RMG Documentation

Release 3.2-RC1

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Please also refer to our website for how to cite RMG in published work.

CHAPTER

ONE

INTRODUCTION TO RMG

RMG is an automatic chemical reaction mechanism generator that constructs kinetic models composed of elementary chemical reaction steps using a general understanding of how molecules react. The model parameters (rate constants and reaction thermodynamics) are estimated using a database and the idea that the behavior of functional groups is somewhat independent of the molecule(s) containing them. The RMG database consists of two parts: kinetic rate rules and thermodynamic group additivity values.

RMG is an object-oriented program written in Java, which provides a stable, robust programming architecture that is easily extended, modified, and improved. At its core, RMG relies on two fundamental data structures: graphs and trees. The graphs represent the chemical structures, and the trees represent the databases of thermodynamic and kinetic data. Currently, RMG can generate reaction mechanisms for species involving carbon, hydrogen, and oxygen, and its mechanisms can contain many hundreds of species and tens of thousands of reactions. It is also capable of performing first-order sensitivity analysis on the rate constants and species thermodynamics.

RMG was originally developed by Dr. Jing Song under the guidance of Prof. William Green in the Department of Chemical Engineering at the Massachusetts Institute of Technology. Currently there are several members of the Green group contributing to RMG's ongoing development. A full list of past and present RMG developers can be found on the *Credits* page.

1.1 Changes

Changes in RMG 3.2 include the following:

- The `RMG_Database` folder has been restructured more logically. (*PrimaryReactionLibrary* and *Seed Mechanism* specifications in condition files will need updating)
- It is possible to specify *forbidden structures* in the input file.
- Various error messages have been improved to give more helpful information to the user.

Changes made in RMG 3.1 include the following:

- *PrimaryReactionLibrary* and *PrimaryThermoLibrary* now both behave as reference libraries from which data are taken (in preference to group additivity estimates), when and if the data are needed.
- *Seed Mechanism* allows the mechanism building to start from a seed mechanism, which is included in its entirety before the simulation starts. (This is how *PrimaryReactionLibrary* behaved in previous

releases.)

- New databases: GRIMech 3.0 and PrIMe-recommended thermodynamic values are included
- Support for Chemkin's P-Log format for *k(T,P) reporting* (in addition to Chebyshev format).
- Added additional options for the input file, including:
  - User-specified limits for number of carbon / oxygen / radical per species
  - User-specified Chebyshev fitting options
- Changed many dependent Fortran codes to use standard input and output, rather than writing temporary files to disk.
- Reduced run-to-run variations by standardizing the order of averaging of values in the kinetics trees.

Bug Fixes:

- Corrected inconsistencies in edge flux evaluation for pressure-dependent reactions.
- Corrected an error in inert gas normalization for runs with multiple temperatures/pressures
- Fixed DASPK interface
- Fixed bugs in peroxide (ROOR) frequency estimation
- Fixed a bug in the gauche correction database for alkenes
- Fixed issues with duplicate reactions and with Chebyshev fitting in writing CHEMKIN input files
- More frequent garbage collection

Changes made in RMG 3.0 include the following:

New features:

- Pressure-dependent reaction network generation
- InChI generation
- Graphical user interface for input file generation
- Generation of reaction mechanisms for multiple reaction conditions (T,P)
- Automatic time stepping option
- Updated RMG Viewer and Editor (including database editing tools)

Functionality changes:

- On the first step of mechanism generation, only one species is added, rather than adding all edge species
- Thermodynamics estimates for non-cyclic species incorporate certain steric effects (1,5-interactions and gauche interactions)

Bug fixes:

- Fixed bug in symmetry number generation (previously could be underestimated in certain cases)
- Fixed differential equations to correctly treat cases where total number of moles changes

CHAPTER

TWO

LICENSE

RMG is intended to be an open source program, available to the general public free of charge. The primary RMG code is distributed under the terms of the MIT/X11 License, reproduced below. Although many of RMG's dependencies are also available under compatible open source licenses, there remain a few dependencies with more restrictive licenses. **It is the user's responsibility to ensure these licenses have been obtained.**

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The FAME module for pressure dependent calculations uses LAPACK, which has the following license:

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That's all there is to it!

CHAPTER

THREE

INSTALLING RMG

3.1 License Requirements

RMG is intended to be an open source program, available to the general public free of charge. The primary RMG code is distributed under the terms of the MIT/X11 License. Although many of RMG's dependencies are also available under compatible open source licenses, there remain a few dependencies with *more restrictive licences*. **It is the user's responsibility to ensure these licenses have been obtained.**

3.2 Installation of Binary Package

Multiple binary releases are available from the RMG website, including Windows 32-bit and Linux x86. The binary packages provides all of the executables necessary for a functional RMG, although some advanced features require additional third-party applications. To install the binary packages, follow steps 1-3 in the source section for your operating system (*Linux Installation* or *Windows Installation*).

A Windows installer is also provided. The user has the option of installing all or part of the binaries, source, documentation, and examples. The installer will automatically set the `RMG` system variable to the installation directory.

Whether you install a binary or a source package, you will need:

The Java SE Runtime Environment (JRE), version 6. This is available from http://java.sun.com/javase/downloads/index.jsp.

To generate InChIs and to convert from InChIs/.mol files to adjacency lists you will need:

The IUPAC International Chemical Identifier InChI version 1 (software version 1.01). This is available from http://www.iupac.org/inchi/download/index.html

Additional information about the advanced RMG features and the third-party software required to install them can be found in the following section.

3.3 Compiling RMG from Source

3.3.1 Compilation Prerequisites

To build a functional version of RMG from source you will need the following:

The Java SE Development Kit (JDK), version 6. This is available from http://java.sun.com/javase/downloads/index.jsp.

The Differential Algebraic System Solver (DASSL). This is available in the public domain from http://www.cs.ucsb.edu/~cse/software.html.

A Fortran 90 compiler. We recommend the free g95 compiler, available from http://www.g95.org/.

A Fortran 77 compiler. The g95 compiler can successfully build the Fortran 77 source code as well.

The Basic Linear Algebra Subprograms (BLAS). This is present in most Linux distributions, and is also available from http://www.netlib.org/blas/. Although only the BLAS source code is required, we recommend installing the full package if possible.

The Linear Algebra PACKage (LAPACK). This is present in most Linux distributions, and is also available from http://www.netlib.org/lapack/. Although only the LAPACK source code is required, we recommend installing the full package if possible.

Although not required, we also recommend that you obtain:

GNU make. This controls the generation of Fortran executables, and is present in most Linux distributions. More information can be found at http://www.gnu.org/software/make/.

Apache Ant. This controls the generation of Java executables. More information can be found at http://ant.apache.org/.

To generate InChIs and to convert from InChIs/.mol files to adjacency lists you will need:

The IUPAC International Chemical Identifier InChI version 1 (software version 1.01). This is available from http://www.iupac.org/inchi/download/index.html

3.3.2 Linux Installation

To install RMG on a Linux computer:

1. Create the directory in which you want to install RMG. For the purposes of this document, we will set the directory to `/usr/local/rmg`. Depending on where you choose to install RMG, you may need superuser privileges.

   ```
   $ mkdir /usr/local/rmg
   ```

2. Set the RMG environment variable as the directory created in the first step. In a bash shell you would type, for our example,

   ```
   $ export RMG=/usr/local/rmg
   ```

In a C shell you would type, for our example,

```
$ setenv RMG /usr/local/rmg
```

To avoid typing this line each time, append it to your `~/.bashrc` (bash shell) or `~/.cshrc` (C shell) file.

1. Obtain the source code (See *Download*). Download the file `rmg-3.2-linux-i386.tar.gz` or `rmg-3.2-source.tar.gz`, ungzip and untar it, and move its contents to the `$RMG` directory.

```
$ tar -xvzf rmg-3.2-source.tar.gz
$ mv rmg3/* $RMG
```

Step 4 is only required if you are working with the source package. Binary packages are available for several platforms and will already contain the compiled executables.

1. Compile the programs. If you are working with the source package, you will need to compile RMG and its supporting Fortran programs. To do this, change to the directory `$RMG` and execute the make-file. The make script will compile four programs: fame, frankie, DASSL, and GATPFit. It will then call the ant build script to compile RMG itself.

```
$ cd $RMG
$ make
```

If you only wish to compile the RMG Java code, you can do so by typing:

```
$ cd $RMG
$ ant jar
```

At this stage you will have a functional version of RMG. The remaining steps are only required to enable some advanced features.

The next few steps are required only if you want RMG to be able to generate InChIs for the species present in the reaction mechanism.

1. Download the InChI version 1 (software version 1.01) source code and Application Program Interface (API).
2. Change to the `InChI-1-API/cInChI/gcc_makefile` directory and execute the makefile. Copy the resulting executable `cInChI-1.exe` to the `$RMG/software/InChI` folder.

```
$ cd InChI-1-API/cInChI/gcc_makefile
$ make
$ cp cInChI-1 $RMG/software/InChI
```

You are now ready to generate InChIs in RMG.

3.3.3 Windows Installation

To install RMG on a Windows computer:

1. Create the directory in which you want to install RMG. Depending on where you choose to install RMG, you may need administrator privileges.
2. Set the RMG environment variable as the directory created in the first step.
   - Go to `Start --> Control Panel --> System` (may need to switch to Classic Control Panel view). Click on the `Advanced` tab, then click on `Environment Variables`.
   - In the lower half of the `Environment Variables` window (System variables), click `New`.
   - In the `New System Variable` window, in the `Variable` name field, type `RMG`. In the `Variable` value field, type the directory in which RMG was installed.
   - Click OK twice to confirm the change.
3. Obtain the source code (See *Download*). Download the file `rmg-3.2-win32-i386.zip` or `rmg-3.2-source.tar.gz`, decompress it, and move its contents to the `%RMG%` directory.

Steps 4 and 5 are only required if you are working with the source package. Binary packages are available for several platforms and will already contain the compiled executables.

1. Obtain BLAS and LAPACK DLL files. You can create these yourself by downloading the BLAS and LAPACK sources, or you can download them from our GitHub downloads page.
2. Compile the programs. If you are working with the source package, you will need to compile RMG and its supporting Fortran programs. The easiest way to do the latter is to execute the file `make.bat` in the `%rmg%` directory. The batch script does not compile the RMG source; for this you will need ant.

