Reaction Mechanism Simulator (RMS)

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The Reaction Mechanism Generator (RMG) Software

- Open source software developed by the Green Research Group at MIT and the CoMoChEng Group at Northeastern University.
- Software aims to **predict** the chemistry of a given system by **automatically** determining the relevant species and reactions under the specified conditions.
- Particularly useful for systems involving pyrolysis and combustion chemistry.

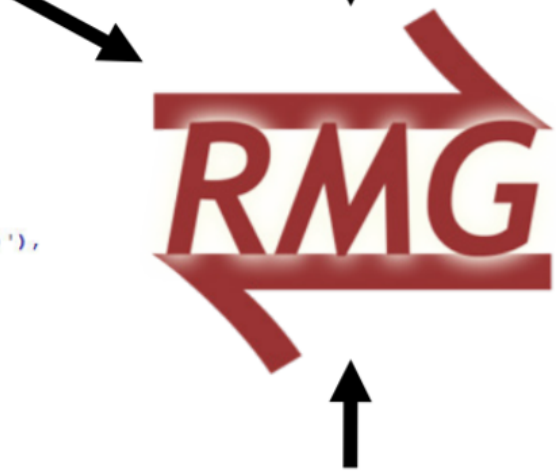
How RMG works

```
entry(
    index = 1,
    label = "H + O2 <=> O + OH",
    degeneracy = 1,
    kinetics = Arrhenius(
        A = (1.0504e+14, 'cm^3/(mol*s)'),
        n = 0,
        Ea = (15310, 'cal/mol'),
        T0 = (1, 'K'),
    ),
)

entry(
    index = 2,
    label = "OH + H2 <=> H + H2O",
    degeneracy = 1,
    kinetics = Arrhenius(
        A = (2.0671e+08, 'cm^3/(mol*s)'),
        n = 1.51,
        Ea = (3437, 'cal/mol'),
        T0 = (1, 'K'),
    ),
)
```

Kinetic and thermodynamic parameters from libraries

Inlet composition and conditions (T, P)



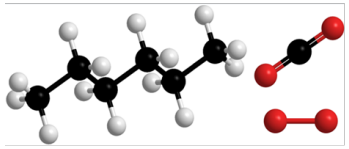
User specified tolerance termination criteria (time and\or conversion)

Kinetic model

reaction DESIGN CHEMKIN

Cantera

Flux-Based Algorithm Overview



Starting species in "core"

Generate all possible reactions

Assign kinetic, thermodynamic, and transport coefficients

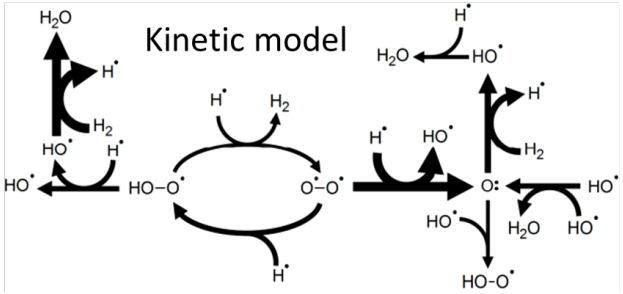
Simulate reactor

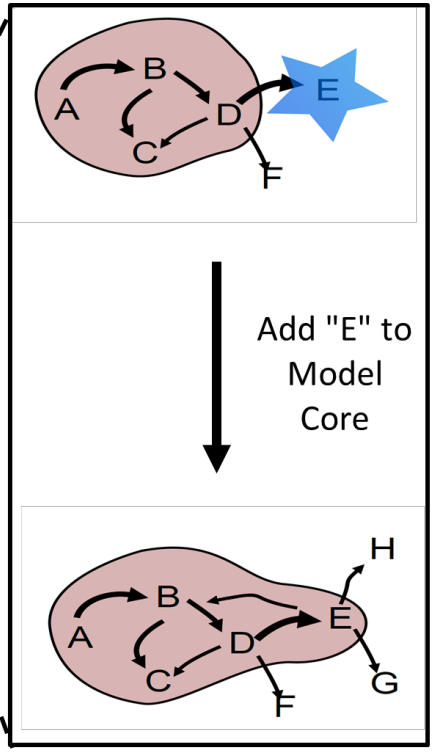
Based on termination criteria, is "core" complete?

