

PCFC QM Subgroup: An introduction to MESS

Mark E. Fuller

Physico-Chemical Fundamentals of Combustion

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- **MESS is the Master Equation System Solver¹, a component of the PAPR suite of chemical kinetics codes**
 - Developers: Y. Georgievskii, C. F. Goldsmith, J. A. Miller, M. P. Burke, and S. J. Klippenstein
 - <https://tcg.cse.anl.gov/papr/codes/mess.html>
- **Conformers on a potential energy surface are connected via transition states**
- **Ab initio calculations provide necessary input information to calculate partition functions and determine rates via transition state theory (TST)**

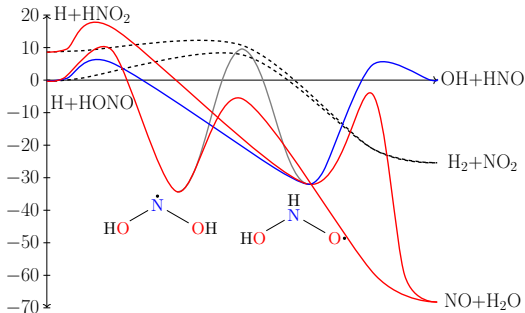
¹Yuri Georgievskii u. a. (2013). "Reformulation and solution of the master equation for multiple-well chemical reactions". In: *The Journal of Physical Chemistry A* 117, S. 12146–12154. DOI: 10.1021/jp4060704.

^aMark E. Fuller und C. Franklin Goldsmith (2019). "On the relative importance of HONO and HNO₂ in low-temperature combustion". In: *Proceedings of the Combustion Institute* 37.1, S. 695–702. DOI: 10.1016/j.proci.2018.06.208.

■ System consists of three kinds of nodes (conformers):

- BIMOLECULAR: a pair of fragments which are lumped together, *e.g.* H+HNO₂
- WELL: a unimolecular intermediate, *e.g.* HONOH
- BARRIER: a transition state (TS) between two wells/bimoleculars

■ Each conformer is described by its geometry and frequencies and (relative) energy



MESS Input File

- **Global section (unnamed header) specifies parameters for solution of the master equation**
- **Specify temperatures, pressures, calculation parameters**
- **Two major choices for calculation method**
 - DIRECT: fuller, more expensive calculations (not so good at low temperature)
 - LOW-EIGENVALUE: assume which eigenvalues are chemical and which are relaxational, numerically cheap, not accurate at high temperatures
- **MODEL definition follows and begins with collision parameters**
- **All conformers are then described to define system**

```

TemperatureList[K]          400.0 450.0 500.0 550.0 600.0 650.0 700.0 750.0 800.0 850.0 900.0 950.0 1000.0 1
PressureList[atm]           0.01 0.1 0.316 1.0 3.16 10.0 31.6 100.0
EnergyStepOverTemperature   .2
ExcessEnergyOverTemperature 30
ModelEnergyLimit[kcal/mol]  400
CalculationMethod            direct #low--eigenvalue #direct
WellCutoff                   10
ChemicalEigenvalueMax        0.2
GlobalCutoff[kcal/mol]      -45.0
Model
  EnergyRelaxation
    Exponential
      Factor[1/cm]           200
      Power                   .85
      ExponentCutoff          15
    End
  CollisionFrequency
    LennardJones
      Epsilons[1/cm]         6.95 285.2
      Sigmas[angstrom]       2.55 5.182
      Masses[amu]             4.0 59
    End
  
