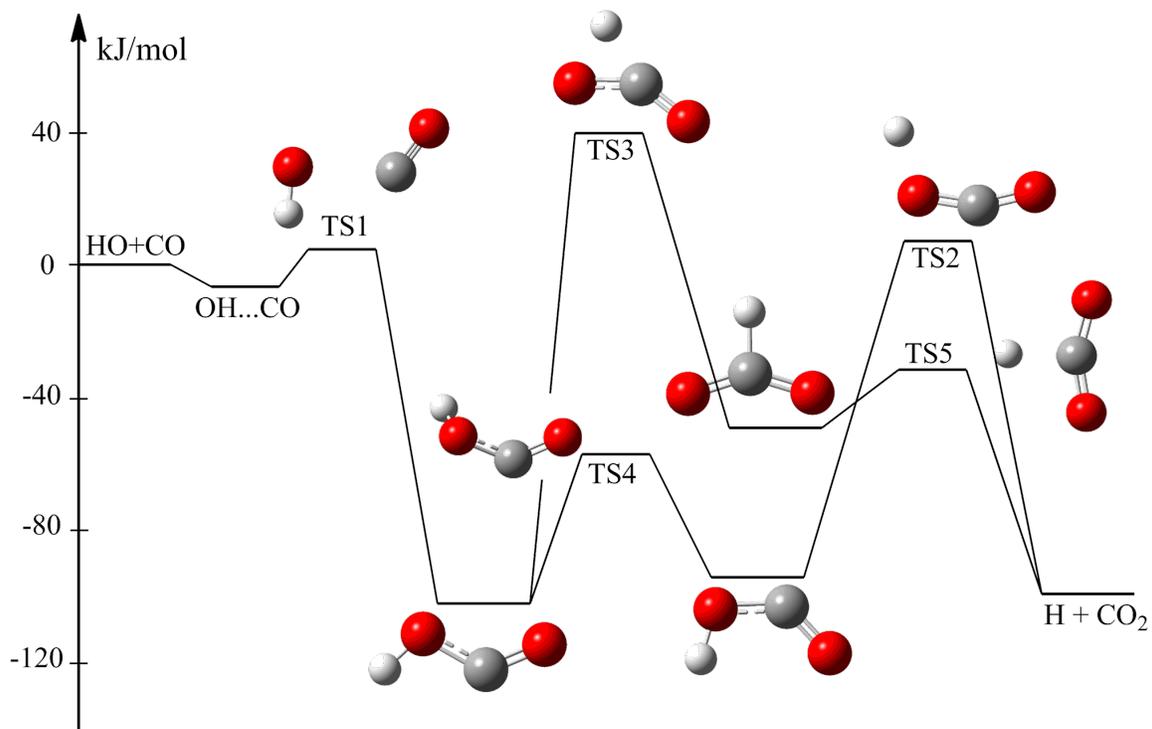


Figure 1: Schematic reaction energy profile for the $\text{HO} + \text{CO} \rightarrow \text{H} + \text{CO}_2$ reaction, adopted from Nguyen et al, *J. Phys. Chem. Lett.* **2012** (Ref. 58).

Line 1: Ceiling (maximum) energy (cm^{-1}), energy bin (cm^{-1})

Line 2: Maximum angular momentum J_{Max} , step size of J

Line 3: Temperature (K), pressure (*default: set at 1 atm*), down energy transfer (cm^{-1})

Line 4: Mass (g/mol), Lennard-Jones collision parameters (σ (Å) and ϵ/k_B (K)) for bath gas

Line 5: Mass (g/mol), Lennard-Jones collision parameters (σ (Å) and ϵ/k_B (K)) for vibrationally excited intermediates

Line 6: $k_\infty(T)$, KEYWORD

k(T): Overall thermal rate constant (in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for a bimolecular reaction, for example OH + CO; or set this to 1 to obtain product yields for each product(s) channel;

KEYWORD represents a model used to compute a collisional integral in computing a Lennard-Jones collisional frequency. It can be either “TROE” or “RPS” models. The latter is default.

Line 7: Number of minima, number of products, unit of energy (in kJ, kcal, or cm^{-1})

Line 8: Index of minimum, *keyword*, name of minimum, name file that comprises three rotational constants (cm^{-1}), energy of minimum, rotational symmetry number, mirror image.

To be continued on a new line until all minima are defined.

Keyword MUST be one of the followings:

- “CRRKM_HO”: conventional RRKM is used to compute sums and densities of states assuming a harmonic oscillator model.
- “EXTERNAL”: sums and densities of states are provided in an external file.

Line 9: Index of product(s), name of product(s), energy of product(s)

To be continued on a new line until all products are defined.