The next few steps are required only if you want RMG to be able to generate InChIs for the species present in the reaction mechanism.

1. Download the InChI version 1 (software version 1.01) source code and Application Program Interface (API) from IUPAC and unzip the file. Navigate to the `InChI-1-API\cInChI\vc6_project\Release` folder. Copy the executable file `cInChI-1.exe` and paste it in the `"%rmg%"\software\InChI` folder.

You are now ready to generate InChIs in RMG.

3.4 RMG Viewer/Editor (RMGVE) Installation

The RMGVE is an accompanying software which can be used for viewing the database of RMG and also the models generated by RMG. The RMGVE is present along with RMG in the `$RMG/RMGVE` directory and need not be downloaded separately. To run the RMGVE just go to the `$RMG/RMGVE` directory and execute `RMGVE 20080101.bat` on the command line. The RMGVE directly reads the RMG database `$RMG/database/RMG_database` which includes the thermo data and the kinetics data. Please refer to *Using the RMGVE* to see how to modify the RMG database.

3.5 Installation of Dependencies for 3D-geometry-based Thermodynamic Property Calculation

Several dependencies are required to use 3D-geometry-based thermodynamic property calculation features of RMG. These include (recommended versions in parentheses):

1. Python (2.x, with x=5 or higher) http://www.python.org/
2. cclib (see below)
3. RDKit (Q2 2009 or later) http://rdkit.org/
4. OpenBabel (2.2.0 or later) http://openbabel.org
5. InChI (1.02beta or 1.03) http://www.iupac.org/inchi/download/index.html
6. SYMMETRY (v. 1.15 or later) http://www.cobalt.chem.ucalgary.ca/ps/symmetry/ (from Serguei Patchkovskii at the University of Calgary)
7. GAUSSIAN03 and/or MOPAC2009 http://www.gaussian.com/ and http://openmopac.net/downloads.html

With the exception of GAUSSIAN03 and MOPAC2009, all of the above may be obtained freely and are open-source. In the case of MOPAC2009, the software may be obtained freely for academic, not-for-profit use.

Below are some notes for each of these and instructions on getting them to work properly with RMG:

Python You should add the Python installation directory to the PATH environment variable such that typing "python" at the command-line brings up the Python prompt. NOTE: This will probably need to be done manually.

cclib Modified portions of the source code for cclib 1.0 (http://cclib.sourceforge.net/) are included in the /source/cclib/ directory (licensed under LGPL 2.1). No action should be required on the part of the user.

RDKit The typical installation process for RDKit should set the RDBASE environment variable and no further action on the part of the user should be required. Note: If installing from the Windows binaries, you will also need to install numpy and set environment variables as described at http://code.google.com/p/rdkit/wiki/InstallingOnWindows .

OpenBabel The OpenBabel installation directory (e.g. C:Program FilesOpenBabel-2.2.0) should be added to the PATH environment variable such that typing "babel" at the command-line produces output (including version information) from OpenBabel. This should be done automatically by the OpenBabel installer, and no manual intervention should be required.

InChI Installation of InChI is described above. The InChI executable should be placed in the /bin/ RMG directory.

SYMMETRY For Windows, it is recommended that the compiled .exe file available from http://www.cobalt.chem.ucalgary.ca/ps/symmetry/ (via symmdos.zip) be used. This file should be copied into RMG's /bin/ directory. On other platforms, you must compile the SYMMETRY.EXE executable yourself and place the executable in RMG's /bin/ directory.

MOPAC2009 The environment variable MOPAC_LICENSE should be set (e.g. c:UsersUser1DocumentsMOPAC). This should be done automatically by the MOPAC installer, and no manual intervention should be required.

GAUSSIAN03 Add the GAUSSIAN03 directory (e.g. "c:/G03W/") to the PATH environment variable. NOTE: This will typically need to be done manually.

CHAPTER

FOUR

CREATING A CONDITION FILE MANUALLY

To run RMG, you must specify the initial conditions and the model generation parameters, all of which are contained in a single file, `condition.txt`. The file `condition.txt` can be located in any directory, although it is advised that you create a special directory for RMG simulations, since each `condition.txt` creates its own subdirectories.

The `condition.txt` file should specify the following conditions, in order:

1. The main *Database*
2. Any *restrictions* on the number of atoms / radicals for all generated species
3. The name and location of all *Primary Transport Libraries*
4. The name and location of all *Primary Thermodynamic Libraries*
5. Optionally, some additional *forbidden structures*
6. The *initial temperature and pressure* of the system
7. The *maximum number* of carbons, oxygens, and radicals any one species may have
8. Whether to generate an *IUPAC International Chemical Identifier (InChI)* for each species
9. The name, concentration, and chemical structure of the *reactants*
10. The specification and concentration of the *inert gas(es)*
11. The method to use to estimate *spectroscopic data* for each species
12. The *Pressure dependence* model
13. The *finish controller*
14. The *dynamic simulator*
15. *Sensitivity analysis* settings
16. The name and location of all *Primary Kinetic Libraries*
17. The name and location of all *Reaction Libraries*
18. The name and location of all *Seed Mechanisms*

19. The *units* for the Arrhenius parameters A and Ea (to be reported in the generated chem.inp file)

The name `condition.txt` is variable. As you'll see in Section *Running RMG from the Command Line in Linux*, you can change the name of the initialization file, so long as it remains a `.txt` file.

4.1 Database

In the main RMG directory is a directory of databases: `$RMG/databases/`. By default, there is one directory within the directory of databases: `$RMG/databases/RMG_database`. It is possible, however, to create multiple databases. For example, you can copy the entire contents of the default database into a new database, `$RMG/databases/my_database`, and change some of the values. Unless you have created your own databases, the Database setting should be left at the default value:

```
Database: RMG_database
```

4.2 Species Restrictions

By default, RMG will allow no more than 30 carbon atoms in any given species (other such default restrictions are: no more than 10 oxygen atoms, no more than 10 radicals, no more than 100 heavy-atoms, etc.). If you would like to change the default settings, the syntax is as follows

```
MaxCarbonNumberPerSpecies: 100
MaxOxygenNumberPerSpecies: 30
MaxRadicalNumberPerSpecies: 10
MaxSulfurNumberPerSpecies: 10
MaxSiliconNumberPerSpecies: 10
MaxHeavyAtomPerSpecies: 100
```

A "Heavy Atom" is defined in RMG as a non-hydrogen atom. Each of these fields is optional; the default values for all fields are listed here.

Changing the default values of these fields, in particular, lowering the maximum value per species, may help you if your simulations are running out of memory. Also, changing the default settings of these fields could be beneficial if you are only concerned with the decomposition of the initial species.

4.3 Primary Thermo Library

By default, RMG will calculate the thermodynamic properties of the species from Benson additivity formulas. In general, the group-additivity results are suitably accurate. However, if you would like to override the default settings, you may specify the thermodynamic properties of species in the primaryThermoLibrary. When a species is specified in the primaryThermoLibrary, RMG will automatically use those thermodynamic properties instead of generating them from Benson's formulas. Multiple libraries may be created, if so desired. The order in which the primary thermo libraries are specified is important: If a species appears in multiple primary thermo libraries, the first instance will be used.

Please see Section *Editing the Thermodynamic Database* for details on editing the primary thermo library. In general, it is best to leave the PrimaryThermoLibrary set to its default value. In particular, the thermodynamic properties for H and H2 must be specified in one of the primary thermo libraries as they cannot be estimated by Benson's method.

In addition to the default library, RMG comes with the thermodynamic properties of the species in the GRI-Mech 3.0 mechanism [GRIMech3.0].

This library is located in the `$RMG/databases/RMG_database/thermo_libraries` directory. All "Locations" for the PrimaryThermoLibrary field must be with respect to the `$RMG/databases/RMG_database/thermo_libraries` directory.:

```
PrimaryThermoLibrary:
Name: Default
Location: primaryThermoLibrary
Name: GRI-Mech 3.0
Location: GRI-Mech3.0
END
```

4.4 Primary Transport Library

By default, RMG will estiamte the transport properties (Lennard-Jones sigma and epsilon parameters) of a species from empirical correlations described by Tee et al. [Tee]; these correlations are functions of the acentric factor, the critical temperature, and the critical pressure. The acentric factor is estimated using the empirical correlation described by Lee et al. [Lee], which itself is a function of the critical pressure, the critical temperature, and the boiling temperature. The critical properties and boiling point are estimated using the Joback group-additivity scheme [Joback], [Reid].

If you would like to override the default settings, you may specify the transport properties of species in the PrimaryTransportLibrary. Similar to the PrimaryThermoLibrary, RMG will automatically use those transport properties instead of estimating them using the methods described above. Multiple libraries may be created, if so desired. The order in which the primary transport libraries are specified is important: If a species appears in multiple primary transport libraries, the first instance will be used.

RMG comes with the transport properties of the species in the GRI-Mech 3.0 mechanism [GRIMech3.0]. This library is located in the `$RMG/databases/RMG_database/transport_libraries` directory. All "Locations" for the PrimaryTransportLibrary field must be with respect to the `$RMG/databases/RMG_database/transport_libraries` directory.

```
PrimaryTransportLibrary:
Name: GRI-Mech 3.0
Location: GRI-Mech3.0
END
```

4.5 Forbidden Structures

It is possible, though not necessary, to specify additional forbidden structures in the condition file. This section should appear after the PrimaryThermoLibrary section. Each adjacency list can be a species, as described in the *Reactants* section, but can contain *wildcards* as described in the *Thermo Database and Adjacency List Notation* section. For example:

```
ForbiddenStructures:
AdjacentBiradicalCs
1 C 1 {2,S}
2 C 1 {1,S}

AdjacentBiradicalCd
1 C 1 {2,D}
2 C 1 {1,D}

END
```

Note that each adjacency list must be followed by an empty line, and that the section must end (after an empty line) with the word *END*.