No

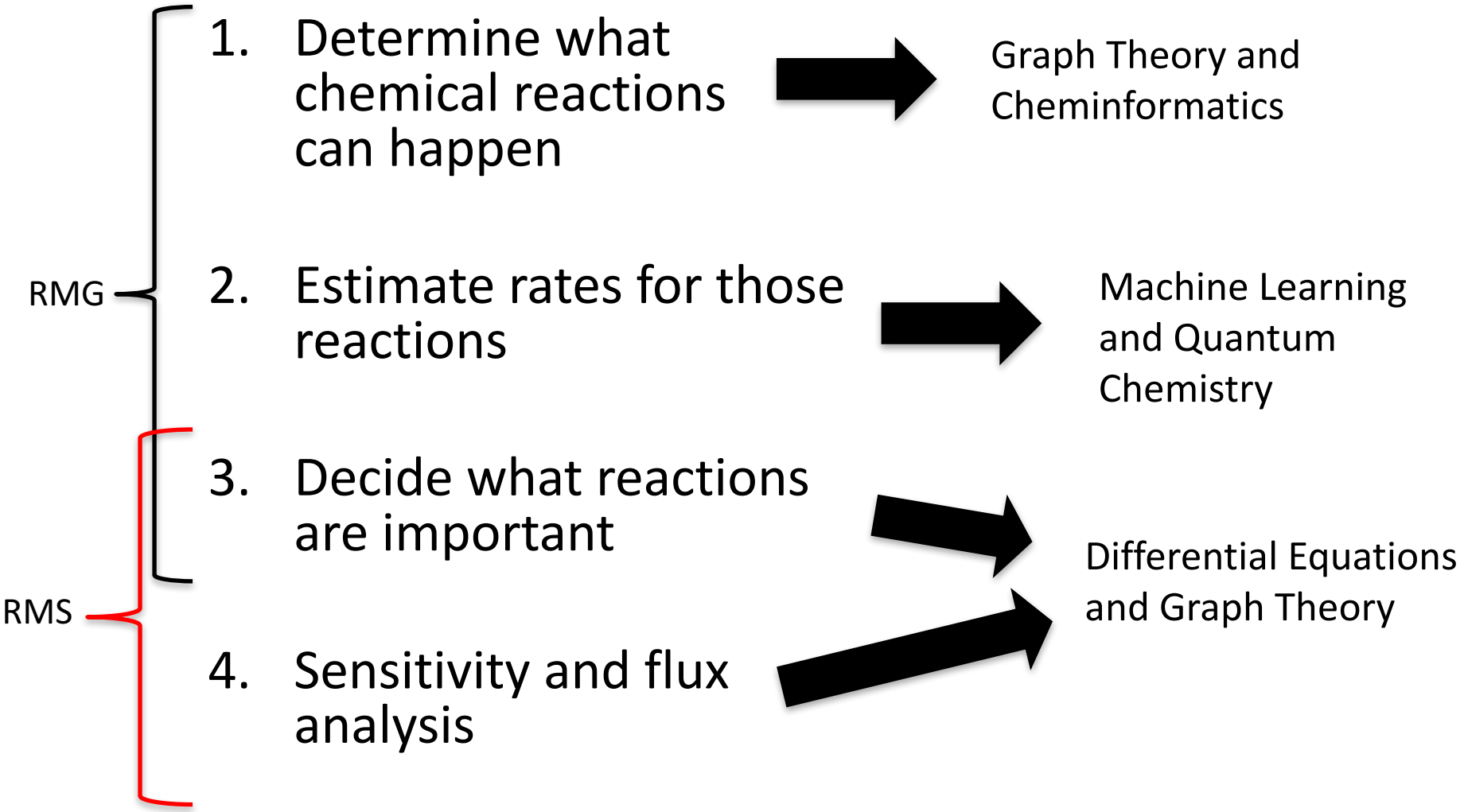
Check fluxes to "edge"; add "edge" species to "core" based on characteristic rate and user tolerance