Line 10: Number of TSs, unit of energy (in kJ, kcal, or cm^{-1})

Line 11: Index of TS, *Keyword*, name of TS, name file that contains three rotational constants (cm^{-1}), TS connects from Well-I to Well-J (or to Products-K), energy of TS, rotational symmetry number, mirror image.

To be continued on a new line until all TSs are defined.

Keyword MUST be one of the followings:

- “**CRRKM_HO**”: conventional RRKM is used to compute sums and densities of states assuming a harmonic oscillator model.
- “**VRRKM_HO**”: variational RRKM is used to compute sums and densities of states assuming a harmonic oscillator model.
- “**EXTERNAL**”: sums and densities of states are provided in an external file.
- “**QRRKM_Eckart**”: conventional RRKM is used to compute sums and densities of states that include an asymmetric Eckart tunneling correction.
- “**QRRKM_WKB**”: conventional RRKM is used to compute sums and densities of states that include a WKB tunneling correction.

Line 12: Keyword that *MUST* be either “DENS M ” or “SPAS M ”

Line 13: Keyword1, Keyword2

Keyword1 must be either “YES” or “NO”. It is used to determine how an initial energy distribution function for a nascent adduct is inputted. “YES” means an external file (named “**FE.EXTERNAL**”) for F(E,J) must be provided by users. “NO” means F(E,J) will be computed by the **TS** program.

Keyword2 is used to define an entrance TS that must be either “TIGHT” or “LOOSE”. This keyword will be activated as long as Keyword1 is equal to “NO”.

Line 14: Keyword that MUST be either “YES” or “NO”; and number of $F(E,J)_{\text{diss}}$ files, which may be useful to study secondary chemistry of products (e.g. energized Criegee), to be written out by the program.

“YES” means these files will be printed out, while “NO” will not.

If this keyword is “YES”, the TS program will move to **Line 15** to read data; otherwise the TS program will not.

Line 15: Index, from Well-I to Product(s)-J

To be continued on a new line until all values are read in.

The first example lists the contents of “TS.INP” file for $\text{HO} + \text{CO} \rightarrow \text{H} + \text{CO}_2$:

(Note that trans-HOCO is defined as **1**; cis-HOCO \equiv **2**; $\text{HO} + \text{CO} \equiv$ **3**; and $\text{H} + \text{CO}_2 \equiv$ **4**. In addition, v.d.W. complex $\text{OH}-\text{CO}$, $\text{H}-\text{CO}_2$, and TS5 are all ignored in chemical kinetic scheme because they do not play an important role under conditions considered here).

Line 1: 50000., 10. !!! The ceiling energy (in cm^{-1}); grain size of energy (energy bin)

Line 2: 200, 5

Line 3: 300., 1., 200. !!! Temperature in K; pressure = 1 atm; down energy transfer (cm^{-1})

Line 4: 4.002602, 2.55, 10. !!! Mass

```

(g/mol); Lennard-Jones collision parameters (sigma;
eps/kb) for bath gas = He
Line 5: 45., 4.1, 210.                !!! Mass
(g/mol); Lennard-Jones collision parameters for HOCO
system
Line 6: 8.20082E-13, 'RPS'           !!! Overall rate
k(T) of bimolecular reaction,H0+CO (or set this value to
1 to obtain yields)

Line 7: 2, 2, 'kJ'                   !!! number of
Minima, number of Products, unit of energy
Line 8: 1, 'EXTERNAL', 't-HOCO', 't-HOCOabc', -103.84,1
1          !!! Index; file name of minimum; file name
contains rotational constants; energy of minimum; rot.
Sym. No.; mirror image.
2, 'EXTERNAL', 'c-HOCO', 'c-HOCOabc', -97.49, 1, 1
Line 9: 3, 'H0 + CO', 0.00           !!! Index; name
of products; energy of products
4, 'H + CO2', -103.29

Line 10: 4, 'kJ'                      !!!
number of TSs; unit of energy
Line 11: 1, 'EXTERNAL', 'TS1', 'TS1abc', 1 3, 3.59, 1, 1
!!! Index; File Name of TS; File Name contains
Rot.Const.; from 1 to 3; energy of TS1; Rot. Sym. No.;
mirror image.
2, 'EXTERNAL', 'TS2', 'TS2abc', 2 4, 8.16, 1, 1
3, 'EXTERNAL', 'TS3', 'TS3abc', 1 4, 40.03, 1, 1
4, 'EXTERNAL', 'TS4', 'TS4abc', 1 2, -69.62, 1, 2

Line 12: 'DENS M'                    !!! (either "DENS M" or "SPASM";
where "DENS M" represents a dense matrix whereas "SPASM"
stands for a sparse matrix)

Line 13: 'NO', 'TIGHT'                !!! (either "YES" or
"NO"; "YES" means to use an external F(E,J), while "NO"
means to compute F(E,J) )

Line 14: 'YES', 2
Line 15: 1, 1 3
         2, 2 4

