Primer to Building Models in RMG

Nth year RMG Users

27th Sept 2013

Outline

We will walk through main sections of a typical RMG input file:

- Databases
- Reactants and reactor conditions
- Pressure dependence parameters
- Model termination
- Guiding RMG Kinetics

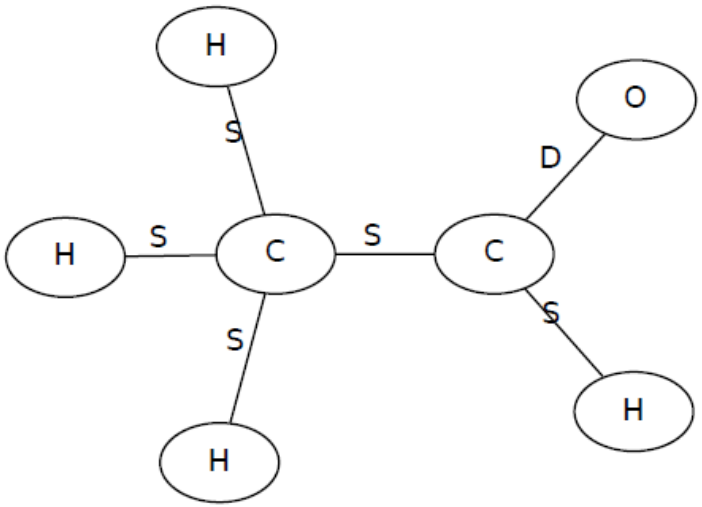
Databases

```
//Example for the oxidation mechanism for nBuOH.

Database: RMG_database

PrimaryThermoLibrary:
Name: RMG-minimal
Location: primaryThermoLibrary
END

PrimaryTransportLibrary:
Name: GRIMech3.0
Location: GRI-Mech3.0
END
```

Reactor Conditions

CH_3CHO

```
1 C 0 {2,S}
2 C 0 {1,S} {3,D}
3 O 0 {2,D}
```



TemperatureModel: Constant (K) 1350
PressureModel: Constant (atm) 1

InitialStatus:

nBuOH (mol/cm3) 0.0338
Reactor conditions
1 C 0 {2,S} 2 C 0 {1,S} {3,S}
3 C 0 {2,S} {4,S}
4 C 0 {3,S} {5,S}
5 O 0 {4,S}