Yes





Automatic Mechanism Generation



RMS Current Features

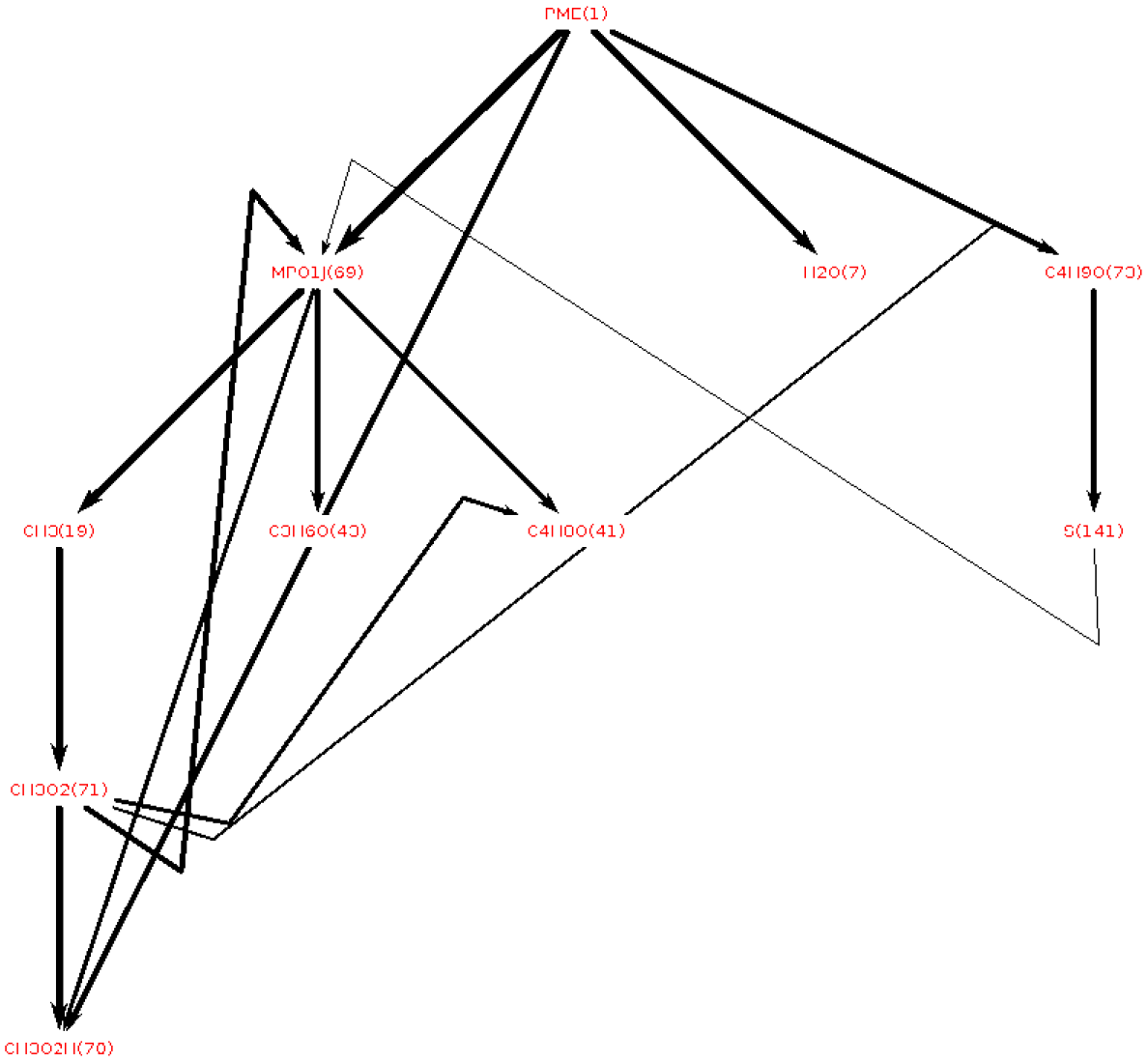
- Extensive and easy to extend rate and thermodynamic property calculators
- Reactors
  - Batch Constant Temperature and Pressure Ideal Gas
  - Batch Constant Temperature and Volume Ideal Dilute Liquid
  - Batch Constant Volume Adiabatic Ideal Gas
  - Ideal Plug Flow Reactor Constant T and P (implicitly)
- Sensitivity analysis for all reactors
- High quality flexible flux diagram generation
- Simulation rate of production analysis and plotting tools
- YAML based input file that is both easy to extend and easy to change