```

The second example is for $O_3 + C_2H_4 \rightarrow CH_2OO + CH_2O$ reaction (see

Figure 2)

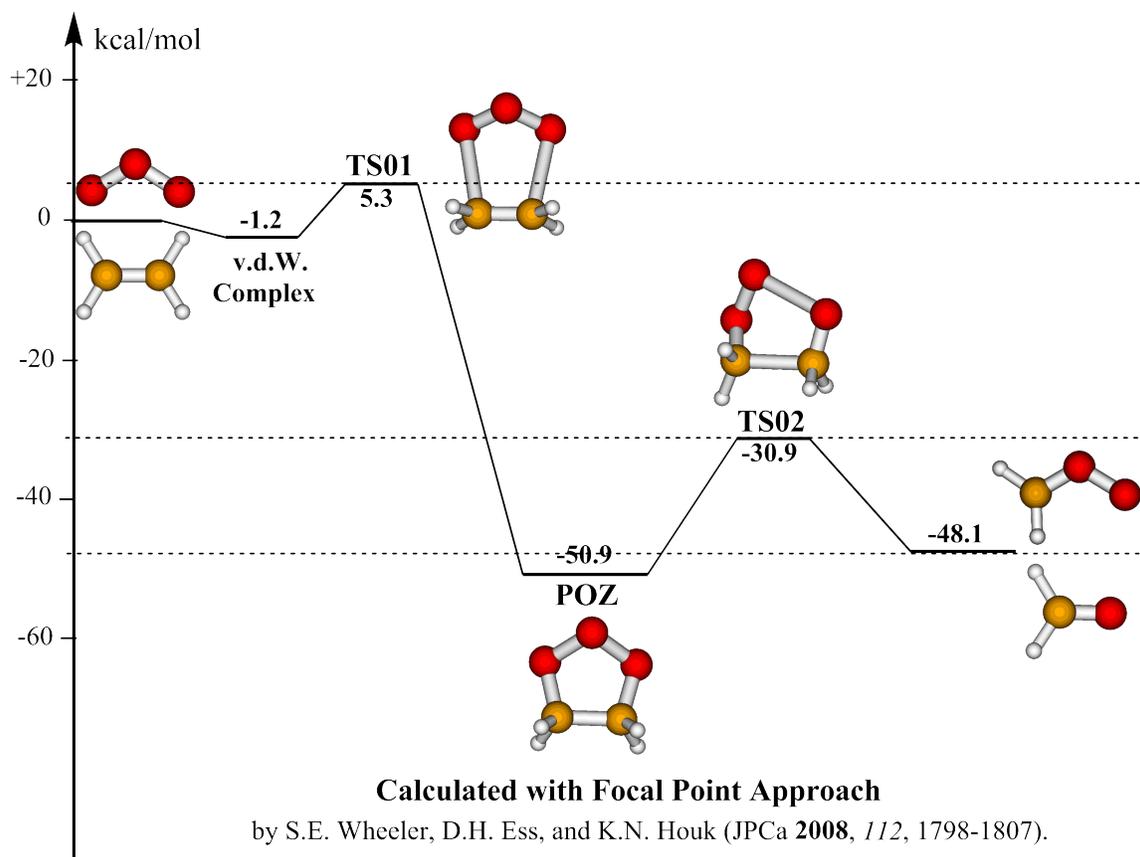


Figure 2: Schematic reaction energy profile for the $O_3 + C_2H_4 \rightarrow CH_2OO + CH_2O$ reaction, adopted from Wheeler et al, *J. Phys. Chem. A* **2008** (Ref. 59).

Note that primary ozonide (POZ) is defined as index **1**, $O_3 + C_2H_4 \equiv$ **2**, and $CH_2OO + CH_2O \equiv$ **3** in the chemical kinetic model in master equation.

Line 1: 50000., 10. !!! Line 1: The ceiling energy; grain size of energy (bin energy)

Line 2: 200, 5 !!! Line 2: Maximum angular momentum number; a step size of J

Line 3: 300., 1., 300. !!! Line 3: Temperature in K; pressure = 1 atm; down energy transfer

(cm⁻¹)

Line 4: 28.8, 3.688, 86.2 !!! Line 4: Mass
(g/mol); Lennard-Jones collision parameters (sigma;
eps/kb) for bath gas = Air(N2/O2)

Line 5: 76., 5.85, 327. !!! Line 5: Mass
(g/mol); Lennard-Jones collision parameters for C2H4O3
system: adopted n-C5H12

Line 6: 1.0E0, 'RPS' !!! Line 6:
Overall rate k(T) of bimolecular reaction, e.g H0+CO (or
set this value to 1 to obtain yields)

Line 7: 1, 2, 'kcal' !!! Line 7:
number of Minima, number of Products, unit of energy

