# Fixed-J Master Equation Model: Parallel Time-Dependent Solution (pTDME)

## MANUAL, pVERSION FEB-1-2023

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**pTDME** is a parallel version of the chemical kinetic program that can be used to solve a fixed-J time-dependent (two-dimensional) master-equation for both *chemically* and *thermally activated* gas-phase reactions in parallel using the deterministic (matrix) method. It is developed, implemented, and maintained by T. L. Nguyen and J. F. Stanton, version Feb-1-2023.

The **pTDME** program can be compiled with OpenMP (or MPI) and it has been tested successfully on the high-performance computer system of the University of Florida (HiPerGator) and on a personal MacBook Pro 2019 (8 cores and 32GB).

In addition to this parallel version, a serial version of the **pTDME** program is also available upon request from the authors.

**Citations for this work should be included:**

1)  J. R. Barker et al. Ann Arbor, Michigan, USA (multiwell.engin.umich.edu), **2023**.
2)  T. L. Nguyen and J. F. Stanton, Pragmatic Solution for a Fully E,J-Master Equation, *J. Phys. Chem. A* **124** (15), 2907-2918 (**2020**).

# Any problems in the use of the pTDME 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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# I.    Input File

The **pTDME** program has a similar input file (named "**pTDME.INP**") as the p**TS** program. So, users may want to refer to the manual of the p**TS** program for further information. Here we briefly describe fourteen lines in "**pTDME.INP**" for a given template (chemically activated) reaction of OH + CO.
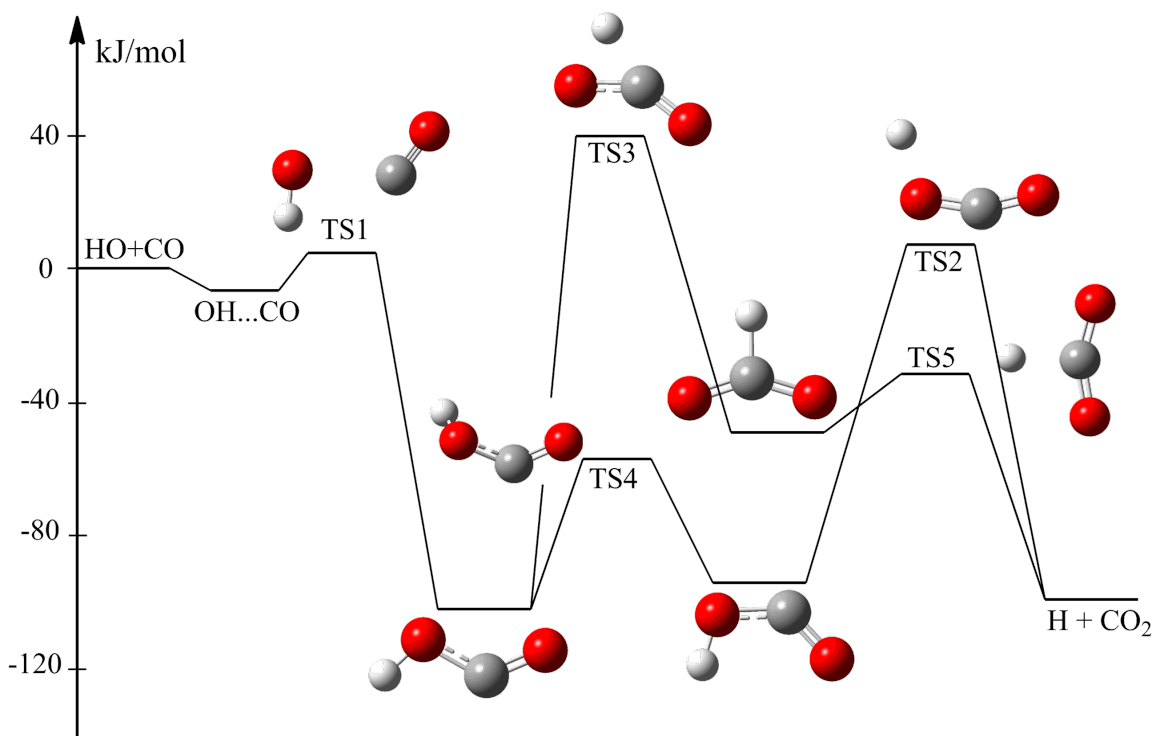


**Figure 1:** Schematic reaction energy profile for the HO + CO → H + CO$_2$ reaction.

**Line 1:** Ceiling (maximum) energy ($cm^{-1}$), energy bin ($cm^{-1}$), **KEYWORD**, guessed/initial eigenvalue ($s^{-1}$, a positive number).

