PCFC QM Subgroup: An introduction to MESS

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Physico-Chemical Fundamentals of Combustion

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What is MESS?

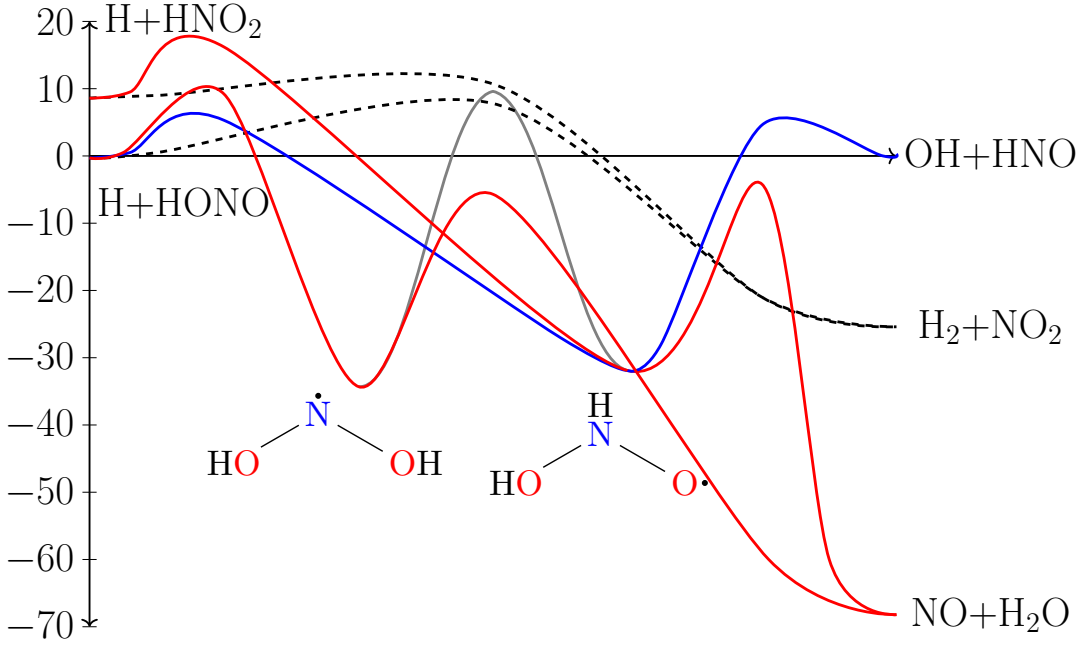
- **MESS is the Master Equation System Solver[1], a component of the PAPR suite of chemical kinetics codes**
  - ➔ Developers: Y. Georgievskii, C. F. Goldsmith, J. A. Miller, M. P. Burke, and S. J. Klippenstein
  - ➔ `https://tcg.cse.anl.gov/papr/codes/mess.html`
- **Conformers on a potential energy 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] Yuri 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.

$H_2N_1O_2$ Potential Energy Surface[a]

[a] Mark E. Fuller und C. Franklin Goldsmith (2019). "On the relative importance of HONO and HNO_2 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+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**



MESS Input File

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**

Header Information

```
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 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.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
      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
```

Well Input

```
!------------------------------------------------------------
!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 potetial 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
```

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/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
```

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

Getting Results

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**

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**

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`

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