Line 8: 1, 'EXTERNAL', 'POZ', 'POZabc', -50.9, 1, 1
!!! Line 8: Index; file name of minimum; file name
contains 3 rotational constants; energy of minimum

Line 9: 2, 'O3+C2H4', 0.0 !!! Line 9:
Index; name of products; energy of products

3, 'CH200+CH20', -48.1 !!! Line 9 (continued
till end)

Line 10: 2, 'kcal' !!! Line 10:
number of TSs; unit of energy

Line 11: 1, 'EXTERNAL', 'TS1', 'TS1abc', 1 2, 5.3, 1, 1
!!! Line 11: Index; file name of TS; file name contains
3 rotational constants; from 1 to 2; energy of TS1; Rot.
Sym. No.; mirror image.

2, 'EXTERNAL', 'TS2', 'TS2abc', 1 3, -30.9, 1, 2 !!!
Line 11 (continued till end)

Line 12: 'DENS M' !!! Line 12:
(either "DENS M" or "SPASM"; where "DENS M" represents a
dense matrix whereas "SPASM" stands for a sparse matrix)

Line 13: 'NO', 'TIGHT' !!!
Line 13: (either "YES" or "NO"; "YES" means to use an
external F(E,J), while "NO" means to compute F(E,J)
inside the program)

Line 14: 'YES', 2 !!! Line 14:
'YES' means to write out F(E)J energy distribution
function at the moment of dissociation; a number of
F(E)J functions

Line 15: 1, 1 3 !!! Line 15:
Index; from Intermediate 1 to Products 3
2, 1 2

II. OUTPUT DATA

The program will generate a number of output files for various purposes.

They include:

1. **TS.out** at each set (T,P,J) is printed out in each subdirectory.
2. **fort.555** that contains J value, $\Sigma F(E)_{J=\text{constant}}$, and a list of thermal rate constants (or product yields). All **fort.555** files will then be combined to generate $k(T,P)$ and/or $Y(T,P)$.

For $\text{HO} + \text{CO} \rightarrow \text{H} + \text{CO}_2$, the contents of **fort.555** look like:

Reaction conditions: $T = 300 \text{ K}$, $P = 760 \text{ Torr}$, and $J = 40$

```
          40      : angular momentum
7.8654225187E-02 :  $\Sigma F(E)_{J=40}$ 
5.09079E-14      :  $k(T,P,J)$  for stabilized t-HOCO
2.76354E-14      :  $k(T,P,J)$  for stabilized s-HOCO
6.34823E-13      :  $k(T,P,J)$  for HO + CO
1.06715E-13      :  $k(T,P,J)$  for H + CO2
```

3. **fort.701**, **fort.702**, **fort.703**, so on... may be used for the purpose of secondary chemistry of product(s). They include an energy distribution of TS population at the moment of dissociation.
4. **fort.444** that mainly summarizes $k(T,P,J)$ or $Y(T,P,J)$.
5. **fort.333** that saves a number of grid points for angular momentum, a number of wells and a number of product(s).
6. **fort.100** that contains only one pressure (in Torr).
7. **fort.101** that comprises only one J value.

C) TO EXECUTE TS PROGRAM

With all files and data mentioned above (in **B section) I. Input Data** section) are available in your current directory, just do the following:

./run_P.sh (and ENTER/RETURN).

This command will generate a number of subdirectories that match with PRESSURES (that were defined in “**run_P.sh**” file) in your current directory. Under each subdirectory of pressure, a list of subdirectories that correspond to each angular momentum number J (that were defined in “**run_J.sh**” file) will be created.

All jobs will then be submitted to your computer cluster automatically.

After all jobs are done, to collect thermal rate constants (or product yields) for each product channel at each pair (T,P), one needs to login each subdirectory of pressure and proceed (under *C-shell*):

./run_collect.sh

Note that one may need to set a PATH for “**run_collect.sh**” and “**xcollect**”. Otherwise, these two files must be copied to the current directory.

D) TO COMPILE TS PROGRAM

To compile, it requires LAPACK/BLAS libraries available in your computer system.

1. make ALL

This command will generate “**xts**” and “**xcollect**”. “**xts**” is the main driver of **TS** program, while “**xcollect**” will be used to collect results printed out by the program.

2. make

This command will give “**xts**” only.

3. make clean

This command will clean all *.o and executable files.

E) How to select a maximum energy and an energy bin?