```

```
!Bimolecular R1: Reactants H + HNO2
```

```
Bimolecular      hno2      # H+HNO2
Fragment      H
! Current data taken from:
! /gpfs/data/cfgoldsm/cfgoldsm/qchem/gas_phase/h/h/ dft/h_b2plypd3_ccpvtz.log
Atom
  Mass[amu]      1
  ElectronicLevels[1/cm]      1
    0      2
End
Fragment      HNO2
! Current data taken from:
! /gpfs/data/cfgoldsm/mfuller/qchem/noh/n1o2/h1n1o2/hno2/hno2_b2plypd3_ccpvtz.log
RPHO
  Geometry[angstrom]      4
    N      0.000000      0.000000      0.000000
    O      0.000000      0.000000      1.219352
    O      0.955111      0.000000      -0.758013
    H      -0.933369      0.000000      -0.450837

  Core      RigidRotor
  SymmetryFactor      2
End

  Frequencies[1/cm]      6
    784.8  1047.3  1365.3
    1513.7  1643.6  3225.1

  ZeroEnergy[kcal/mol]      0.0
  ElectronicLevels[1/cm]      1
    0      1
End
GroundEnergy[kcal/mol]      8.56
End
```

```
! Well 2: honho
```

```
Well      honho      # HONHO
Species
```

```
! Current data taken from:
```

```
! /gpfs/data/cfgoldsm/mfuller/qchem/noh/n1o2/h2n1o2/honho/honho_b2plypd3_ccpvtz.log
```

```
RRHO
```

```
Geometry [angstrom]      5
N      0.000000      0.000000      0.000000
O      0.000000      0.000000      1.242823
O      1.246970      0.000000      -0.684257
H      -0.604321      0.645919      -0.510082
H      1.844105      -0.334291      0.001465
```

```
Core      RigidRotor
```

```
SymmetryFactor      1
```

```
End
```

```
Rotor      Hindered
```

```
Group      5      # atoms in rotating group excluding the atom on the axis
```

```
Axis      1 3      # rotational axis
```

```
Symmetry      1      # 360/angle of rotation to recover the initial structure
```

```
Potential [kcal/mol]      36      # number of equidistant point on the potential energy curve with
```

```
0.00 0.01 0.08 0.20 0.34 0.49 0.65 0.84 1.06 1.33 1.65 2.03 2.48 2.98 3.54 4.16 4.79 5.41 5.9
6.27 6.36 6.16 5.69 5.05 4.34 3.63 3.00 2.44 1.98 1.58 1.24 0.94 0.66 0.41 0.20 0.06
```

```
End
```

```
Frequencies [1/cm]      8
```

```
544.7 785.8
```

```
956.3 1298.7 1415.2
```

```
1519.8 3406.8 3749.3
```

```
! Torsional frequencies: 279.4
```

```
ZeroEnergy [kcal/mol]      -31.94
```

```
ElectronicLevels [1/cm]      1
```

```
0 2
```

```
End
```

```
!TS abstraction: h+hno2 <=> honho
```

Barrier	B4	hno2	honho	#
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```
! Current data taken from:
```

```
! /gpfs/data/cfgoldsm/mfuller/qchem/noh/n1o2/h2n1o2/ts/ts_h_hno2_to_honho/ts_h_hno2_to_honho_b2plypd3_ccpvt
```

```
RRHO
```

Geometry [angstrom]	5		
N	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.211134
O	0.972148	0.000000	-0.753057
H	-0.921040	0.065743	-0.468641
H	1.786284	1.415784	-0.743167

Core	RigidRotor	
	SymmetryFactor	1
End		

Frequencies [1/cm]	8
220.2	518.6 793.0
1038.6	1355.2 1501.6
1619.2	3235.5
! Imaginary mode: -1352.8	

ZeroEnergy [kcal/mol]	16.16
ElectronicLevels [1/cm]	1
0	2

Tunneling	Eckart
ImaginaryFrequency [1/cm]	1352.8
WellDepth [kcal/mol]	7.60
WellDepth [kcal/mol]	48.10

```
End
End
```

- While you could, it is tedious and error-prone to write input files manually
- The utility program `WRITEMESS` reads a `GAUSSIAN` output (log) file and writes a conformer template
- Optionally, hindered rotors (`GAUSSIAN` log files) and energy from a single-point calculation (`ORCA`, currently) may also be added and written concurrently

Getting Results

- **Assuming everything is installed correctly, job submission on the HPC with slurm is simple: we call MESS on the input file**
 - If we have an input file for a network of bimoleculars, wells, and barriers, then we call MESS on the input file
 - For two bimoleculars connected by a single transition state, we call ABSTRACTION on the input file
- **A log file and output file will be generated by MESS**
- **Output file can be split into three sections:**
 1. System network at the top
 2. Rate tables at each temperature and pressure condition
 3. Rate tables for each species pair
- **The output file requires conversion to a recognized format for inclusion in chemical kinetic mechanisms**

- **A function to fit the output data to pressure-dependent, modified Arrhenius expressions is posted on the MESS webpage,**
`http://tcg.cse.anl.gov/papr/codes/mess/mess_aux/mod_arr.tgz`
- **You will likely need to make some small changes for your specific system, but this will output CHEMKIN-format PLOG fits for all of the conformer pairs**

- **The MESS manual:** `http://tcg.cse.anl.gov/papr/codes/mess/messmanual_3_23_16.pdf`
- **More examples to run and test:**
`http://tcg.cse.anl.gov/papr/codes/mess/MESS_Examples.tgz`

Mark E. Fuller – fuller@pcfc.rwth-aachen.de

Physico-Chemical Fundamentals of Combustion
RWTH Aachen University
Schinkelstr. 8
52062 Aachen

www.pcfc.rwth-aachen.de