Dominant Other Codes

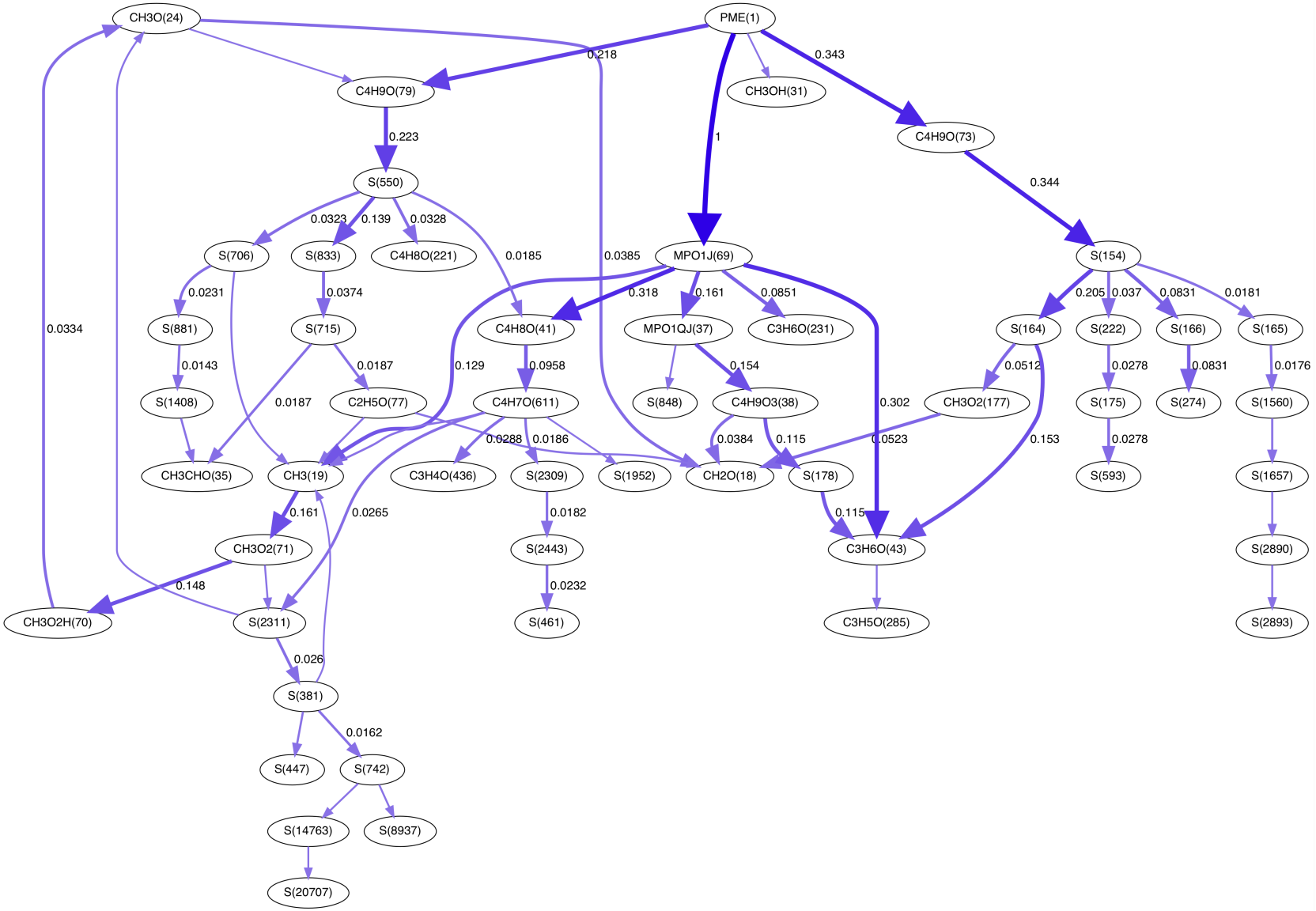
- Chemkin Pro
  - Commercial code
  - Based on a Department of Energy code that first released in 2001
  - Fortran
- Cantera
  - Open source code
  - Development started in 1998 first released in 2003
  - C++