**KEYWORD** must be either "**CAT1**" or "**CAT2**" or "**THERMO**".

#1 "**CAT1**" is used for the chemically activated bimolecular reaction **type-I**, which assumes that an association of OH and CO leading to highly vibrationally excited adduct (e.g. trans-HOCO*), which then carries out unimolecular dissociations (in competition with energy-transfer processes via collisions) to yield various products (e.g. H + $CO_2$) or thermalized HOCO, which is collisionally stabilized.

#2 "**CAT2**" is used for the chemically activated bimolecular reaction **type-II**, which starts with the (pseudo fist-order) decay of OH, assuming that $[CO]_o \gg [OH]_o$, thus [CO] remains almost unchanged during the decay of OH. In this work, $[CO]_o = 10^{15}$ molecules $cm^{-3}$ was selected.

#3 "**THERMO**" is used for the thermally activated unimolecular reaction model, assuming that "initial" reactant has Boltzmann thermal energy distribution before the unimolecular decay (in competition with energy-transfer processes via collisions) occurs.

**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 ($\sigma$ (Å) and $\varepsilon/k_B$ (K)) for bath gas

**Line 5:** Mass (g/mol), Lennard-Jones collision parameters ($\sigma$ (Å) and $\varepsilon/k_B$ (K)) for vibrationally excited intermediates

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

- **$k_\infty(T)$:** Overall (capture) thermal rate constant (in $cm^3$ molecule$^{-1}$ s$^{-1}$) for a bimolecular reaction, for example OH + CO. A value must be input when "**CAT2**" model is used, otherwise set $k_\infty(T) = 1$.

- **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 (RPS stands for Reid-Prausnitz-Sherwood) 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-1**, name of minimum, name file that comprises three rotational constants (cm$^{-1}$), energy of minimum, rotational symmetry number, mirror image, **KEYWORD-2**.

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

**KEYWORD-1** MUST be one of the followings:

- "**CRRKM_HO**": conventional RRKM is used to compute sums and densities of states inside the pTDME program assuming a harmonic oscillator model. A list of vibrational frequencies must be provided (by users) in a file named "name of minimum".

-  "**EXTERNAL**": sums and densities of states are provided (by users) in an external file (named "name of minimum").

**KEYWORD-2** MUST be either "**NLINEAR**" or "**LINEAR**" for non-linear or linear molecule, respectively.

**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-1**, 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, **KEYWORD-2**.

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

**KEYWORD-1** 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 (by users) 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 1D-WKB tunneling correction.

**KEYWORD-2** MUST be either "**NLINEAR**" or "**LINEAR**" for non-linear or linear TS, respectively.

**Line 12:** Keyword-1 and Keyword-2

- Keyword-1: that *MUST* be either "ASYM" or "SYMM"

  "ASYM" stands for an asymmetric relaxation matrix $\mathbb{M}$;

  "SYMM" stands for a symmetric relaxation matrix $\mathbb{M}$.

- Keyword-2: that *MUST* be either "ARPACK" or "LAPACK".

  "ARPACK" is used to obtain chemically significant eigenvalues/eigenfunctions (i.e. CSEs);

  "LAPACK" is used to compute a full set of eigenvalues/eigenfunctions, from which $C_i$(time) can be calculated.

**Line 13:** Keyword-1, Keyword-2

- Keyword-1 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 **pTDME** program.

- Keyword-2 is used to define an entrance TS (e.g. for a bimolecular reaction) that must be either "TIGHT" or "LOOSE". This keyword will be activated as long as Keyword-1 is equal to "NO".

**Line 14:** Beginning-Time, Ending-Time

- "Beginning-Time" is the time to start the reaction simulation;

- "Ending-Time" is time to stop the reaction simulation.