O2 (mol/cm3) 0.4056
1 O 1 {2,S}
2 O 1 {1,S}

END

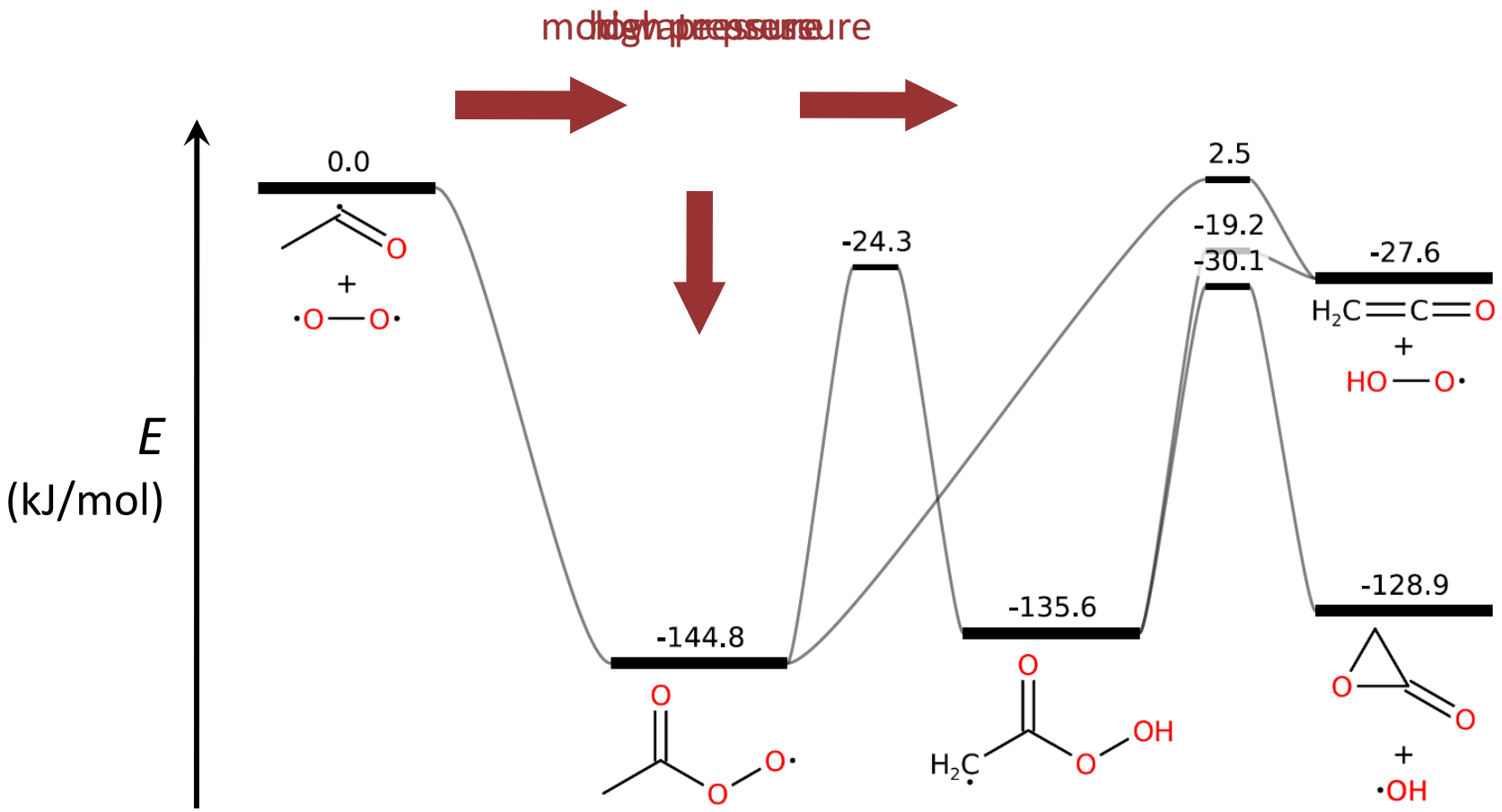
InertGas:
N2 (mol/cm3) 0.5606
Ar (mol/cm3) 0.0

END

Pressure Dependence

```
//Pressure dependence specific parameters
SpectroscopicDataEstimator: FrequencyGroups
PressureDependence: ModifiedStrongCollision

MaxAtomsForPressureDependence: 20
// Size of adduct above which pdep will not be performed

PDepKineticsModel: Chebyshev 6 4
TRange: (K) 290.0 3000.0 8
PRange: (bar) 0.01 100.0 5
```

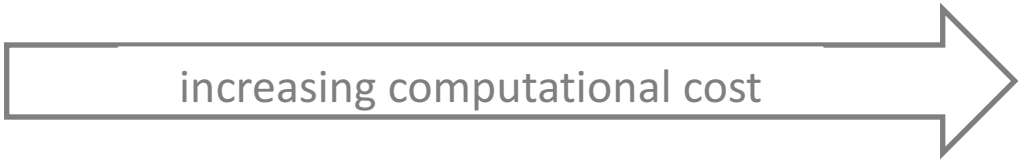
Changing pressure can dramatically change product branching ratios in multi-well networks.