It depends on reaction conditions (i.e. particularly temperature) and complexities of reaction mechanism, a ceiling (maximum) energy and an energy bin in an energy-grained master equation can be selected. There is a relative correlation between a maximum energy and reaction temperature: the higher temperature is, the higher maximum energy is. In the atmosphere, temperature is typically within 190-340 K, a maximum energy of $35 \times 10^3 \text{ cm}^{-1}$ (*ca.* 100 kcal/mol) relative to the lowest-lying intermediate on PES may be sufficient. Whereas, in combustion, temperature is much higher and may occasionally reach up to 4000 K. Therefore, a maximum energy must be higher; and a typical value of $7 \times 10^4 \text{ cm}^{-1}$ (*ca.* 200 kcal/mol) may be acceptable for most of cases. Also, there is a close correlation between an accuracy of result and an energy bin: the smaller bin is, the better result is. However, a smaller bin will generate a larger matrix, which in turn takes more computer time to solve it. As a result, one needs to compensate between a required accuracy of result and a size of bin. In general, an energy bin is selected in such a way that it is reduced until the calculated results (e.g. thermal rate constants or product yields) converge. Although the TS program can handle a matrix that has dimensions as large as 46000×46000 , to speed up the calculations the following values for a maximum energy and an energy bin are recommended for a matrix with dimensions of $10^4 \times 10^4$.

Atmospheric conditions		General purposes		Combustion conditions	
$E_{\max} = 3.5 \times 10^4 \text{ cm}^{-1}$		$E_{\max} = 5 \times 10^4 \text{ cm}^{-1}$		$E_{\max} = 7 \times 10^4 \text{ cm}^{-1}$	
N_{well}	$\Delta E_{\text{bin}} (\text{cm}^{-1})$	N_{well}	$\Delta E_{\text{bin}} (\text{cm}^{-1})$	N_{well}	$\Delta E_{\text{bin}} (\text{cm}^{-1})$
≤ 2	10	≤ 2	10	≤ 2	15
3	15	3	15	3	25
4	15	4	20	4	30
5	20	5	25	5	35
6	25	6	30	6	45
7	25	7	35	7	50
8	30	8	40	8	60
9	35	9	45	9	65
10	35	10	50	10	70
16	60	16	80	16	120
20	75	20	100	20	150

Our experience indicates that:

- i) Differences between $\Delta E_{\text{bin}} = 1 \text{ cm}^{-1}$ and 10 cm^{-1} are negligibly small for most of cases in realistic calculations.
- ii) $\Delta E_{\text{bin}} = 35 \text{ cm}^{-1}$ may be acceptable for most purposes, given that potential energy surfaces those are currently (by 2020) constructed using quantum chemistry methods may not be more accurate than 0.1 kcal/mol ($\sim 35 \text{ cm}^{-1}$). In any case, a sensitivity analysis should be used to estimate a possible error bar for the theoretical results.
- iii) For applications in the atmosphere, an energy bin as small as possible should be used. For applications in combustion, a large energy bin may be applied to speed up the calculations.
- iv) A maximum number of intermediates (also called wells) are currently set to 20. Complexities of reaction mechanism may

frequently be reduced (or eliminated) by, for example, treating hindered internal rotors for multiple rotamers and/or disregarding reaction paths that are kinetically unimportant.

F) THEORETICAL BACKGROUNDS

1. One-Dimensional Master-Equation (1DME):

Solution of the 1DME, which depends only on internal energy (or vibrational energy), is well documented in textbooks.^{1-11,36-41} It is briefly summarized below for chemically activated reactions, although solutions for thermally activated reactions or other scenarios can be obtained in a similar manner.

The one-dimensional energy-grained master equation that describes the competing processes of population loss and gain of hot intermediates by unimolecular reactions (i.e. dissociation/isomerization) and collisional energy transfer processes of vibrationally excited intermediates with bath gases is expressed by¹⁻¹¹

$$\frac{d[C_i]}{dt} = R \cdot f_i - k(E_i)[C_i] - \omega[C_i] + \omega \sum_{j=1}^n P_{ij}[C_j], \quad (Eq. 1)$$

where $[C_i]$ is the population of the vibrationally excited intermediate in state i . ω is the collisional frequency of an energized intermediate with a third body, and $k(E)$ is the microcanonical rate constant for a dissociation/isomerization step. Note that the dissociation of energized intermediates leading to fragmented products is assumed to be irreversible while the isomerization from one well to another well is treated reversibly. P_{ij} represents the probability of energy transfer from state j to

state i . $R \cdot f_i$ is the source term; R is the total rate of the entrance flux leading to the formation of the energized adduct. f represents the initial energy distribution function of the energized adduct just formed from a chemical association reaction and is given by⁷⁻¹¹

$$f(E) = \frac{G(E) \exp\left(-\frac{E}{RT}\right)}{\int_0^\infty G(E) \exp\left(-\frac{E}{RT}\right) dE} \quad (\text{Eq. 2})$$

where G is the sum of vibrational states of the entrance transition structure. T is the temperature and R is the gas constant.