Comparison With Other Codes

Chemkin Flux Diagram

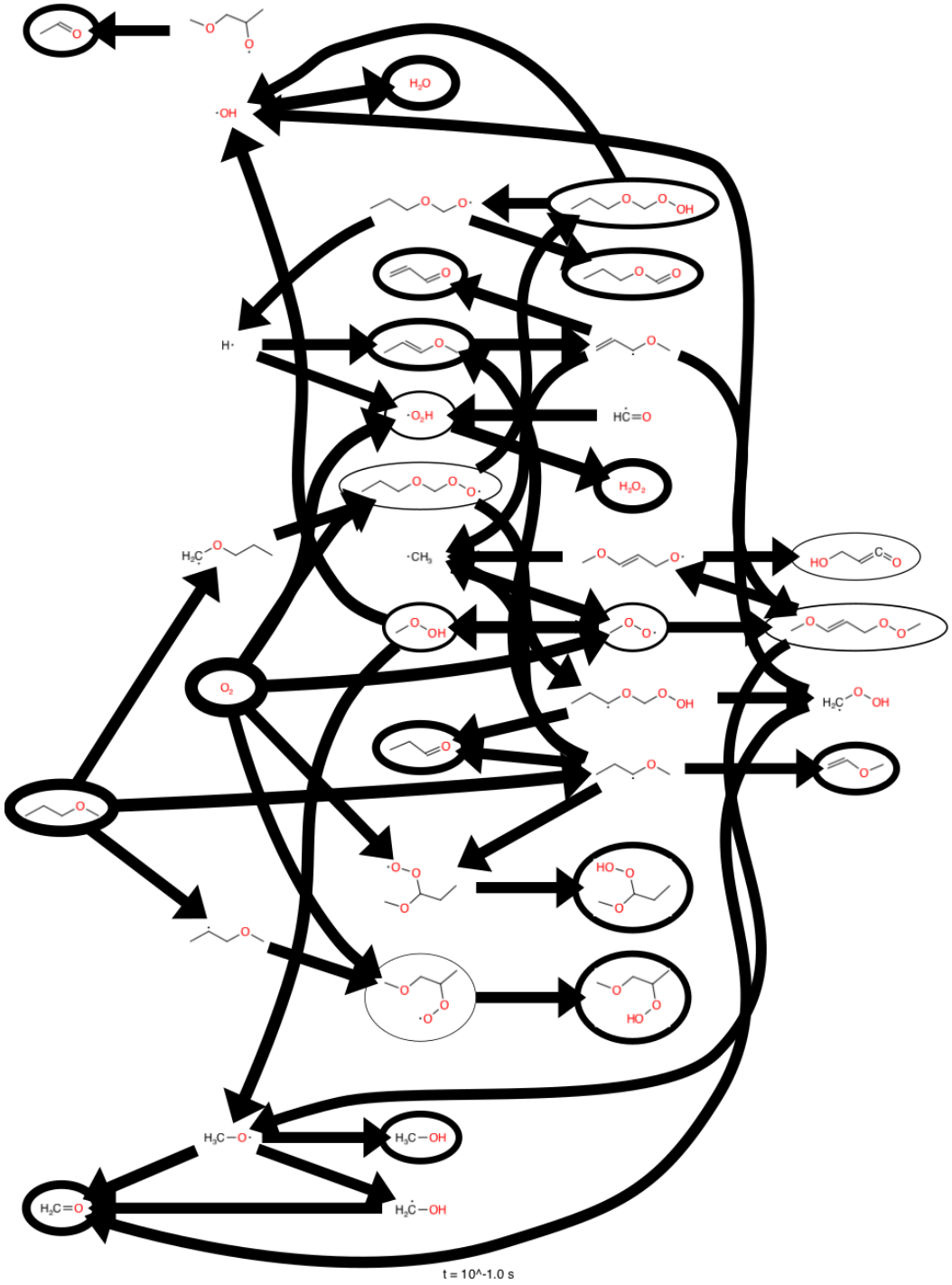


Cantera Flux Diagram



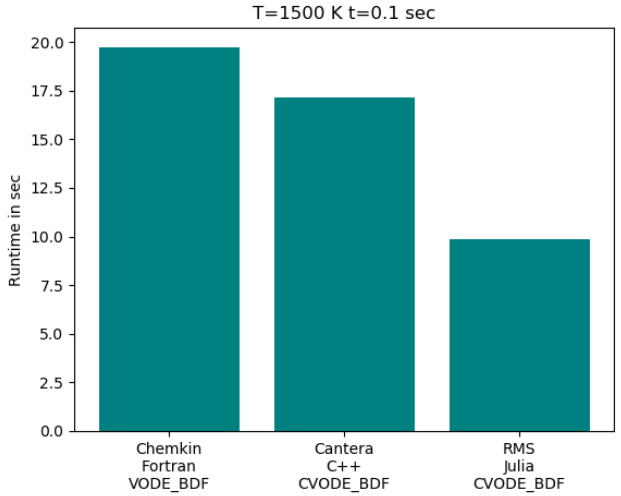
Scale = 0.0084
Reaction path diagram following C