Methods for estimating pressure dependence kinetics in RMG

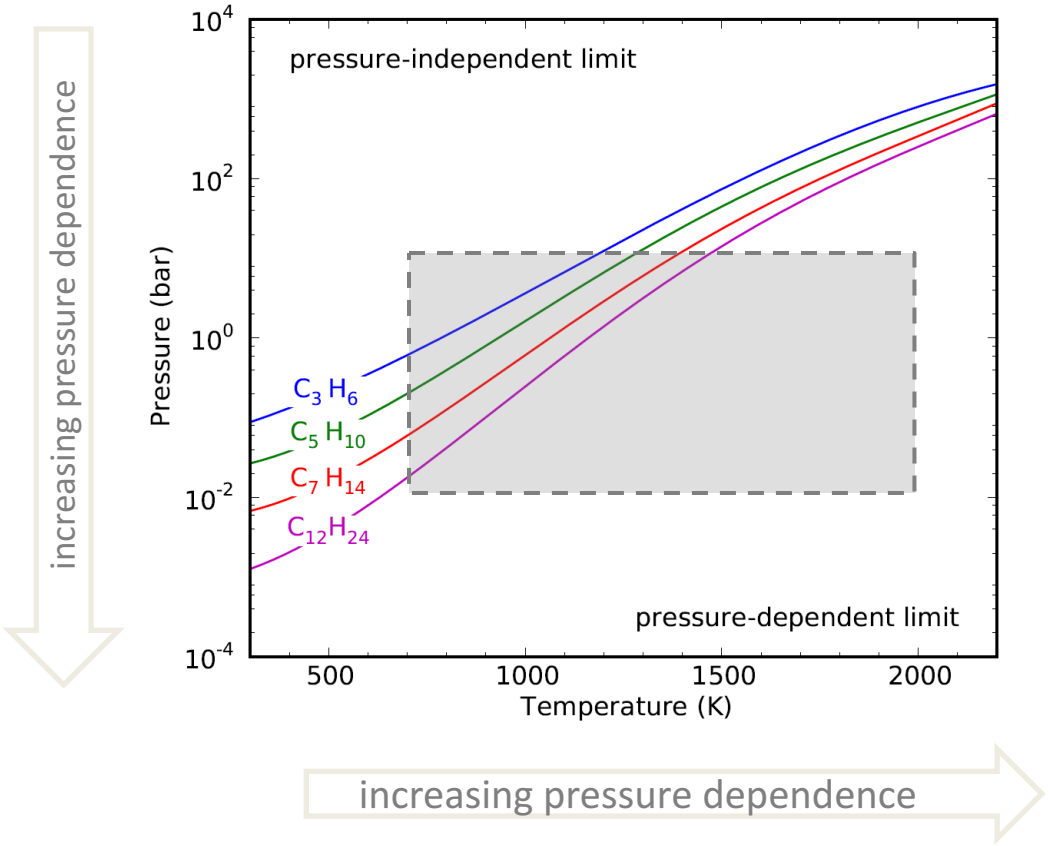
PressureDependence: ModifiedStrongCollision
PressureDependence: ReservoirState

	MSC	RS	CSE
accuracy	okay	good (low T) bad (high T)	very accurate
speed	very fast	fast	very slow
robustness	very robust	robust	not robust



Maximum size for pressure dependent networks

MaxAtomsForPressureDependence: 20



switchover pressure – indicating the onset of pressure dependence as a function of temperature and molecular size

B. M. Wong, D. M. Matheu, and W. H. Green. *J. Phys. Chem. A* **2003**, 107, p. 6206-6211.

Interpolation model for pressure dependent kinetics

PDepKineticsModel: Chebyshev 6 4
PDepKineticsModel: PDepArrhenius

- Option #1: Chebyshev
  - Output is in CHEB parameters no physical significance
  - 6 points in Temperature and 4 points in Pressure has been found to be quite accurate and avoids overfitting
- Option #2: PLOG
  - Easier to understand the output
  - Usually the fit is not very accurate

Termination Criteria

FinishController:
(1)Goal Conversion: nBuOH 0.9
//(1) Goal ReactionTime: 0.1 (sec)
(2) Error Tolerance: 0.1

DynamicSimulator: DASSL
Conversions: AUTO
Atol: 1e-18
Rtol: 1e-8

Guiding RMG Kinetics

```
PrimaryKineticLibrary:
END

ReactionLibrary:
Name: nBuOH
Location: nBuOH
END

SeedMechanism:
Name: GRIMech3.0
Location: GRI-Mech3.0
GenerateReactions: yes
END
```