4.6 Initial Conditions

The next item in the initialization file is the initial temperature and pressure. Currently, RMG can only model constant temperature and pressure systems. Future versions will allow for variable temperature and pressure. Please note that the temperature and pressure must be accompanied by a unit (in parentheses). Suitable temperature units are: K, F, and C. Suitable pressure units are: atm, torr, pa, and bar. The following example assumes that the system begins at 600 Kelvin and 200 atmospheres:

```
TemperatureModel: Constant (K) 600
PressureModel: Constant (atm) 200
```

You may also list multiple temperature and pressure conditions, as the example below shows:

```
TemperatureModel: Constant (K) 600 700 800 900
PressureModel: Constant (atm) 1 200
```

For cases in which multiple temperatures and pressures are listed, the model generator will simulate the system (still using an isothermal, isobaric model) at all possible combinations of the specified temperatures and pressures. Thus, the resulting reaction mechanism will be valid (within the given error tolerances, estimates, and various other assumptions) at all the conditions specified. (Note, however, that reported concentrations in the `Final_Model.txt` output file will only correspond to the first T/P combination.)

4.7 Maximum Number of Atoms/Radicals Per Species

The next item in the initialization file allows the user to override the maximum number of carbons, oxygens, and/or radicals any species in the model may have. To override the default values, the syntax is:

```
MaxCarbonNumberPerSpecies: 20
MaxOxygenNumberPerSpecies: 6
MaxRadicalNumberPerSpecies: 3
```

If any of these fields are not present in the `condition.txt` file, RMG will use the default values.

4.8 InChI Generation

The next item in the initialization file is the InChI generation command. An InChI, or IUPAC **In**ternational **Ch**emical **I**dentifier, is an unique species identifier, with the exception of differing electronic or spin states, developed by IUPAC and NIST. An example of an InChI string (which represents the species caffeine) is:

```
InChI=1/C8H10N4O2/c1-10-4-9-6-5(10)7(13)12(3)8(14)11(6)2/h4H,1-3H3
```

The InChI is composed of layers, separated by a forward-slash (/):

1. Chemical formula layer
2. Connectivity layer
3. Hydrogen layer
4. ...

For the current release, the InChIs are used as another way to represent a molecule. In future releases, the InChIs will link RMG with an online thermochemical database: PrIMe, or **Pr**ocess **I**nformatics **M**ode**l**. The union will allow RMG to search for a community-recommended thermochemical data entry (e.g. Arrhenius parameters, NASA polynomials) before using estimation techniques.

If this field is turned on, the InChI for each species in the model is located in the `RMG_Dictionary.txt` file.

More information on the InChI project may be found at http://www.iupac.org/inchi/. More information on the PrIMe project may be found at http://primekinetics.org/

To enable the InChI generation, the item should read:

```
InChIGeneration: on
```

To disable the InChI generation, the item should read:

```
InChIGeneration: off
```

4.9 Reactants

The name, concentration, and structure of each reactant must be specified. For each reactant, the first line should include the reactant number (e.g. `(1)`), its name (e.g. `C2O2`), and it's concentration with units (e.g. `4.09e-3 (mol/cm3)`). Acceptable units for concentration are "mol/cm3", "mol/m3", and "mol/l". Furthermore, RMG will not accept a species name that begins with a number.

The next line defines the reactant structure, described by an adjacency list. The *RMG Viewer and Editor* is a useful tool for generating adjacency lists. Please note that you may choose the simplified adjacency list in which the hydrogen atoms are omitted (shown below):

```
InitialStatus:

(1) CH3OH 4.09e-3 (mol/cm3)
1  C 0 {2,S}
2  O 0 {1,S}

(2) O2 1.1E-7 (mol/cm3)
1  O 1 {2,S}
2  O 1 {1,S}

END
```

Please note that the keyword `END` must be placed at the end of the InitialStatus section.

If one of the reactants is a resonance isomer, you only need to define one of the resonance structures, and RMG will automatically detect the others.

Represent molecular oxygen, O_2, **as shown above.** This is a deviation from versions of the RMG database prior to RMG 3.2. For more detail, please see this discussion on *representing oxygen*.

4.10 Inert Gases

Following InitialStatus, the initialization file specifies which inert gases, if any, are used. Currently RMG can handle four inert gases: N_2, Ne, He, and Ar. If one of the gases is not used, set the concentration to 0.0 (mol/cm3). If no bath gas is used, set all concentrations to zero. In the example below, there is no nitrogen, the neon and helium are omitted, and the argon concentration is 2.21E-6 (mol/cm3):

```
InertGas:
N2 0.0 (mol/cm3)
Ar 2.21E-6 (mol/cm3)
END
```

To create valid CHEMKIN files, ensure that any 3rd-body collider molecules used in your Seed Mechanisms or Primary Reaction Libraries are either declared in their species.txt files (if they are reactive) or in this section. (i.e. it's a good idea to list all of N2, Ne, He and Ar, even if their concentrations are 0)

Please note that the keyword `END` must be placed at the end of the InertGas section.

4.11 Spectroscopic Data

The next item in the initialization file is the method to use to estimate the spectroscopic data (i.e. rovibrational modes) of each species. At present there is only one method available, which utilizes approximate frequencies based on functional groups in the molecule when possible, then fits remaining degrees of freedom to heat capacity data. This can also be set to off if spectroscopic data is not needed (i.e. when pressure dependence is off).

When pressure dependent calculations are not desired, this item should read:

```
SpectroscopicDataEstimator: off
```

When pressure dependent calculations are desired, this item should read:

```
SpectroscopicDataEstimator: FrequencyGroups
```

4.12 Pressure Dependence

This flag is used to specify whether the model should account for pressure dependent rate coefficients. If pressure dependence is not desired, this item should read:

```
PressureDependence: off
```

If pressure dependence is desired, this item can take one of two values, based on the method used to approximate the pressure-dependent kinetics: `ModifiedStrongCollision` and `ReservoirState`. The former utilizes the modified strong collision approach of Chang, Bozzelli, and Dean [Chang2000], and works reasonably well while running more rapidly. The latter utilizes the steady-state/reservoir-state approach of Green and Bhatti [Green2007], and is more theoretically sound but more expensive.

To specify the modified strong collision approach, this item should read:

```
PressureDependence: ModifiedStrongCollision
```

To specify the reservoir state approach, this item should read:

```
PressureDependence: ReservoirState
```

For more information on the two methods, consult the following resources:

When pressure dependence is on, you must also specify a linear interpolation model to use to evaluate $k(T, P)$ and output to the Chemkin file. (This line is not required if pressure dependence is set to off.) This line must immediately follow the previous one.

To disregard all temperature and pressure dependence and simply output the rate at the provided temperature and pressure, use the line

```
PDepKineticsModel: Rate
```

To use logarithmic interpolation of pressure and Arrhenius interpolation for temperature, use the line

```
PDepKineticsModel: PDepArrhenius
```

The auxillary information printed to the Chemkin chem.inp file will have the "PLOG" format. Refer to Section 3.5.3 of the `CHEMKIN_Input.pdf` document and/or Section 3.6.3 of the `CHEMKIN_Theory.pdf` document. These files are part of the CHEMKIN manual.

To fit a set of Chebyshev polynomials on inverse temperature and logarithmic pressure axes mapped to [-1,1], use the line

```
PDepKineticsModel: Chebyshev
```

You should also specify the number of temperature and pressure basis functions by adding the appropriate integers. For example, the following specifies that five basis functions in temperature and four in pressure should be used

```
PDepKineticsModel: Chebyshev 5 4
```

The auxillary information printed to the Chemkin chem.inp file will have the "CHEB" format. Refer to Section 3.5.3 of the `CHEMKIN_Input.pdf` document and/or Section 3.6.4 of the `CHEMKIN_Theory.pdf` document.

To generate the $k(T, P)$ interpolation model, a set of temperatures and pressures must be used. RMG can do this automatically, but it must be told a few parameters. Following the previous line, you should provide a line to specify the minimum and maximum temperature and number of temperatures to use in the grid, e.g.

```
TRange: (K) 300.0 2000.0 8
```

A similar line should follow for pressures:

```
PRange: (bar) 0.01 100.0 5
```

If you prefer, you can also specify the grid of temperatures and pressures manually using lines similar to the following:

```
Temperatures: 8 (K) 300.0 400.0 500.0 600.0 800.0 1000.0 1500.0 2000.0
Pressures: 5 (bar) 0.01 0.1 1.0 10.0 100.0
```

You should specify either a `TRange` or `Temperatures` line and either a `PRange` or `Pressures` line.

4.13 Finish Controller

The Finish Controller defines the termination rules for model growth. Additionally, it includes the precision parameters such as reaction time, conversion, and error tolerance. The finish controller item should begin with a line that contains only `FinishController:`.

Below the Finish Controller line, you must specify the goal. The goal tells the program when to terminate the reaction model expansion. There are two goal options: `ReactionTime` and `Conversion`.

`ReactionTime` must be followed by a number and a time unit. Acceptable units of time are "sec", "min", "hr", and "day". `Conversion` must be followed by a reactant species name and a number between 0 and 1.

Beneath the goal, you must specify the error tolerance. Typical values for the error tolerance are between 0.0001 and 0.5. A smaller error tolerance generally corresponds to a larger model and longer model generation times. In the first example, the reaction will run for 0.001 seconds:

```
FinishController:
(1) Goal ReactionTime: 0.001 (sec)
(2) Error Tolerance: 0.1
```

In the second example, the reaction will run until 90% of the C_2H_6 reactant is consumed and has a much tighter error tolerance:

```
FinishController:
(1) Goal Conversion: C2H6 0.90
(2) Error Tolerance: 0.0001
```

For the initial model run, it is often preferable to use `Goal Conversion` instead of `Goal ReactionTime`, since it is difficult to judge *a priori* what the reaction time should be.

For a more detailed description on rate-based model enlargement, please consult [Susnow1997].

4.14 Dynamic Simulator

RMG uses the DASSL or DASPK dynamic solver. DASSL is recommended, as RMG uses DASPK in a way that requires the use of the proprietary DAEPACK library, which is not distributed with RMG. Future versions of RMG might include the CHEMKIN dynamic solver.

The first line beneath the solver should be either `TimeStep` or `Conversions`, depending on whether you chose Goal Conversion or Goal ReactionTime as your finish controller criterion.