A template "**pTDME.INP**" given below is for the OH + CO $\to$ HOCO* $\to$ H + CO$_2$ reaction:

(Note that trans-HOCO is defined as **1**; cis-HOCO $\equiv$ **2**; HO + CO $\equiv$ **3**; and H + CO$_2$ $\equiv$ **4**. In addition, v.d.W. complex OH—CO, H–CO$_2$, and TS5 are all ignored in the chemical kinetic scheme considered here for simplification).

```
Line 1: 50000., 10., "CAT1", 1.0          !!! 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,HO+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, "NLINEAR"       !!! 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,
"NLINEAR"
Line 9: 3, 'HO + 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, "NLINEAR"      !!! 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,
"NLINEAR"
3, 'EXTERNAL', 'TS3', 'TS3abc', 1 4, 40.03, 1, 1,
"NLINEAR"
4, 'EXTERNAL', 'TS4', 'TS4abc', 1 2, -69.62, 1, 2,
"NLINEAR"

Line 12: 'ASYM', 'LAPACK'        !!!

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: 1.0E-18, 1.0E00  !!! A time to start the
reaction simulation, a time to stop the reaction
simulation.

## II.    Get Compiled and Started

The **pTDME** program has been compiled and tested successfully on a high-performance computer (HPC, the HiPerGator) of the University of Florida and on a personal MacBook Pro 2019 (2.4GHz, 8 cores and 32GB) using gfortran (or ifort) and openMPI. Here we describe how to compile and run the **pTDME** program on these two computer systems. For different computer systems, users must modify "Makefile" and "qsub_file" accordingly.

### II.1) Get started on a HPC (or cluster):

**Step 1:** Copy "Makefile.Cluster" to "Makefile"

**Step 2:** Edit "Makefile";
The **pTDME** program requires gfortran (or ifort), openMPI, and Lapack/Blas libraries available.
Users must provide paths/directions to these libraries in "Makefile".

**Step 3:** Compile the **pTDME** program by typing "make" (or make ALL).
This will give an executable file, named "xptdme".

**Step 4:** Examples are given in the sub-directory "EXAMPLES". There are three files that must be modified before running the **pTDME.**

1) "pTDME.INP": this is the input file of the **pTDME** code. it depends on the reaction under consideration, so it must be created beforehand (see below).

2) "run0.dummy": this is a template SLURM script for the submission; users MUST modify this file accordingly to the "qsub" computer system.

3) "run_P.sh": this C-shell file contains a list of pressures (in the units of Torr, e.g. 1 atm = 760 Torr

and 1 bar = 750 Torr) for the ME simulation, which MUST be input by users.

**Step 5:** To run the **pTDME** code (in user's working directory) under C-shell environment, just type

<span style="color:red">**./run_P.sh (and RETURN/ENTER).**</span>


This command will create all subdirectories associated with pressures that are defined in "run_P.sh". And then, it will automatically submit all jobs to the HPC.

**Step 6:** when the calculations are done, all output files will be generated and copied (back) to these (pressures) subdirectories.

"pTDME.out" includes main results of the pTDME program.
"pTDME_J.out" contains all results at a fixed-J angular momentum value.
"population.i" lists the mole fraction for each (relevant) species as a function of time.
"rate.i" lists the flux rate coefficient for each reaction channel as a function of time.


## II.2) Get started on a MacBook Pro computer:

**Step 1:** Copy "Makefile.Mac" to "Makefile"

**Step 2:** Edit "Makefile";
The **pTDME** program requires gfortran (or ifort) and openMPI installed in advance on a MacBook Pro.
Xcode of Apple (for MacBook Pro 2017 or later) already has Lapack/Blas libraries.

**Step 3:** Compile the **pTDME** program by typing "make" (or make ALL).
This will give an executable file, named "xptdme".

**Step 4:** Examples are given in the sub-directory "EXAMPLES". There are two files that need to be modified before running the **pTDME** code.

1) "pTDME.INP": this is an input file of the **pTDME** code.

2) "run_P.sh": this C-shell file contains a list of pressures, which MUST be input by users.

Note that users must provide a path in "run_P.sh" to call the executable "xptdme".

**Step 5:** To run the **pTDME** code in user's working directory under C-shell environment, just type

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

This command will make all subdirectories associated with pressures that are defined in "run_P.sh".

**Step 6:** all output files will be created in these (pressures) subdirectories when the calculations are done.

"pTDME.out" includes main results of the pTDME program. "pTDME_J.out" contains all results at a fixed-J angular momentum value.
"population.i" lists the mole fraction for each (relevant) species as a function of time.
"rate.i" lists the flux rate coefficient for each reaction channel as a function of time.

## III. Output Files

When the **pTDME** program finishes perfectly, it will create several output files, including "pTDME.out", "pTDME_J.out", "population.i", and "rate.i".