Reaction Libraries & Seed Mechanisms

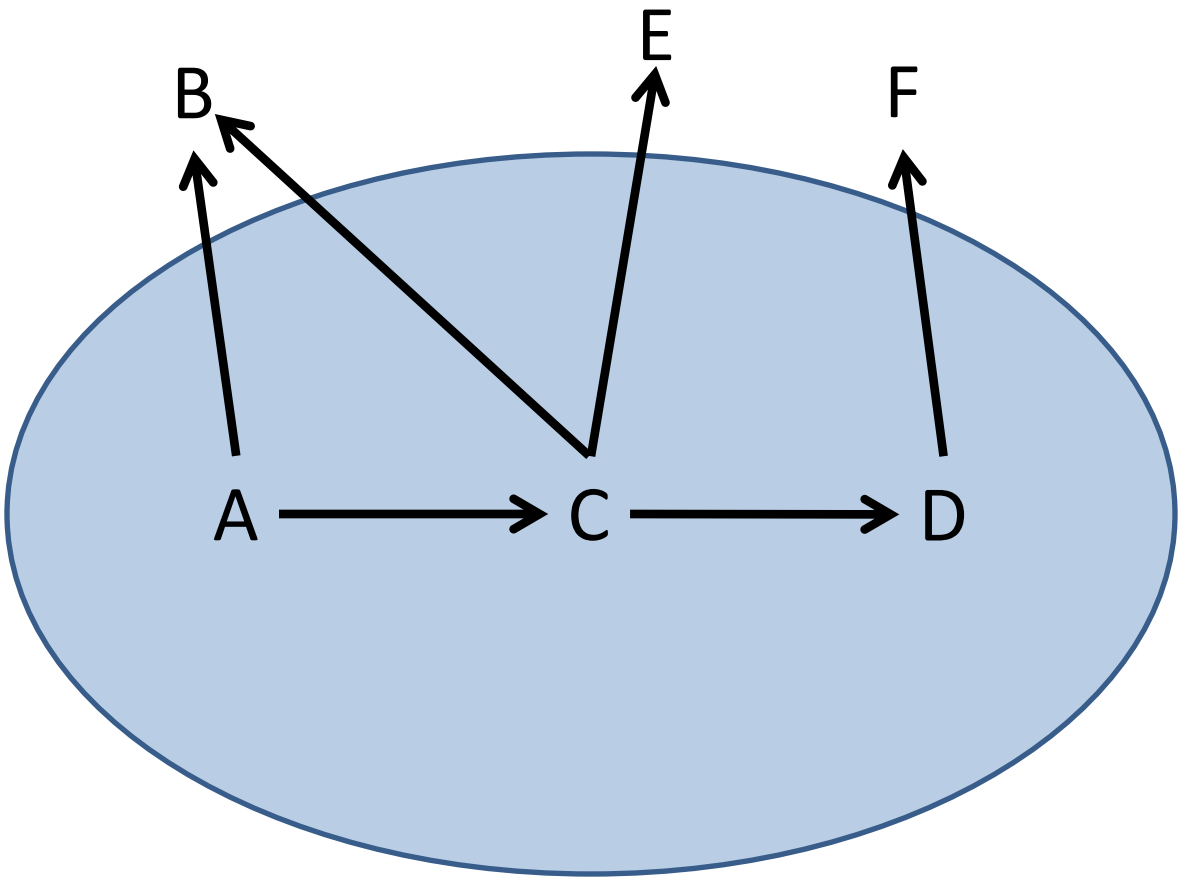
Many are already available in RMG_database/kinetics_libraries

Contain trusted kinetic parameters calculated via experiments or quantum chemistry

Include mechanisms for small and large(-ish) molecules in combustion and pyrolysis