The `TimeStep` indicates at what time steps RMG should check to see if the model needs to be enlarged. By default the units of time steps is **always** seconds. For example in the example shown below RMG will stop at 0.0001 sec, 0.0002 sec ... and so on to see whether the error tolerance is satisfied:

```
DynamicSimulator: DASSL
TimeStep: 0.0001 0.0002 0.0004 0.0006 0.0008 0.0009
```

The other option is to specifiy the Conversions. In this option the conversion of the FinishController species (in this case, C_2H_6) is monitored and RMG will stop at conversions of 0.1, 0.2, ... and so on to see whether the error tolerance is satisfied:

```
DynamicSimulator: DASSL
Conversions: 0.1 0.2 0.4 0.6 0.8 0.9
```

For both `TimeStep` or `Conversions`, in addition to determining when RMG will stop to check whether error tolerances are satisfied, the concentrations and flux at the points specified will be reported in the `Final_Model.txt` file.

If you would not like to specify time steps or conversions, you may have them determined using the "automated time stepping" feature by specifying `AUTO` as follows:

```
DynamicSimulator: DASSL
TimeStep: AUTO
```

or:

```
DynamicSimulator: DASSL
Conversions: AUTO
```

The automated time stepping feature is described in greater detail in the Theory and Implementation Details appendix. When using automated time stepping, it is also possible to perform mechanism generation with pruning of "unimportant" edge species to reduce memory usage. This option is requested by specifying `AUTOPRUNE` in place of `AUTO`. When using `AUTOPRUNE`, this must be followed by four lines specifying pruning parameters, as the example below shows:

```
TerminationTolerance: 1.0E4
PruningTolerance: 1.0E-15
MinSpeciesForPruning: 1000
MaxEdgeSpeciesAfterPruning: 1000
```

`TerminationTolerance` and `PruningTolerance` are compared with the same quantity as `Error Tolerance` in the `FinishController` section (i.e. they are all compared with ratios of edge species flux to characteristic reaction model flux). `TerminationTolerance` indicates how high the edge flux ratio must get to interrupt the simulation (before reaching the `Goal Conversion` or `Goal ReactionTime` described earlier). Pruning won't occur if the simulation is interrupted before reaching the goal criteria, so set this high to increase pruning opportunities. The value should be greater than or equal to `Error Tolerance`. `PruningTolerance` indicates how low the edge flux ratio for a species must get before the species is pruned (removed) from the edge (regardless of edge size relative to `MaxEdgeSpeciesAfterPruning`). The value should be (significantly) lower than `Error Tolerance`. `MinSpeciesForPruning` indicates the minimum total number of species (edge and core) that must be present for pruning (due to low edge flux ratio relative to `PruningTolerance` or due to `MaxEdgeSpeciesAfterPruning`) to occur. `MaxEdgeSpeciesAfterPruning` indicates the upper limit for the size of the edge. Pruning will continue until the edge is at least this small, regardless of `PruningTolerance` (though lowest fluxes are pruned first).

When using pruning, RMG will not prune unless all reaction systems reach the goal reaction time or conversion without first exceeding the termination tolerance. Therefore, you may find that RMG is not pruning even though the model edge size exceeds `MaxEdgeSpeciesAfterPruning`. In order to increase the likelihood of pruning in such cases, you can try increasing `TerminationTolerance` to an arbitrarily high value. Alternatively, if you are using a conversion goal, because reaction systems may reach equilibrium below the goal conversion, it may be helpful to reduce the goal conversion or switch to a goal reaction time.

The next two lines specify the absolute and relative tolerance for the ODE solver, respectively. Common values for the absolute tolerance are 1e-15 to 1e-25. Relative tolerance is usually 1e-4 to 1e-8:

```
Atol: 1e-20
Rtol: 1e-4
```

Note: You have the option of using sensitivity analysis only if you have the DASPK solver and the DAEPACK library. If you are using DASSL solver then skip the Sensitivity Analysis section.

One option when dealing with NegativeConcentrationException issues is to use the "non-negative" option with DASSL. This option is requested with the line "DynamicSimulator: DASSL: non-negative". See the FAQ for further details.

4.15 Sensitivity Analysis

As long as DASPK is chosen for the dynamic solver, RMG can perform sensitivity analysis and generate error bars on the concentration profiles. As mentioned above, however, RMG uses DASPK in a way that requires the use of the proprietary library DAEPACK (which provides automatic differentiation capabilities for the sensitivity analysis). If you do not have access to this library, an alternative is to perform sensitivity analysis in CHEMKIN, using the ''chem.inp" file produced by RMG.

The sensitivity analysis is based upon first-order sensitivity coefficients and uncertainties in the rate constants. To use the sensitivity analysis, either the first or second line must be set to `on`. If both `Error bars` and `Display sensitivity coefficients` are set to off, then RMG will not perform a sensitivity analysis.

When the option to generate error bars is turned on, RMG calculates the upper and lower bounds on the concentration profiles for all core species. These upper and lower bounds are generated by the first-order sensitivity equation:

$$\ln C_i\left(t, \overrightarrow{k} + \Delta\overrightarrow{k}\right) \approx \ln C_i\left(t, \overrightarrow{k}\right) + \sum_j \frac{\partial \ln C_i}{\partial \ln k_j}\Delta \ln k_j$$

where C_i is the concentration of the i^{th} species, and $\overrightarrow{k}$ is the vector of rate constants.

If the option to display sensitivity coefficients is turned on, you must specify a list of species for which the sensitivities should be displayed. The output file will then include the sensitivities of those species with respect to all the rate constants, all the heats of formations, and the initial concentrations of all the reactants. Additionally, if you choose to display the sensitivity coefficients, RMG will print a list of the five reactions that contribute the most to the uncertainty in the concentration (for each species selected by the user).

Sensitivities to rate constants are normalized sensitivities ($\partial \ln C_i/\partial \ln k_j$), and sensitivities to heats of formation are semi-normalized ($\partial \ln C_i/\partial \Delta H_f$). The contribution of a reaction to the uncertainty is estimated as the product of the normalized sensitivity and the uncertainty in the rate constant ($\Delta \ln k$). In the following example, RMG will perform a sensitivity analysis. Error bars will be generated for all the species, and the sensitivity coefficients will be generated for carbon monoxide, carbon dioxide, methane, and water:

```
Error bars: On
Display sensitivity coefficients: On
Display sensitivity information for:
```

```
CO
CO2
CH4
H2O
END
```

Please note that the keyword `END` must be placed at the end of the Error bars section.

4.16 Primary Kinetic Library

The next section of the `condition.txt` file specifies which, if any, primary kinetic libraries should be used. When a reaction is specified in a primary kinetic library, RMG will use these kinetics instead of the kinetics located in the `RMG_database/kinetics_groups/<RxnFamily>/rateLibrary.txt` directory.

For details of the kinetics libraries included with RMG that can be used as a primary kinetic library, see *Kinetics Libraries*. You can specify your own primary kinetic library in the location section. In the following example, the user has created her own primary kinetic library with a few additional reactions specific to n-butane, and these reactions are to be used in addition to the Leeds' oxidation library:

```
PrimaryKineticLibrary:
Name: nbutane
Location: nbutane
Name: Leeds
Location: combustion_core/version5
END
```

If a user wished to use the GRI-Mech 3.0 mechanism as a primary kinetic library, the syntax is:

```
Name: GRI-Mech 3.0
Location: GRI-Mech3.0
```

The libraries are stored in `$RMG/databases/RMG_database/kinetics_libraries/` and the *Location:* should be specified relative to this path.

Please note that the keyword `END` must be placed at the end of the Primary Kinetic Library section. Because the units for the Arrhenius parameters are given in each library, the different libraries can have different units.

If the same reaction occurs more than once in the combined library, the instance of it from the first library in which it appears is the one that gets used. Changed in version 3.2: In previous versions this feature was called "PrimaryReactionLibrary" it has been renamed to "PrimaryKineticLibrary" to better represent its functionality.

4.17 Reaction Library

The next section of the `condition.txt` file specifies which, if any, Reaction Library should be used. When a reaction library is specified, RMG will first use the reaction library to generate all the relevant

reactions for the species in the core before going through the reaction templates. This feature can be used as a Primary Kinetic Library and in addition also use to specify those reactions which the user wants to consider while building the mechanism but do not match any of RMG templates. In Reaction Library unlike the seed mechanism these reactions do not need to be included in the core from the start.

For details of the kinetics libraries included with RMG that can be used as a reaction library, see *Kinetics Libraries*. You can specify your own reaction library in the location section. In the following example, the user has created a reaction library with a few additional reactions specific to n-butane, and these reactions are to be used in addition to the Glarborg C3 library:

```
ReactionLibrary:
Name: nbutane
Location: nbutane
Name: Glarborg
Location: Glarborg/C3
END
```

The reaction library are stored in `$RMG/databases/RMG_database/kinetics_libraries/` and the *Location:* should be specified relative to this path.

Please note that the keyword `END` must be placed at the end of the Reaction Library section. Because the units for the Arrhenius parameters are given in each mechanism, the different mechanisms can have different units.

Note: While using a Reaction Library the user must be careful enough to provide all instances of a particular reaction in the library file, as RMG will ignore all reactions generated by its templates.

In case the user has specified a reaction as only irreversible RMG will ignore all instances it generates even if they are reversible.

4.18 Seed Mechanisms

The next section of the `condition.txt` file specifies which, if any, Seed Mechanisms should be used. If a seed mechanism is passed to RMG, every species and reaction present in the mechanism will be placed into the core, in addition to the species that are listed in the *Reactants* section.

For details of the kinetics libraries included with RMG that can be used as a seed mechanism, see *Kinetics Libraries*.

You can specify your own seed mechanism in the location section. Please note that the oxidation library should not be used for pyrolysis models. The syntax for the seed mechanisms is similar to that of the primary reaction libraries, except for the `GenerateReactions` line, explained below.:

```
SeedMechanism:
Name: GRI-Mech 3.0
Location: GRI-Mech3.0
GenerateReactions: yes
Name: Leeds
Location: combustion_core/version5
GenerateReactions: yes
END
```

The seed mechanisms are stored in `$RMG/databases/RMG_database/kinetics_libraries/` and the *Location:* should be specified relative to this path.

There is a new required `GenerateReactions` line in seed mechanisms that controls how RMG adds the seed species and reactions to the model core. If set to `yes`, RMG will use its reaction families to react all seed species with one another; the generated reactions will supplement the seed reactions. If set to `no`, RMG will not generate reactions of the seed species. In either case, RMG will react the species in the condition file with one another and with all species in the seed mechanism.