In a matrix form, eq. 1 can be rewritten as:

$$\frac{d\mathbb{C}}{dt} = R\mathbb{F} - \mathbb{K}\mathbb{C} - \omega\mathbb{I}\mathbb{C} + \omega\mathbb{P}\mathbb{C} \quad (\text{Eq. 3a})$$

or

$$\frac{d\mathbb{C}}{dt} = R\mathbb{F} - \mathbb{A}\mathbb{C}, \quad \text{with } \mathbb{A} = \mathbb{K} + \omega\mathbb{I} - \omega\mathbb{P}, \quad (\text{Eq. 3b})$$

viz.

$$\mathbb{A} = \begin{pmatrix} k(E_1) + \omega - \omega P_{1,1} & -\omega P_{1,2} & \dots & \dots & -\omega P_{1,n-1} & -\omega P_{1,n} \\ -\omega P_{2,1} & k(E_2) + \omega - \omega P_{2,2} & \dots & \dots & -\omega P_{2,n-1} & -\omega P_{2,n} \\ \dots & \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \\ -\omega P_{n-1,1} & -\omega P_{n-1,2} & \dots & \dots & k(E_{n-1}) + \omega - \omega P_{n-1,n-1} & -\omega P_{n-1,n} \\ -\omega P_{n,1} & -\omega P_{n,2} & \dots & \dots & -\omega P_{n,n-1} & k(E_n) + \omega - \omega P_{n,n} \end{pmatrix}$$

Note that eq. 1 is intended for a single well master equation. The extension to a multiple-intermediate master equation is straightforward and can be found in the literature.^{42,43} For the $O(^1D) + CH_4$ reaction, there

are two intermediates including CH₃OH and vdW complex (¹CH₂-H₂O); thus eq. 1 can be rewritten as eqs. 1a and 1b to take these two intermediates into account:

$$\begin{aligned} \frac{d[C_i]_{CH_3OH}}{dt} = R \cdot f_i - \{ \sum k_{CH_3OH}(E_i) + k_{2 \leftarrow 1}(E) \} [C_i]_{CH_3OH} - \omega [C_i]_{CH_3OH} + \\ \omega \sum_{j=1}^n P_{ij} [C_j]_{CH_3OH} + k_{1 \leftarrow 2}(E) [C_i]_{vdW}, \end{aligned} \quad (\text{Eq. 1a})$$

$$\begin{aligned} \frac{d[C_i]_{vdW}}{dt} = - \{ \sum k_{vdW}(E_i) + k_{1 \leftarrow 2}(E) \} [C_i]_{vdW} - \omega [C_i]_{vdW} + \omega \sum_{j=1}^n P_{ij} [C_j]_{vdW} + \\ k_{2 \leftarrow 1}(E) [C_i]_{CH_3OH}, \end{aligned} \quad (\text{Eq. 1b})$$

where $k_{2 \leftarrow 1}(E)$ and $k_{1 \leftarrow 2}(E)$ are the microcanonical rate coefficients for isomerization step from CH₃OH* to vdW* and vice versa.

The \mathbb{A} matrix for two-intermediate master equation now becomes:

$$\mathbb{A} = \begin{pmatrix} \mathbb{A}_{11} & \mathbb{A}_{1 \leftarrow 2} \\ \mathbb{A}_{2 \leftarrow 1} & \mathbb{A}_{22} \end{pmatrix} = \begin{pmatrix} \mathbb{A}_{11} & \ddots \\ \vdots & \mathbb{A}_{22} \end{pmatrix},$$

with

$$\mathbb{A}_{2 \leftarrow 1} = \begin{pmatrix} * & \dots & 0 \\ \vdots & * & \vdots \\ 0 & \dots & * \end{pmatrix} =$$

$$\begin{pmatrix} k_{2 \leftarrow 1}(E_1) & 0 & \dots & \dots & 0 & 0 \\ 0 & k_{2 \leftarrow 1}(E_2) & \dots & \dots & 0 & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & \dots & k_{2 \leftarrow 1}(E_{n-1}) & 0 \\ 0 & 0 & \dots & \dots & 0 & k_{2 \leftarrow 1}(E_n) \end{pmatrix}$$

where \mathbb{A}_{11} and \mathbb{A}_{22} matrices have the same structure and property as the \mathbb{A} matrix in the one-well case and represent CH_3OH and vdW , respectively. $\mathbb{A}_{2\leftarrow 1}$ and $\mathbb{A}_{1\leftarrow 2}$ are the diagonal matrices that contain microcanonical rate constants for the $\text{CH}_3\text{OH}^* \rightarrow \text{vdW}^*$ and $\text{vdW}^* \rightarrow \text{CH}_3\text{OH}^*$ steps, respectively.