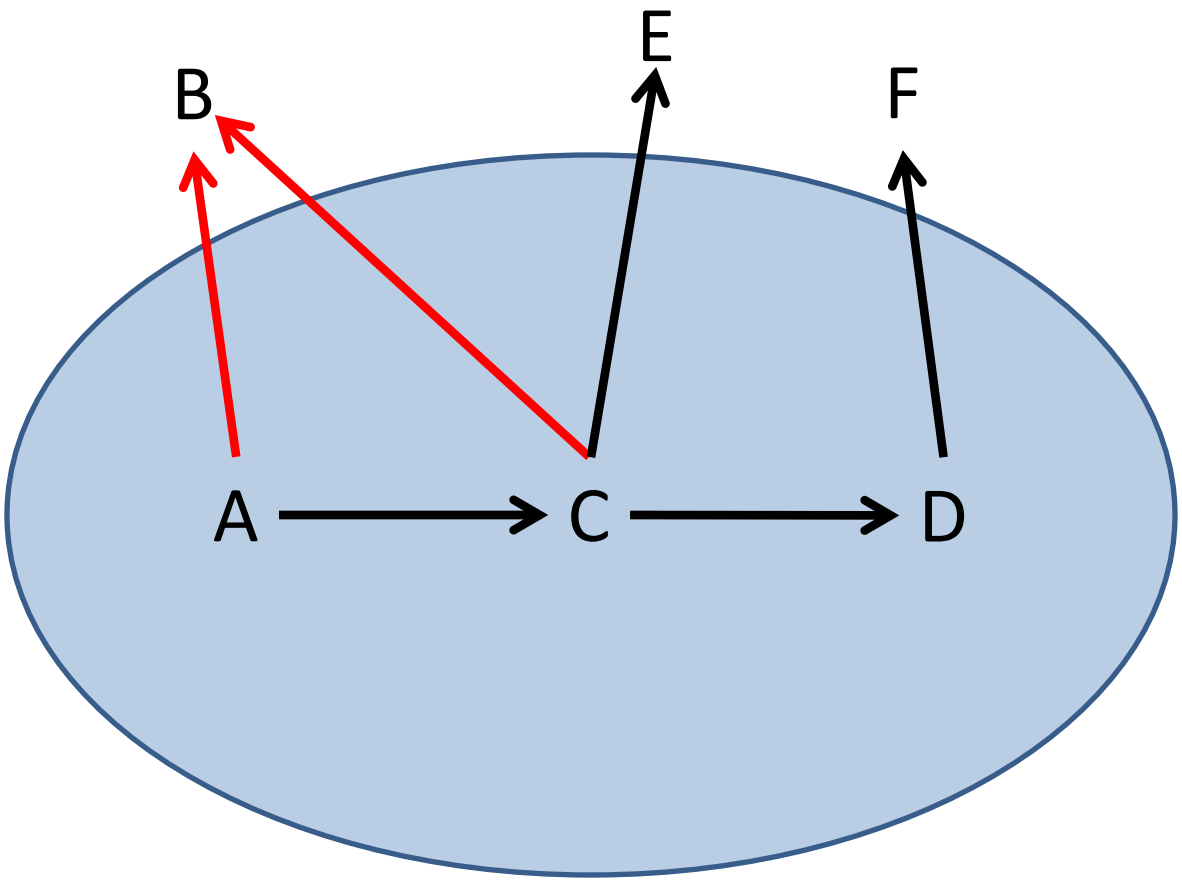
What's the difference?

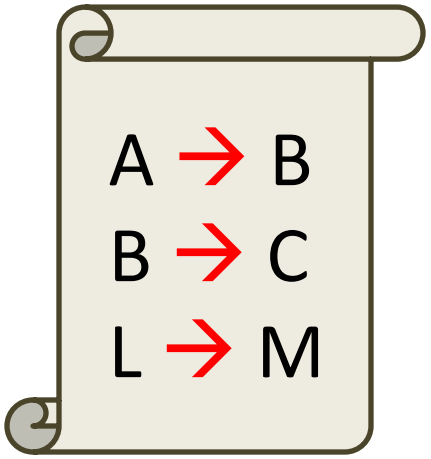
General RMG Algorithm



What's the difference?