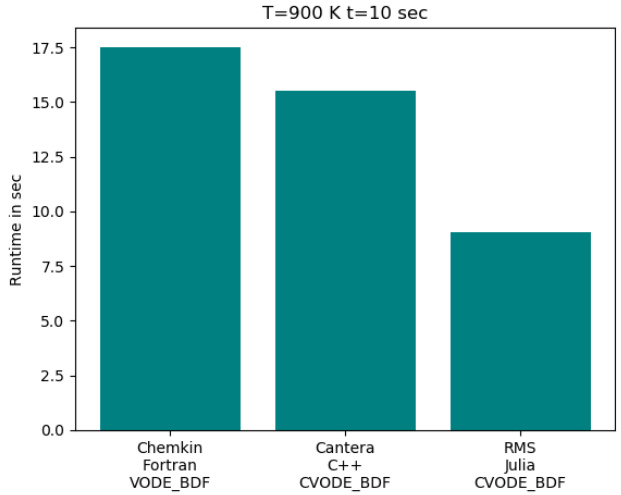
RMS Flux Diagram:

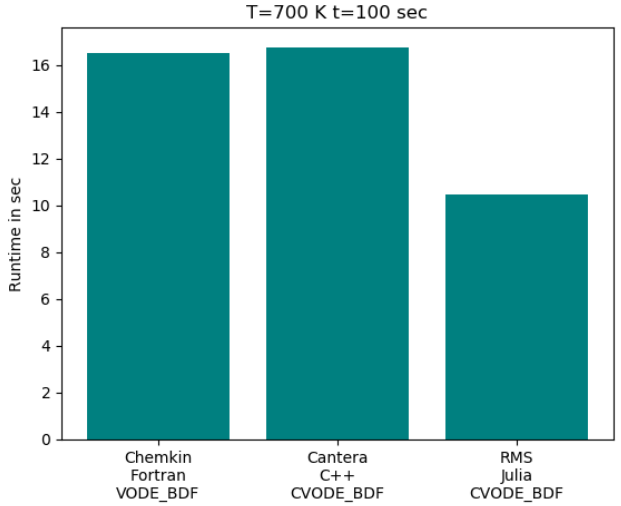


Timings

Methyl Propyl Ether Combustion
403 species, 9712 reactions
Stoichiometric with O2
Constant Temperature and Pressure at 10 bar
Averages of 10 runs







RMS is ~1.7x faster than Cantera or Chemkin

RMS Improvements over Chemkin and Cantera

- More flexible and easier to manipulate input file format
- More informative and and more flexible flux diagram generation
- API is much easier to write
- API is much easier to use
- New objects are automatically recognized by the parser after they are added to the API
- Faster solve
- When analytic jacobians are not available falls back to automatic differentiation using ForwardDiff
- Features
  - Diffusion limitations
  - Constant concentration species

RMS Current Dependencies

- DifferentialEquations
- Parameters
- Unitful
- ForwardDiff
- StaticArrays
- LinearAlgebra
- MathProgBase
- Clp
- PyCall
  - rdkit
  - rmgpy
  - pydot
- Images
- YAML
- SpecialFunctions
- PyPlot
- Test

Codes used in testing

- Chemkin Pro
- Cantera

RMS Future Features

- Analytic Jacobians (mostly done)
- Domains with parameterized temperature, pressure and volume (very soon)
- Interfaces
  - Inlets
  - Outlets
  - Pipes
  - Heat sources
  - Flows and Diffusive Fluxes
- Multi-phase reactors (gas-liquid and catalysis)