There are three common approaches used to solve the 1DME, namely the Monte-Carlo (e.g. stochastic) method, eigenvalue/eigenvector matrix technique, and the steady-state approach.¹⁰ To facilitate the objectives of this paper, the steady-state (SS) approach^{7,11} will be applied here.

$$\frac{d\mathbb{C}^{SS}}{dt} = \mathbb{R}\mathbb{F} - \mathbb{A}\mathbb{C}^{SS} = 0 \rightarrow \mathbb{R}\mathbb{F} = \mathbb{A}\mathbb{C}^{SS} \rightarrow \mathbb{C}^{SS} = \mathbb{A}^{-1}\mathbb{R}\mathbb{F} \quad (\text{Eq. 4})$$

The linear equation above is solved for \mathbb{C}^{SS} , a vector of steady-state populations, using standard techniques.⁴⁴⁻⁴⁶

Once the vector of steady-state population (\mathbb{C}^{SS}) is known, phenomenological reaction rate coefficients as functions of both temperature and pressure can be calculated via⁷

$$k(T, P) = \frac{\sum_{i=1}^n k(E_i)C_i^{SS}}{\sum_{i=1}^n C_i^{SS}} \quad (\text{Eq. 5})$$

Finally, the product fraction (i.e. yield, branching ratio) for each channel can then be computed as a ratio of reaction rate coefficient for each

channel to the overall reaction rate constant of the entrance flux. It should be mentioned that eq. 5 is the definition of a reaction flux coefficient. The reaction flux coefficient can be identified with a phenomenological rate constant only under restrictive conditions: for example, the energy distribution must be at steady-state (that is considered here) and the reaction must be irreversible (for example, the dissociation of an energized adduct to fragmented products).⁴⁷ Thus, eq. 5 cannot be used to compute phenomenological rate coefficients $k(T,P)$ for reversible well-to-well reactions.⁴⁷ This is the limitation of the steady-state approach; in such a case, the Bartis-Widom approach⁴⁷ may be used.

2. Two-Dimensional Master Equation (2DME):

When the total angular momentum J is incorporated, the master equation then assumes the somewhat more complicated form:

$$\begin{aligned} \frac{d[C_1(E_i, J_i)]}{dt} = & Rf(E_i, J_i) - \left\{ \sum k_1(E_i, J_i) + k(E)_{2 \leftarrow 1} \right\} [C_1(E_i, J_i)] - \omega [C_1(E_i, J_i)] \\ & + \omega \sum_{J_k=0}^{\infty} \sum_{E_k=0}^{\infty} P(E_i, J_i | E_k, J_k) [C_1(E_k, J_k)] \\ & + k(E)_{1 \leftarrow 2} [C_2(E_i, J_i)] \end{aligned} \quad (\text{Eq. 6a})$$

$$\begin{aligned}
\frac{d[C_2(E_i, J_i)]}{dt} = & - \left\{ \sum k_2(E_i, J_i) + k(E)_{1 \leftarrow 2} \right\} [C_2(E_i, J_i)] - \omega [C_2(E_i, J_i)] \\
& + \omega \sum_{J_k=0}^{\infty} \sum_{E_k=0}^{\infty} P(E_i, J_i | E_k, J_k) [C_2(E_k, J_k)] \\
& + k(E)_{2 \leftarrow 1} [C_1(E_i, J_i)] \qquad \qquad \qquad (Eq. 6b)
\end{aligned}$$

where initial energy and angular momentum distribution functions for the energized adduct are now given by¹¹

$$f(E, J) = \frac{(2J + 1)G(E, J)\exp\left(-\frac{E}{RT}\right)}{\sum_{J=0}^{\infty} \int_0^{\infty} (2J + 1)G(E, J)\exp\left(-\frac{E}{RT}\right)dE}, \qquad (Eq. 7)$$

which should be compared to eq. 2. Given that the form of a probability function of energy and angular momentum transfer $P(E_i, J_i | E_k, J_k)$ from the state k (E_k, J_k) to the state i (E_i, J_i) is unknown (even a simpler 1D-form $P(E_i | E_k)$ is not well established),⁹ heuristics must be applied. There have been a number of attempts to fit a 2D-form $P(E_i, J_i | E_k, J_k)$ using data sets obtained from classical trajectory calculations.⁴⁸ The results of such works are promising, but must be regarded as preliminary. Further studies are clearly needed. Theoretically, one might not need an analytical 2D-functional form of $P(E_i, J_i | E_k, J_k)$, instead the energy transfer parameters can be computed “*on-the-fly*” from first principles using a classical trajectory simulation program,⁴⁹ interfaced with a master equation code that is based on the stochastic method. Because of the above

considerations, current calculations of master-equation kinetics remain semi-empirical, rather than truly ab initio. Nevertheless, it is useful to have an approximate, and expedient, solution of the 2DME to monitor the effects of angular momentum. There are a number of such solutions available in the literature, as mentioned in the Introduction, see also Smith and coworkers,³⁰ Klippenstein and Miller,³² Pilling and coworkers,³³ Venkatesh et al.^{34,35}