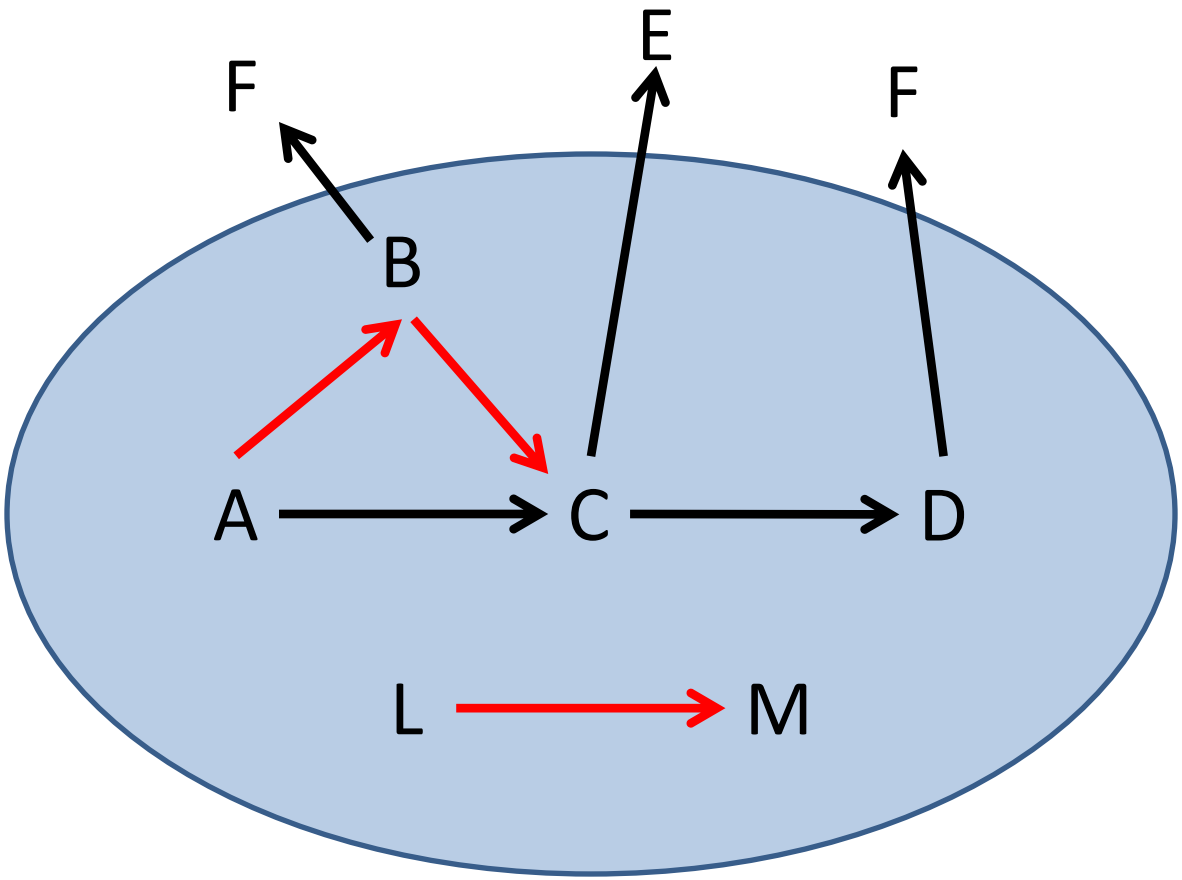
Reaction Library

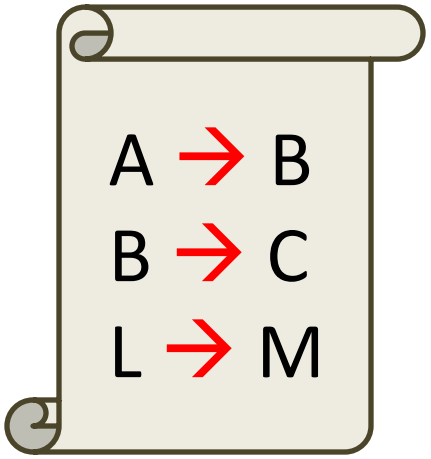




What's the difference?

Seed Mechanism





Reaction Libraries & Seed Mechanisms

In a folder within RMG_database/kinetics_libraries/

Must contain three files

- reactions.txt
- pdepreactions.txt
- species.txt

Sometime in the future: advanced tips for efficient model generation

- Imposing constraints on:
  - Molecular structure of products
  - Allowed chemical reactions
- Guiding RMG model generation:
  - Seed mechanisms
  - Kinetic/thermo libraries
  - Adding species to input file
- Playing around with termination criteria