Chemkin Input File:

```
S(57646)                H   7C   6O   7     G   100.000  5000.000  930.55      1
 2.60731665E+01 3.01691197E-02-1.35915619E-05 2.56478697E-09-1.78057094E-13    2
-1.06097782E+05-9.07484194E+01-2.85785835E+00 1.54530408E-01-2.14056246E-04    3
 1.46182504E-07-3.87622509E-11-1.00713443E+05 4.67445374E+01                   4

S(57973)                H   7C   6O   7     G   100.000  5000.000 1238.28      1
 3.95079084E+01 6.14018762E-03 1.92299232E-07-2.15997189E-10 1.86253004E-14    2
-1.11956420E+05-1.66880769E+02-3.97484999E+00 1.55544782E-01-1.91623080E-04    3
 1.08886092E-07-2.31858219E-11-1.01873267E+05 4.94232688E+01                   4

S(57974)                H   7C   6O   7     G   100.000  5000.000 1375.33      1
 4.39340203E+01-1.57543668E-03 5.13224088E-06-1.23046003E-09 9.00209141E-14    2
-1.13670663E+05-1.91064481E+02-4.77540591E+00 1.62646391E-01-1.98576227E-04    3
 1.09438211E-07-2.21943286E-11-1.02405589E+05 5.16983689E+01                   4

END



REACTIONS    KCAL/MOLE   MOLES

H(3)+O2(2)=OH(5)+O(4)                                1.040000e+14 0.000     15.286

H2(6)+O(4)=OH(5)+H(3)                                3.818000e+12 0.000     7.948
DUPLICATE
H2(6)+O(4)=OH(5)+H(3)                                8.792000e+14 0.000     19.170
DUPLICATE


OH(5)+H2(6)=H2O(7)+H(3)                              2.160000e+08 1.510     3.430

OH(5)+OH(5)=H2O(7)+O(4)                              3.340000e+04 2.420     -1.930

H2(6)+M=H(3)+H(3)+M                                  4.577e+19 -1.400    104.380
CO2(13)/3.80/ H2O(7)/12.00/ H2(6)/2.50/ He(9)/0.00/ CO(12)/1.90/ Ar(8)/0.00/

H2(6)+Ar(8)=Ar(8)+H(3)+H(3)                          5.840000e+18 -1.100    104.380

H2(6)+He(9)=He(9)+H(3)+H(3)                          5.840000e+18 -1.100    104.380

O(4)+O(4)+M=O2(2)+M                                  6.165e+15 -0.500    0.000
CO2(13)/3.80/ H2O(7)/12.00/ H2(6)/2.50/ He(9)/0.00/ CO(12)/1.90/ Ar(8)/0.00/

Ar(8)+O(4)+O(4)=Ar(8)+O2(2)                          1.886000e+13 0.000     -1.788

He(9)+O(4)+O(4)=He(9)+O2(2)                          1.886000e+13 0.000     -1.788

H(3)+O(4)+M=OH(5)+M                                  4.714e+18 -1.000    0.000
CO2(13)/3.80/ H2O(7)/12.00/ H2(6)/2.50/ He(9)/0.75/ CO(12)/1.90/ Ar(8)/0.75/

H2O(7)+M=OH(5)+H(3)+M                                6.064e+27 -3.322    120.790
CO2(13)/3.80/ H2O(7)/0.00/ H2(6)/3.00/ He(9)/1.10/ O2(2)/1.50/ N2/2.00/ CO(12)/1.90/

H2O(7)+H2O(7)=OH(5)+H2O(7)+H(3)                      1.006000e+26 -2.440    120.180

H(3)+O2(2)(+M)=HO2(10)(+M)                           4.651e+12 0.440     0.000
CO2(13)/3.80/ H2O(7)/14.00/ H2(6)/2.00/ He(9)/0.80/ O2(2)/0.78/ CO(12)/1.90/ Ar(8)/0.67/
    LOW/ 6.366e+20 -1.720    0.525    /
    TROE/ 5.000e-01 1e-30     1e+30    /

HO2(10)+H(3)=H2(6)+O2(2)                             2.750000e+06 2.090     -1.451
```

Cantera Input File:

```
species(name=u'S(117474)',
        atoms='H:5 C:4 O:5',
        thermo=(NASA([100.00, 1355.96],
                     [-9.32154322E-01,  9.24590680E-02, -1.00927691E-04,
                       5.16967734E-08, -1.00098286E-11, -8.51414276E+04,
                       3.42204119E+01]),
                NASA([1355.96, 5000.00],
                     [ 2.58818270E+01,  8.22784427E-03, -2.07207046E-06,
                       3.02738915E-10, -1.96623441E-14, -9.19414117E+04,
                      -1.01567108E+02])),
        transport=gas_transport(geom='nonlinear',
                                diam=7.873,
                                well_depth=664.505))

#-------------------------------------------------------------------------------
# Reaction data
#-------------------------------------------------------------------------------

# Reaction 1
reaction('H(3) + O2(2) <=> O(4) + OH(5)', [1.040000e+14, 0.0, 15.286])

# Reaction 2
reaction('O(4) + H2(6) <=> H(3) + OH(5)', [3.818000e+12, 0.0, 7.948],
         options='duplicate')

# Reaction 3
reaction('O(4) + H2(6) <=> H(3) + OH(5)', [8.792000e+14, 0.0, 19.17],
         options='duplicate')

# Reaction 4
reaction('OH(5) + H2(6) <=> H(3) + H2O(7)', [2.160000e+08, 1.51, 3.43])

# Reaction 5
reaction('OH(5) + OH(5) <=> O(4) + H2O(7)', [3.340000e+04, 2.42, -1.93])

# Reaction 6
three_body_reaction('H2(6) + M <=> H(3) + H(3) + M', [4.577000e+19, -1.4, 104.38],
                    efficiencies='He(9):0.0 CO(12):1.9 H2(6):2.5 CO2(13):3.8 Ar(8):0.0 H2O(7):12.0')

# Reaction 7
reaction('H2(6) + Ar(8) <=> H(3) + H(3) + Ar(8)', [5.840000e+18, -1.1, 104.38])

# Reaction 8
reaction('H2(6) + He(9) <=> H(3) + H(3) + He(9)', [5.840000e+18, -1.1, 104.38])

# Reaction 9
three_body_reaction('O(4) + O(4) + M <=> O2(2) + M', [6.165000e+15, -0.5, 0.0],
                    efficiencies='He(9):0.0 CO(12):1.9 H2(6):2.5 CO2(13):3.8 Ar(8):0.0 H2O(7):12.0')

# Reaction 10
reaction('O(4) + O(4) + Ar(8) <=> Ar(8) + O2(2)', [1.886000e+13, 0.0, -1.788])

# Reaction 11
reaction('O(4) + O(4) + He(9) <=> He(9) + O2(2)', [1.886000e+13, 0.0, -1.788])

# Reaction 12
three_body_reaction('H(3) + O(4) + M <=> OH(5) + M', [4.714000e+18, -1.0, 0.0],
                    efficiencies='He(9):0.75 CO(12):1.9 H2(6):2.5 CO2(13):3.8 Ar(8):0.75 H2O(7):12.0')

# Reaction 13
three_body_reaction('H2O(7) + M <=> H(3) + OH(5) + M', [6.064000e+27, -3.322, 120.79],
```

