PCFC QM Subgroup: An introduction to MESS

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1 Introduction

1.1 What is MESS?

- MESS is the **M**aster **E**quation **S**ystem **S**olver (Publication[1]), 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
  - PAPR: `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)

1.2 $H_2N_1O_2$ Potential Energy Surface

Consider simple PES as example system (Publication[2])

- System consists of three kinds of nodes (conformers):
  - BIMOLECULAR: a pair of fragments which are lumped together, *e.g.* H+HNO_2
  - 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

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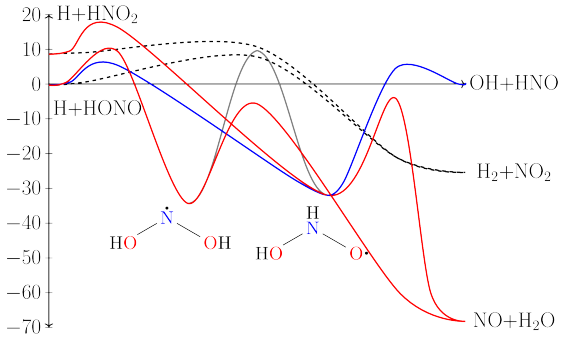

2 MESS Input File

2.1 Input file overview

- 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

2.1.1 Header Information

```
TemperatureList[K]                400.0 450.0 500.0 550.0 600.0 650.0 700.0 750.0
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
```

2.1.2 Bimolecular Input

```
!-----------------------------------------------------
!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.l
      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_ccp
      RRHO
        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
```

2.1.3 Well Input

```
!-----------------------------------------------------
!Well 2: honho
```

```
!-------------------------------------------------
  Well      honho          # HONHO
   Species
      ! Current data taken from:
      !/gpfs/data/cfgoldsm/mfuller/qchem/noh/n1o2/h2n1o2/honho/honho_b2plypd3_c
      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 exclu
          Axis                     1 3            # rotational axis
          Symmetry                 1              # 360/angle of rotation to reco
          Potential[kcal/mol]      36             # number of equidistant point c
 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   5.93   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
```

2.1.4 Barrier Input

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

  Barrier        B4       hno2     honho    #

      ! Current data taken from:
      !/gpfs/data/cfgoldsm/mfuller/qchem/noh/n1o2/h2n1o2/ts/ts_h_hno2_to_honho/
```

```
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
```

2.2 Generating MESS Input Blocks

- 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

3 Getting Results

3.1 Job Submission and Output

- 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

3.2 Fitting the Output

- 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

4 Additional Resources

- 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`

References

[1] Y. Georgievskii, J. A. Miller, M. P. Burke, S. J. Klippenstein, Reformulation and solution of the master equation for multiple-well chemical reactions, The Journal of Physical Chemistry A 117 (2013) 12146–12154. doi:10.1021/jp4060704.

[2] M. E. Fuller, C. F. Goldsmith, On the relative importance of HONO and HNO_2 in low-temperature combustion, Proceedings of the Combustion Institute 37 (1) (2019) 695–702. doi:10.1016/j.proci.2018.06.208.