Here, we present another approach that could be viewed as a 2DME approach that is carried by solving a set of 1DMEs. For each fixed angular momentum J , we solve the 1DME described in eq. 1 to obtain $k(T,P,J)$, assuming that J does not change in collisions (i.e. a **fixed-J** model). In other words, when the energized adduct collides with the bath gas molecules, the total internal energy (E) is allowed to vary, but the total angular momentum (J) is fixed. This assumption is of course not a particularly well-founded one and is only correct at the low- and high-pressure limits, but not in the fall-off region. However, it is worth noting that this assumption is already tacitly applied in the 1DME case where only the total internal energy (or vibrational energy) is allowed to change during collision. In this work, the total angular momentum J is considered as a conventional parameter (i.e. not a variable) that will be considered in computing expectation values for properties of chemical kinetics. A complete solution of a 2DME, where both E and J are coupled and allowed to vary in collisions (i.e. a fully explicit 2DME), is a considerably more

difficult and involved task, and is well beyond the scope of this work. Although the model outlined in this work is quite simple, practical test cases done by us show that it has considerable promise. Moreover, this technique can easily be implemented in parallel (calculations for different values of J are completely independent), thus it can provide solutions for a wide range of temperature and pressure. Provided that total angular momentum is not altered by collisions (i.e. the **fixed-J** model), the 2DME problem reduces to several 1DMEs, whose solutions are well established. By doing a loop from $J=0$ to a ceiling angular momentum J_c , we solve the 1DME $J_c/\Delta J + 1$ times, where ΔJ is the step size of J . J_c should be chosen in the range of 50 to 500. J_c must be smaller than a maximum angular momentum (J_{\max}) that determines when an intermediate has all of its internal energy in rotation and is consequently unreactive. So, J_{\max} depends on the reaction system and temperature in interest. Finally, the rate constant leading to product(s) can then be computed as an expectation value:

$$\langle k(T, P) \rangle = \frac{\sum_{J=0}^{\infty} k(T, P, J) \times \int_0^{\infty} f(E, J) dE}{\sum_{J=0}^{\infty} \int_0^{\infty} f(E, J) dE} \quad (\text{Eq. 8})$$

It should be mentioned that the fixed-J model, which is similar to the approach used in this paper, was first suggested by Penner and Forst.^{50,51} These authors tested the model on thermally activated dissociations of H_2 and H_2O_2 where collisional energy transfer is the rate-determining step

and found good results. In this work, we have extended this work by adapting the fixed-J model to chemically activated multiple-product, multiple-intermediate reaction systems.

For simplification, the stationary points (transition states and intermediates) on the potential energy surface are assumed to be symmetric tops²⁷ (this is another expedient that can be used with three external rotors), so the rotational energy levels are given by eq. 9. Moreover, three external (rigid) rotors are assumed to be active; thus, they can freely exchange energy with vibrations. Consequently, the quantum states of three rotors can then be convolved with those of vibrations (see eq. 10 or eq. 11).^{8,11,27}

$$E_{rot} = \bar{B}J(J + 1) + (A - \bar{B})K^2 \quad ; \quad \text{with } \bar{B} = \sqrt{B \cdot C} \quad \text{and } |K| \leq J \quad (\text{Eq. 9})$$

$$\rho(E, J)_{rv} = \int_0^E \rho_{vib}(E - E_{rot}) \rho_{rot}(E_{rot}) dE_{rot} \quad (\text{Eq. 10})$$

$$\rho(E, J)_{rv} = \sum_{K=-J}^{K=+J} \rho_{vib}(E - E_{rot}(J, K)) \quad (\text{Eq. 11})$$

Previous studies have demonstrated that eq. 10 is equivalent to eq. 11.²⁷⁻²⁹

The active rotor model, eq. 11, is also named the J-shifting approximation and is often used in quantum dynamic calculations.⁵³⁻⁵⁵

A hybrid model, which is a mixture of active and inactive models, has also been recommended. The hybrid model assumes that the K-rotor (i.e.

1D-rotor) is active while the 2D-rotor is adiabatic.^{7,28,29} In this work, the model assuming three active rotors, eqs. 10 or 11, is used because it is computationally more efficient.

The approach used in this work gives an exact solution at the high-pressure limit, but only a *nearly* exact, converged solution at the low-pressure limit. This is due to the fact that at low-pressure conditions, the actual rate of formation of the unimolecular products is the difference between stabilization from the populations above the barrier (which are dictated by the reactive influx) and collisional reactivation from below the barrier (which requires a full ME solution). This point has been discussed in reversibility relationships some time ago by Smith et al.^{56,57}

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