RMS Input File:

```
  - name: CC(=O)C(=O)C(O)(O[O])C(O)=CO
    smiles: CC(=O)C(=O)C(O)(O[O])C(O)=CO
    thermo:
      polys:
      - Tmax: 1375.33
        Tmin: 100.0
        coefs: [-4.77540591, 0.162646391, -0.000198576227, 1.09438211e-07, -2.21943286e-11,
          -102405.589, 51.6983689]
        type: NASApolynomial
      - Tmax: 5000.0
        Tmin: 1375.33
        coefs: [43.9340203, -0.00157543668, 5.13224088e-06, -1.23046003e-09, 9.00209141e-14,
          -113670.663, -191.064481]
        type: NASApolynomial
      type: NASA
    type: Species
  name: phase
Reactions:
- kinetics: {A: 104000000.00000001, Ea: 63956.623999999996, n: 0.0, type: Arrhenius}
  products: [OH, O]
  reactants: [H, O2]
  type: ElementaryReaction
- kinetics:
    arrs:
    - {A: 3818000.0000000005, Ea: 33254.432, n: 0.0, type: Arrhenius}
    - {A: 879200000.0000001, Ea: 80207.28000000001, n: 0.0, type: Arrhenius}
    type: MultiArrhenius
  products: [OH, H]
  reactants: [H2, O]
  type: ElementaryReaction
- kinetics: {A: 216.00000000000003, Ea: 14351.12, n: 1.51, type: Arrhenius}
  products: [H2O, H]
  reactants: [OH, H2]
  type: ElementaryReaction
- kinetics: {A: 0.033400000000000006, Ea: -8075.12, n: 2.42, type: Arrhenius}
  products: [H2O, O]
  reactants: [OH, OH]
  type: ElementaryReaction
- kinetics:
    arr: {A: 45770000000000.01, Ea: 436725.92, n: -1.4, type: Arrhenius}
    efficiencies: {Ar: 0.0, CO: 1.9, CO2: 3.8, H2: 2.5, H2O: 12.0, He: 0.0}
    type: ThirdBody
  products: [H, H]
  reactants: [H2]
  type: ElementaryReaction
- kinetics: {A: 5840000000000.001, Ea: 436725.92, n: -1.1, type: Arrhenius}
  products: [Ar, H, H]
  reactants: [H2, Ar]
  type: ElementaryReaction
- kinetics: {A: 5840000000000.001, Ea: 436725.92, n: -1.1, type: Arrhenius}
  products: [He, H, H]
  reactants: [H2, He]
  type: ElementaryReaction
- kinetics:
    arr: {A: 6165.000000000001, Ea: 0.0, n: -0.5, type: Arrhenius}
    efficiencies: {Ar: 0.0, CO: 1.9, CO2: 3.8, H2: 2.5, H2O: 12.0, He: 0.0}
    type: ThirdBody
  products: [O2]
  reactants: [O, O]
  type: ElementaryReaction
- kinetics: {A: 18.860000000000003, Ea: -7480.992, n: 0.0, type: Arrhenius}
  products: [Ar, O2]
```