Please note that the keyword `END` must be placed at the end of the Seed Mechanism section. Because the units for the Arrhenius parameters are given in each mechanism, the different mechanisms can have different units. Additionally, if the same reaction occurs more than once in the combined mechanism, the instance of it from the first mechanism in which it appears is the one that gets used.

Note: For more information on what files to include in a Primary Kinetic / Reaction Library or Seed Mechanism, visit *Building a Primary Kinetc Library / Reaction Library / Seed Mechanism*

4.19 Chemkin Units

The last section of the `condition.txt` file specifies the units for the Arrhenius A and Ea parameters reported in the `chem.inp` file. The acceptable units for A are "moles" and "molecules"; the acceptable units for Ea are "kcal/mol", "cal/mol", "kJ/mol", "J/mol", and "Kelvins":

```
ChemkinUnits:
A: moles
Ea: kcal/mol
```

Another option available to the user is to specify whether the comments following each set of Arrhenius parameters in the `chem.inp` file are concise or verbose. The verbose comments describe how the reported A, n, and Ea Arrhenius parameters were calculated in the event RMG could not find an exact match for the functional groups.:

```
ChemkinUnits:
Verbose: on
A: moles
Ea: kcal/mol
```

If the Verbose field is not present, RMG will default to "off".

Note: The `chem.inp` file generated with the Verbose field turned "on" may have a comment that spans hundreds of characters. These verbose comments may cause the CHEMKIN interpreter to throw an error when running the Pre-Processor.

CHAPTER

FIVE

EXAMPLE CONDITION FILES

5.1 1,3-hexadiene pyrolysis

This is our first example. Somebody should write something wise about it:

```
//tracks the consumption of 1,3-hexadiene in presence of N2, Methane and hydrogen.
//notice the primary reaction library is turned off because this is not
//a oxidation mechanism. Also the sensitivity analysis section is missing
//because we are using the dassl solver.

//This example should take roughly 15-20 minutes to run to completion.


Database: RMG_database

//MaxCarbonNumberPerSpecies:
//MaxOxygenNumberPerSpecies:
//MaxRadicalNumberPerSpecies:
//MaxSulfurNumberPerSpecies:
//MaxSiliconNumberPerSpecies:
//MaxHeavyAtomPerSpecies:

PrimaryThermoLibrary:
Name: GRIMech3.0
Location: GRI-Mech3.0
Name: RMG-old
Location: primaryThermoLibrary
END

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

ReadRestart: no
WriteRestart: yes

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

```
InitialStatus:

(1) HXD13 6.829e-4 (mol/cm3)
1 C 0 {2,D}
2 C 0 {1,D} {3,S}
3 C 0 {2,S} {4,D}
4 C 0 {3,D} {5,S}
5 C 0 {4,S} {6,S}
6 C 0 {5,S}

(3) CH4 0.104 (mol/cm3)
1 C 0

(6) H2 1.56e-2 (mol/cm3)
1 H 0 {2,S}
2 H 0 {1,S}

END

InertGas:
N2 0.8797 (mol/cm3)
Ar 0.0e-6 (mol/cm3)
END

SpectroscopicDataEstimator: FrequencyGroups
PressureDependence: ReservoirState
PDepKineticsModel: Chebyshev 4 4
TRange: (K) 300.0 2000.0 8
PRange: (bar) 0.01 100.0 5

FinishController:
(1) Goal Conversion: HXD13 0.9
(2) Error Tolerance: 0.5

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

PrimaryKineticLibrary:
//Name: RMG-example
//Location: Example
END

ReactionLibrary:
//Name: GRIMech3.0
//Location: GRI-Mech3.0
END


SeedMechanism:
//Name: Leeds
```

```
//Location: combustion_core/version5
//GenerateReactions: yes
//Name: GRIMech3.0
//Location: GRI-Mech3.0
//GenerateReactions: yes
END

ChemkinUnits:
A: moles
Ea: kcal/mol
```

5.2 Butane oxidation with pruning

This example illustrates the use of pruning, as well as multiple reaction conditions. The example should take at least several hours to run and may require allocation of a large amount of memory (e.g. 1500 MB) to complete:

```
//tracks the consumption of Butane in presence of O2.

//This example illustrates the use of pruning, as well
//as multiple reaction conditions. The example should
//take at least several hours to run and may require allocation
//of a large amount of memory (e.g. 1500 MB) to complete.

Database: RMG_database

//MaxCarbonNumberPerSpecies:
//MaxOxygenNumberPerSpecies:
//MaxRadicalNumberPerSpecies:
//MaxSulfurNumberPerSpecies:
//MaxSiliconNumberPerSpecies:
//MaxHeavyAtomPerSpecies:

PrimaryThermoLibrary:
Name: GRIMech3.0
Location: GRI-Mech3.0
Name: RMG-old
Location: primaryThermoLibrary
END

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

ForbiddenStructures:


END
```

```
ReadRestart: no
WriteRestart: yes

TemperatureModel: Constant (K) 800 1000 2000
PressureModel: Constant (atm)  20 30 40

InitialStatus:

(1) C4H10 1 (mol/cm3)
1 C 0 {2,S}
2 C 0 {1,S} {3,S}
3 C 0 {2,S} {4,S}
4 C 0 {3,S}

(2) O2 6.5 (mol/cm3)
1 O 1 {2,S}
2 O 1 {1,S}

END

InertGas:
N2 24.399 (mol/cm3)
Ar 0 (mol/cm3)
END

SpectroscopicDataEstimator: off
PressureDependence: off
//PressureDependence: ModifiedStrongCollision
//PDepKineticsModel: Chebyshev

FinishController:
(1) Goal Conversion: C4H10 0.9
(2) Error Tolerance: 0.1

DynamicSimulator: DASSL
//Conversions: AUTO
Conversions: AUTOPRUNE
TerminationTolerance: 10
PruningTolerance: 1.0E-18
MinSpeciesForPruning: 1000
MaxEdgeSpeciesAfterPruning: 10000
Atol: 1e-18
Rtol: 1e-8

PrimaryKineticLibrary:
//Name: RMG-example
//Location: RMG_database/primaryReactionLibrary/Example
END

ReactionLibrary:

END
```

```
SeedMechanism:
//Name: Leeds
//Location: RMG_database/SeedMechanisms/combustion_core/version5
//GenerateReactions: yes
Name: GRIMech3.0
Location: GRI-Mech3.0
GenerateReactions: yes
//Name: Glarborg
//Location: RMG_database\SeedMechanisms\Glarborg\C3_light
//GenerateReactions: yes

END

ChemkinUnits:
A: moles
Ea: kcal/mol
```

5.3 Quantum mechanics calculations

This is an example illustrating the use of on-the-fly thermo calculations. Gaussian03 is used to estimate thermodynamic properties of cyclic species, like cyclopropane. In particular, the semi-empirical PM3 method, with RRHO treatment of partition functions is used. Without this feature, RMG would try to estimate thermodynamic properties of cyclic species using the typical Benson groups, and would only apply an appropriate ad hoc ring correction if it is in Ring_Library.txt. The example should take roughly 45 minutes to run and requires several additional dependencies, as described in the documentation.

```
//This is an example illustrating the use of on-the-fly thermo
//calculations. Gaussian03 is used to estimate thermodynamic
//properties of cyclic species, like cyclopropane. In particular,
//the semi-empirical PM3 method, with RRHO treatment of partition
//functions is used. Without this feature, RMG would try to estimate
//thermodynamic properties of cyclic species using the typical Benson
//groups, and would only apply an appropriate ad hoc ring correction
//if it is in Ring_Library.txt. The example should take roughly 45
//minutes to run and requires several additional dependencies, as
//described in the documentation.

Database: RMG_database

//MaxCarbonNumberPerSpecies:
//MaxOxygenNumberPerSpecies:
//MaxRadicalNumberPerSpecies:
//MaxSulfurNumberPerSpecies:
//MaxSiliconNumberPerSpecies:
//MaxHeavyAtomPerSpecies:

PrimaryThermoLibrary:
Name: GRIMech3.0
Location: GRI-Mech3.0
Name: RMG-old
```

```
Location: primaryThermoLibrary
END

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

ReadRestart: no
WriteRestart: no

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

ThermoMethod: QM Gaussian03
QMForCyclicsOnly: on
MaxRadNumForQM: 0

InitialStatus:

(1) Cyclopropane 6.829e-4 (mol/cm3)
1 C 0 {2,S} {3,S}
2 C 0 {1,S} {3,S}
3 C 0 {1,S} {2,S}

END

InertGas:
N2 0.8797 (mol/cm3)
Ar 0.0e-6 (mol/cm3)
END

SpectroscopicDataEstimator: off FrequencyGroups
PressureDependence: off ModifiedStrongCollision
//PDepKineticsModel: Chebyshev

FinishController:
(1) Goal Conversion: Cyclopropane 0.9
(2) Error Tolerance: 0.1

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

PrimaryKineticLibrary:
//Name: RMG-example
//Location: Example
END

ReactionLibrary:
//Name: RMG-example
//Location: RMG_database/primaryReactionLibrary/Example
```

```
END

SeedMechanism:
//Name: Leeds
//Location: RMG_database/SeedMechanisms/combustion_core/version5
//GenerateReactions: yes
//Name: GRIMech3.0
//Location: RMG_database/SeedMechanisms/GRI-Mech3.0
//GenerateReactions: yes
END

ChemkinUnits:
A: moles
Ea: kcal/mol
```

CHAPTER

SIX

CREATING A CONDITION FILE USING THE GRAPHICAL USER INTERFACE

A user may construct the `condition.txt` file by hand or by using the Graphical User Interface.

6.1 Launching the Graphical User Interface

First, change to the directory where you want the output files to be stored; for the following example, we will store the output in the directory `rmgRun`, located in the $RMG directory.

For Linux users, run the following commands to launch the GUI:

```
cd $RMG/rmgRun
java -Xmx500m -classpath $RMG/software/rmg/RMG.jar GUI > output &
```

For Windows users, run the following commands to launch the GUI:

```
cd "%rmg%"\rmgRun
java -Xmx500m -classpath "%rmg%"\software\rmg\RMG.jar GUI > output &
```

6.2 The "Initial Conditions" tab

This tab of the GUI allows the user to enter the *Reactants*, *Inert Gases*, and *Initial Conditions* for the simulation.

6.2.1 Reactants and Inert Gases

For each species, a "Name," "Concentration," "Units," and "Reactivity" must be specified. The three options for "Reactivity" are:

- "Inert" - a species for which RMG will not build a reaction mechanism for
- "Reactive-User" - a species for which RMG will build a mechanism for, but only according to the list of reactions the user has provided

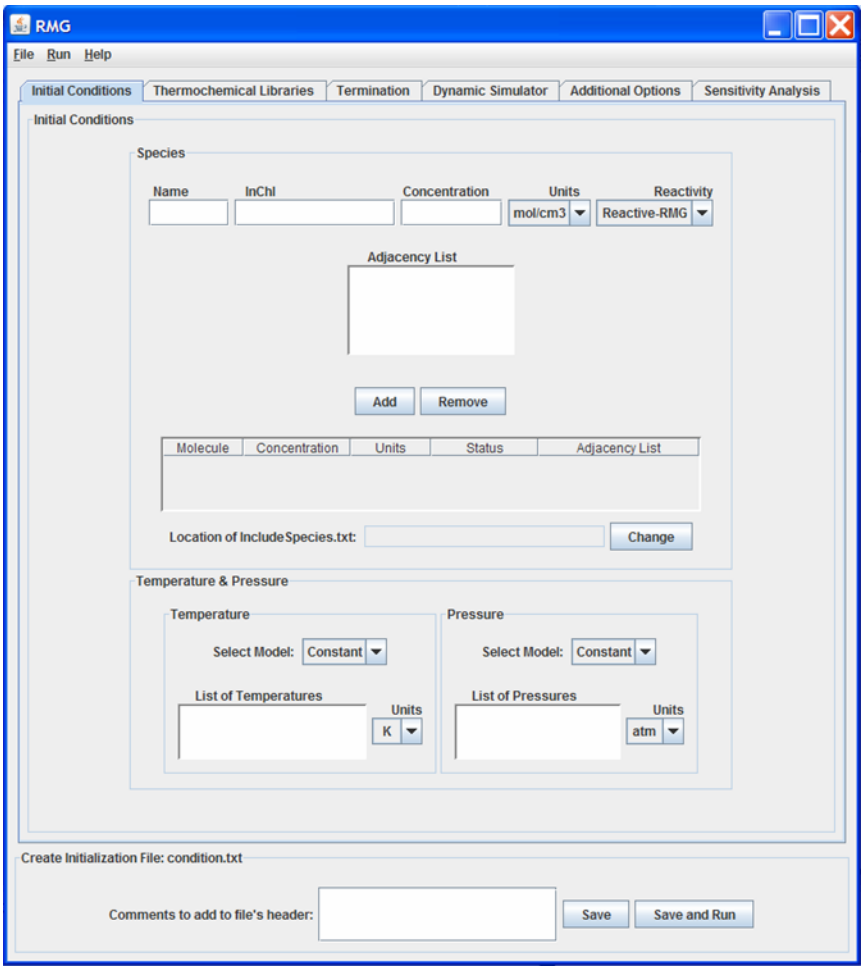


Figure 6.1: Initial Conditions tab

- "Reactive-RMG" - a species for which RMG will build a mechanism for, according to the reaction family templates located in the `RMG_database/kinetics` folder

If the species is selected as "Inert", no structural information for the molecule is necessary. RMG only recognizes the following Inerts: N2, He, Ne, Ar.

If the species is selected as either "Reactive-User" or "Reactive-RMG", the user must supply structural information about the molecule. This information may be provided in one of three ways: adjacency list, InChI, or .mol file.

An example of an adjacency list (for methane) is:

```
1 C 0 {2,S} {3,S} {4,S} {5,S}
2 H 0 {1,S}
3 H 0 {1,S}
4 H 0 {1,S}
5 H 0 {1,S}
```

An equally valid adjacency list for methane (with the Hydrogen atoms removed) is:

```
1 C 0
```

If the user knows the InChI of the molecule (and the InChI executable is located in the `RMG/software/InChI` folder), the GUI will convert the InChI to an adjacency list upon pushing the "Add" button. If using either InChI software version 1.01 or software version 1.02beta, the InChI for methane is:

```
InChI=1/CH4/h1H4
```

However, if using the InChI software version 1.02 for Standard InChI/InChIKey, the InChI for methane is:

```
InChI=1S/CH4/h1H4
```

Please make sure the InChI you pass to the RMG GUI is consistent with the InChI version located in the `$RMG\software\InChI` folder. Upon pushing the "Add" button, if neither an adjacency list nor InChI have been provided, the GUI will ask the user for the location of the .mol file associated with this species. If the InChI executable is in the proper folder, the GUI will convert the .mol file to an adjacency list.

The user may add/remove species to the model by clicking the appropriate buttons.

6.2.2 Reactive-User Species

If a "Reactive-User" species is added to the model, the GUI will ask the user for the location of the `IncludeSpecies.txt` file. If no "Reactive-User" species are added to the model, the "Location of IncludeSpecies.txt" field will remain inactive.

6.2.3 Initial Conditions

RMG currently only has one pressure/temperature model: "Constant". However, the user may specify a list of temperatures and pressures for which to build the reaction mechanism. The list of temperatures (or pressures) should be separated from one another with a blank space or a return carriage.

6.3 The "Thermochemical Libraries" tab

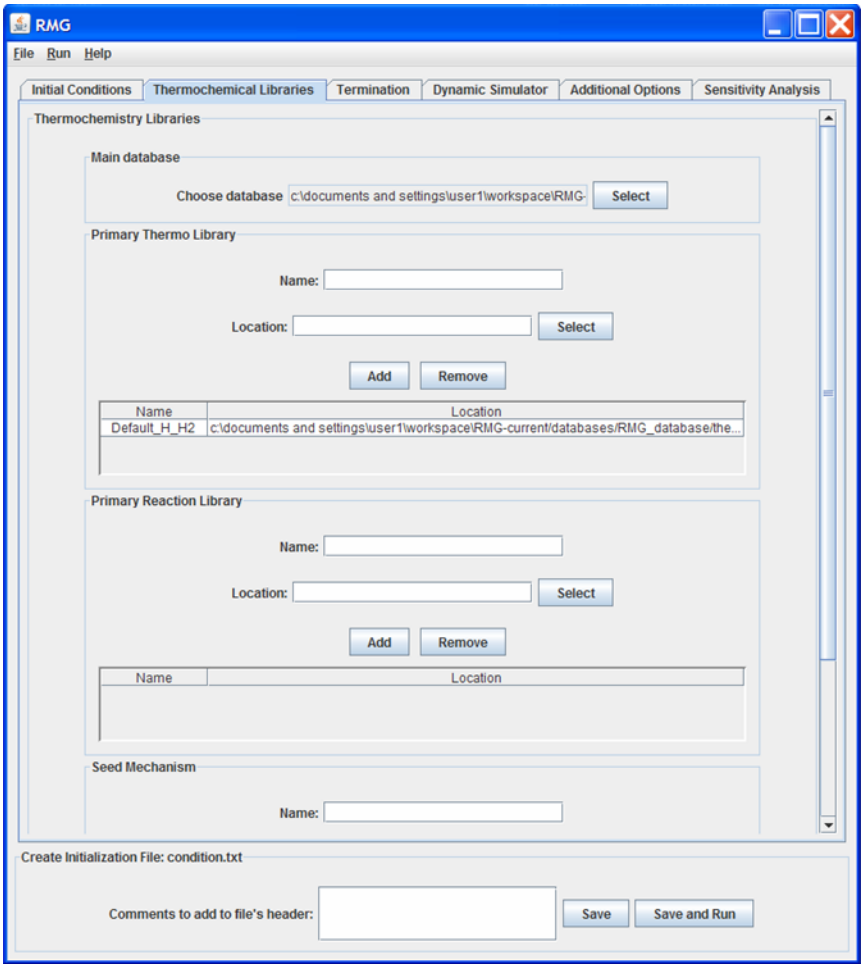


Figure 6.2: Thermochemical Libraries tab

This tab of the GUI allows the user to enter the location of the thermochemical libraries RMG will use in building the model.

The default location of the *Main Database* is the `RMG/database/RMG_database` folder. We recommend to use the default settings.

The default location of the *Primary Thermo Library* is the `RMG/database/RMG_database/thermo/PrimaryTherr` folder. We recommend to include this default primary thermo library. To add additional primary thermo libraries: Supply a Name, select the directory by pressing the "Select" button, and then push "Add".

To add a *Primary Reaction Library* or *Seed Mechanism*: Supply a Name, select the directory by pressing the "Select" button, and then push "Add".

Note: The order of the "Primary Thermo Libraries", "Primary Reaction Libraries", and "Seed Mechanisms" in the tables are important. The order established in the table will be conserved when writing the `condition.txt` file. For any reactions that appear in multiple "Primary Reaction Libraries" (or "Seed Mechanisms"), RMG will use the information contained in the first "Primary Reaction Library" (or "Seed Mechanism") and ignore all others. Similarly, for any species that appear in multiple "Primary Thermo Libraries", RMG will use the information contained in the first "Primary Thermo Library" and ignore all others.

6.4 The "Termination" tab

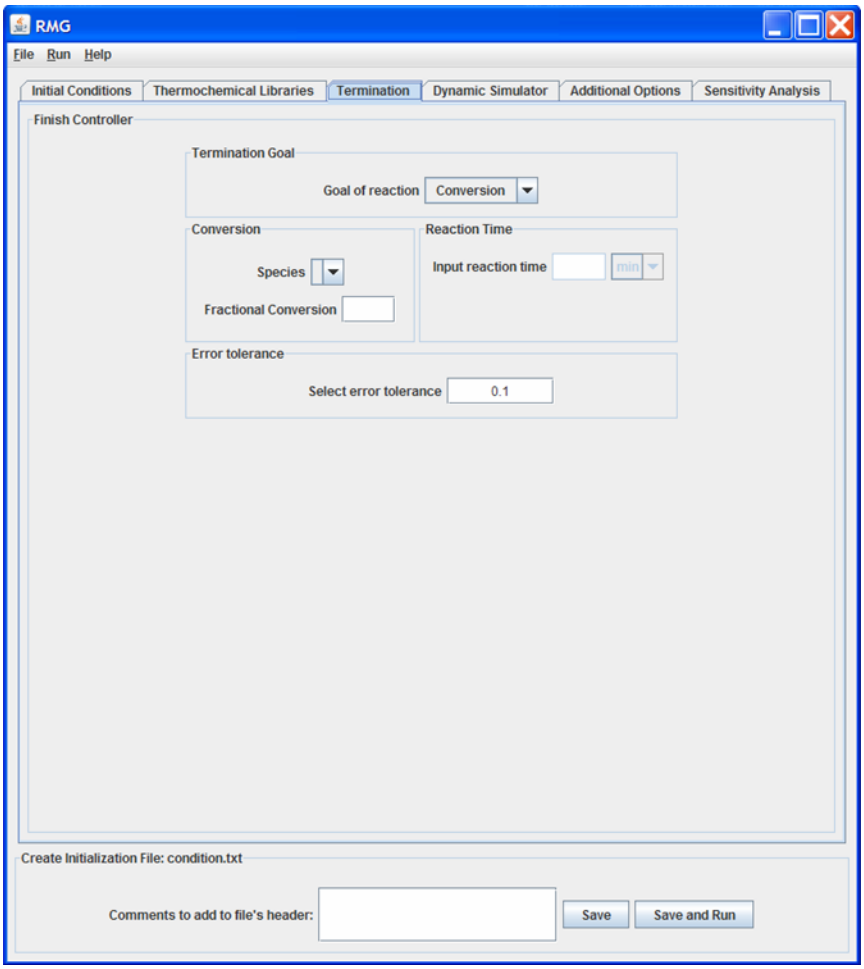


Figure 6.3: Termination tab

This tab of the GUI allows the user to specify the *termination criteria* for the model. A user may specify either the desired "ReactionTime" or "Conversion".

If "Conversion" is selected, the user must specify a species and a fraction conversion (ranging from 0 to 1). The "Species" drop-down menu will only contain the "Reactive-RMG" and "Reactive-User" species

specified in the Initialization tab.

If “ReactionTime” is selected, the user must specify the value and units of the desired reaction time.

Lastly, the user must specify an “Error tolerance” for the model. If building a mechanism for a new system, we recommend starting with a high “Error tolerance” (e.g 0.1).

6.5 The “Dynamic Simulator” tab

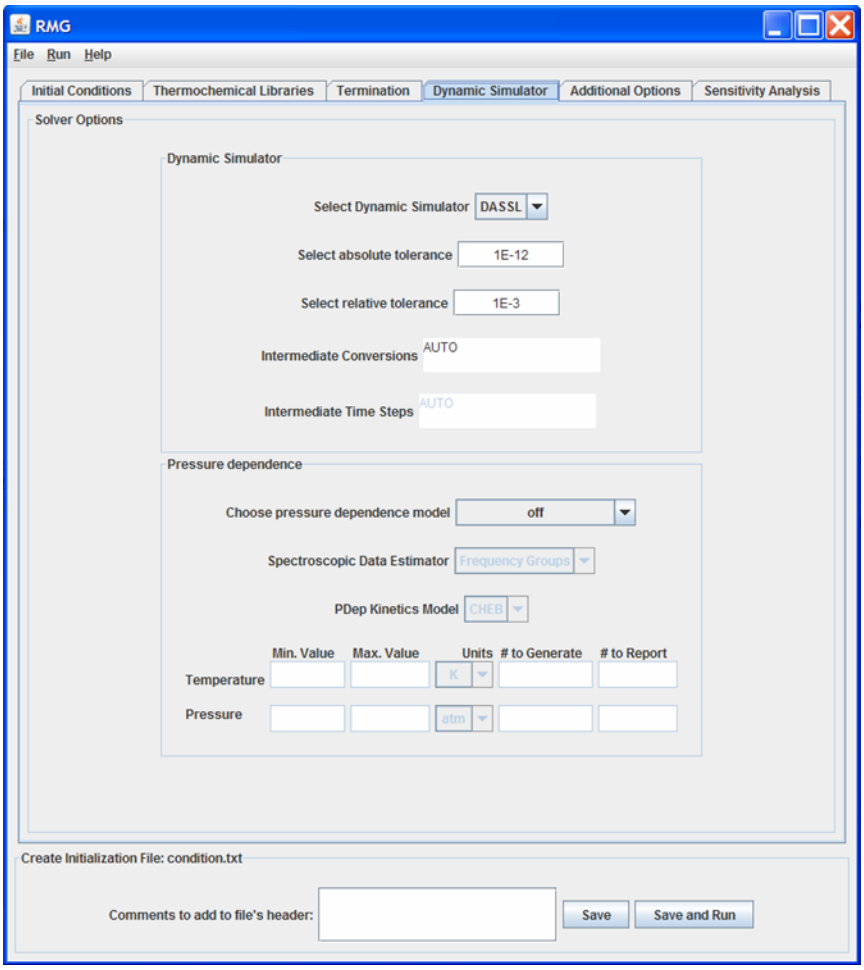


Figure 6.4: Dynamic Simulator tab

This tab of the GUI allows the user to specify options for:

- *the ODE solver*
- *building a pressure dependent mechanism*

6.5.1 The ODE Solver

The user must select a "Dynamic Simulator" and set the Absolute and Relative Tolerances for that Dynamic Simulator. The user may also select Intermediate times or conversions for RMG to check whether the reaction mechanism needs to be enlarged. We recommend using the automatic time stepping, which is invoked by typing "AUTO" in the "Intermediate" time/conversion fields.

The "Intermediate Conversions" field will be enabled (and the "Intermediate Time Steps" field will be disabled) if the "Termination Goal" was chosen as "Conversion" on the *Termination* tab.

Note: If the user specifies "Intermediate Time Steps," the values must have units of Seconds.

6.5.2 The pressure dependence model

The user must specify a *pressure dependence model*. The options are:

- off
- Modified Strong Collision
- Reservoir State

If the user specifies a pressure dependent model, the "Spectroscopic Data Estimator" and "PDep Kinetics Model" fields will be enabled. The only option for the "Spectroscopic Data Estimator" are:

- Frequency Groups

The options for the "PDep Kinetics Model" are:

- CHEB - resulting in Chebyshev polynomials as auxiliary information for pressure-dependent reactions
- PLOG - resulting in Modified Arrhenius parameters at different pressures as auxiliary information for pressure-dependent reactions
- Rate - resulting in no auxiliary information and modified Arrhenius parameters of A 0.0 0.0, where A = k(T,P)

If CHEB is selected as the "PDep Kinetics Model", the fields near the bottom of this tab will become enabled. These fields are optional. However, if data is entered into any of the eight fields, all eight fields must be filled.

6.6 The "Additional Options" tab

This tab allows the user to specify additional (and usually optional) information to RMG.

6.6.1 Species properties

The user may choose to override any of the following species properties, by entering data into the appropriate field:

- Maximum carbon number per species

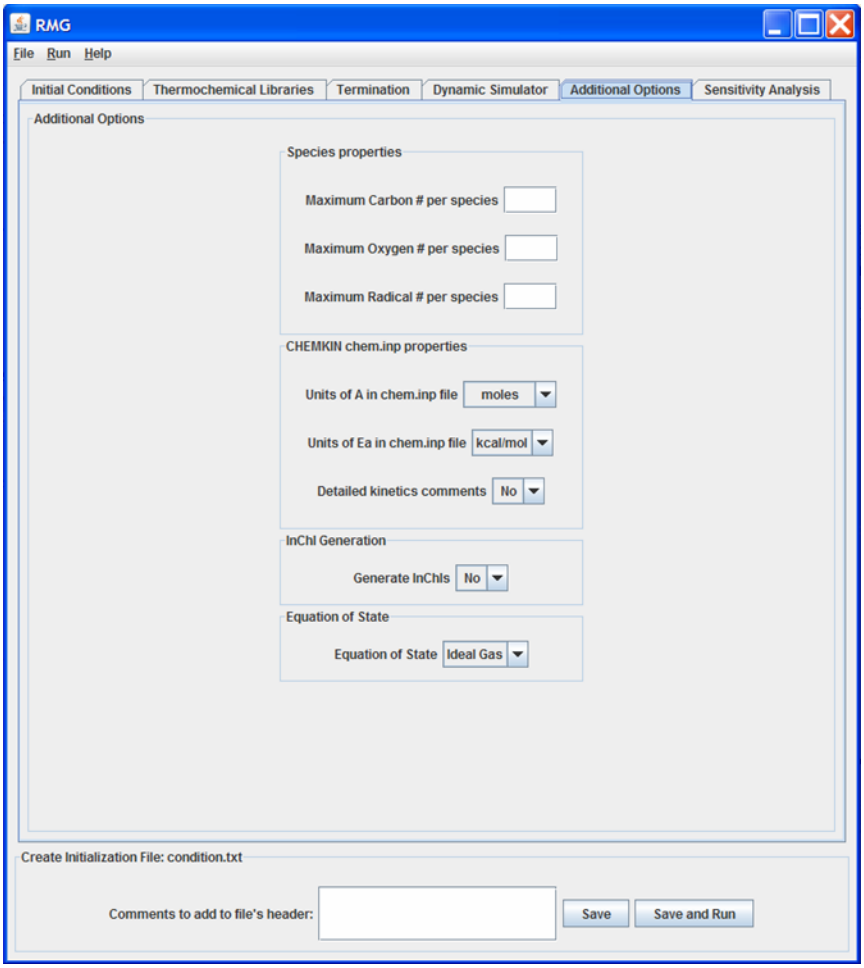


Figure 6.5: Additional Options tab

- Maximum oxygen number per species
- Maximum radical number per species

The user has the option to enter data for none, one, two, or all three of these fields. If left blank, RMG will use the default values.

6.6.2 CHEMKIN chem.inp properties

The next set of fields allow the user to specify the units of the Arrhenius parameters 'A' and 'Ea' for the `chem.inp` file generated by RMG. The user may also specify if they want the concise or verbose comments for each reaction in the `chem.inp` file. Refer to *Chemkin options* for more details.

6.6.3 Optional fields

Some optional fields the user may change are:

- Equation of State
- InChI generation

The user may also choose to turn off/on the generation of *InChIs*. If the user chooses to turn InChI generation on, the InChI executable (v 1.01) must be located in the `RMG/software/InChI` folder.

The user currently has only one option for the "Equation of State":

- Ideal Gas

6.7 The "Sensitivity Analysis" tab

This tab of the GUI allows the user to specify options for error bars and sensitivity coefficients. The features of this tab will only be active if "DASPK" is selected as the "Dynamic Simulator" on the *Dynamic Simulator* tab.

The user may turn the generation of error bars "on" or "off." If turned on, upper and lower error bars will be generated for all species in the model.

The user may also turn the generation of sensitivity coefficients "on" or "off." The sensitivity coefficients will only be generated for the species listed in the "Molecule" table. The order in which the species appear in the table is not important.

6.8 Saving the file

To save the file, the user can either press the "Save" button near the bottom of the GUI or by selecting "File" –> "Save" from the navigation toolbar. The file does not have to be named condition.txt. Also, the user may add additional comments to the `condition.txt` file by adding information to the text field at the bottom of the GUI. These comments will be added to the header of the saved file.

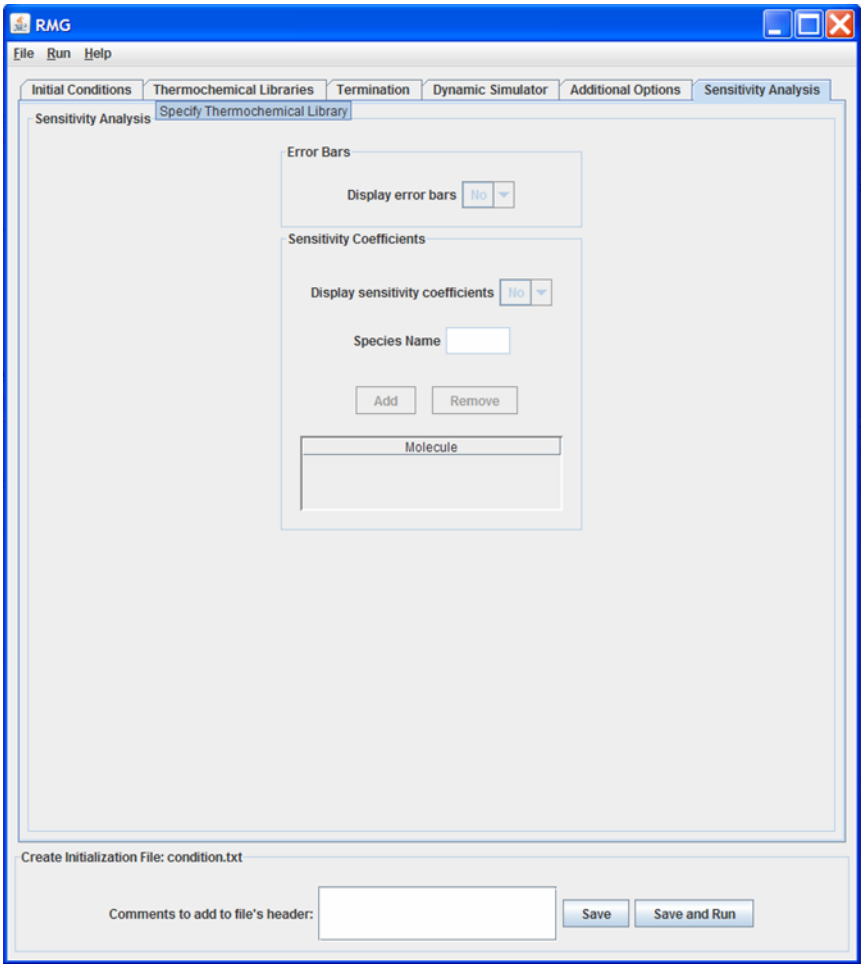


Figure 6.6: Sensitivity Analysis tab

To save and immediately run a file, the user can press the "Save and Run" button near the bottom of the GUI.

6.9 Opening a file

To open and import the information from an already written `condition.txt` file, the user can select "File" –> "Open" from the navigation toolbar.

Note: The comments in the header of the file will not be imported.

6.10 Running the file

To run a file without viewing it, the user can select "Run" –> "Run RMG" from the navigation toolbar.

CHAPTER

SEVEN

KINETICS LIBRARIES

The seed mechanisms are stored in `$RMG/databases/RMG_database/kinetics_libraries/`

Currently, the reaction library that are included in RMG are: the Leeds' oxidation library the GRI-Mech 3.0 mechanism (w/o the nitrogen-containing species and the lumped C3H7 species) and the Glarborg combustion mechanism for C1 - C3 species.

7.1 GRI-Mech 3.0

GRI-Mech 3.0 mechanism (w/o the nitrogen-containing species and the lumped C3H7 species)

7.2 Glarborg

RMG provides the option to use the rate coefficients in the master chemical mechanism developed by Peter Glarborg and coworkers at the Technical University of Denmark. The data are in the directory databases/kinetic_libraries/Glarborg. Within this directory are four subdirectories – C0, C1, C2, and C3 – where the index refers to the carbon number. The mechanisms are hierarchical in nature, so the contents of C0 are contained in C1, C1 in C2, and so forth. The C0 and C1 mechanisms include many small molecule reactions that would not necessarily fit the reaction families of RMG; consequently, they are useful Seed Mechanisms. The C2 and C3 mechanisms are optimized for high-temperature oxidation, and many of the species in the C2 and C3 mechanisms are relevant only for high-temperature chemistry. Therefore, if you are developing a mechanism for low- or moderate-temperature oxidation, it is suggested that you use C2 or C3 as a Primary Kinetic Library, rather than a Seed Mechanism. Details of the mechanism can be obtained in these three papers and references therein.

Experimental measurements and kinetic modeling of CO/H-2/O-2/NO, conversion at high pressure. Rasmussen CL, Hanson J, Marshall P, Glarborg P IJCK, 2008, 40, 8, 454-480 DOI: 10.1002/kin.20327

Experimental Measurements and Kinetic Modeling of CH4/O-2 and CH4/C2H6/O-2 Conversion at High Pressure. Rasmussen CL, Jakobsen JG, Glarborg P IJCK, 2008, 40, 12, 778-807 DOI: 10.1002/kin.20352

Experimental and kinetic modeling study of C2H4 oxidation at high pressure. Lopez JG, Rasmussen CL, Alzueta MU, Gao Y, Marshall P, Glarborg P Proc. Comb. Inst. 2009, 32, 367-375 DOI: 10.1016/j.proci.2008.06.188

CHAPTER

EIGHT

RUNNING RMG

8.1 Running RMG from the Command Line in Linux

This section assumes that RMG is already installed according to the directions in Section *Linux Installation*. Additionally, it is assumed that you have created a directory (either in your home directory or elsewhere) in which the initialization file `condition.txt` has been placed. In the example, we assume that we have created a directory `/hexane_pyro`, which contains the condition file `hexane_pyro.txt`.

1. Change the current working directory to the directory with the condition file:

   ```
   $ cd /hexane_pyro/
   ```

2. Run the following Java command to launch the program (all one line):

   ```
   $ java -Xmx500m -classpath $RMG/bin/RMG.jar RMG hexane_pyro.txt > output.log &
   ```

When RMG is started, it creates ten subdirectories in the directory containing the condition file: `therfit`, `chemkin`, `fame`, `chemdis`, `fit3p`, `frankie`, `GATPFit`, `ODESolver`, `InChI` and `Restart`.

In this example, all of the output from RMG is piped to a file `output.log`. The `> output` part of the command is optional but recommended. The Java option `-Xmx500m` is hardware specific. In this example, we assume that we can allot five hundred megabytes of memory for Java Virtual Machine running RMG; please consult a guide to Java for more information. On unix systems we recommend allocating less than half of your available virtual memory, because of the way the Java Virtual Machine forks processes.

To see the content of the output file as it is being generated, use the command: `$ tail -f output.log`.

8.2 Running RMG from the Command Line in Windows

To run RMG in Windows: Open a DOS-prompt, change the current working directory to the directory with the condition file, and run the following Java command to launch the program. In this example, the condition file is located in a (new) folder named conditionFiles:

```
cd "%rmg%"\conditionFiles
java -Xmx500m -jar "%rmg%"\bin\RMG.jar condition.txt
```

Note: The name of the input file does not have to be `condition.txt`

8.3 Running RMG using Batch Scripts in Windows

As of version 3.2, several batch scripts have been provided to make running RMG on Windows more straightforward. These can be found along with the example condition files in the `examples` directory. There are currently three such scripts:

- `RMG.bat` - For running general RMG mechanism generation jobs
- `PopulateReactions.bat` - For generating possible reactions and kinetics of a set of species
- `ThermoDataEstimator.bat` - For estimating the thermodynamics of a set of species

The easiest way to use them is:

1. Create the condition or input file for the job you wish to run. For general RMG jobs this file should be named `condition.txt`. For other jobs this file should be named `input.txt`.
2. Copy the batch script corresponding to the job you wish to run to the folder containing the condition file. For best results, this folder should only contain the condition file and the batch script at this step. The batch script will happily overwrite existing files if they correspond to files created by RMG, including the results of a previous RMG run.
3. Double-click the batch script to start the job. A console window will appear. After a few seconds a line of text should appear that tells you the job has been started. If RMG is not setup correctly, an error message will appear instead telling you what needs to be done. As the job runs, output will be sent to the file `RMG.log` in the same directory as the condition file.
4. Close the console window when the job is finished. The batch script will print a line of text when the job is completed. This line of text does not reflect whether or not the job was successful; check the tail of `RMG.log` for that information.

CHAPTER

NINE

ANALYZING THE OUTPUT

9.1 RMG Output Files

RMG will generate several types of output files, each with a different purpose. These files will be located in the directory which contains the condition file. Generally, there are five outputs from RMG (six if pressure-dependence is turned on):

1. `output.txt`. This is a large file that shows the many steps RMG went through to build the model, including the addition of each new species, concentrations and fluxes at all of the reported integration time steps, and generally the details as RMG builds the mechanism. It is useful for debugging if a problem occurs, but other output files are better if all you care about is the final model and its behavior. This file also lists the input file at the beginning.

2. `Final_Model.txt`. As its name would imply, this file contains the details of the final model created by RMG. This file reports the concentration and mole fraction profiles of all "core" species, based on the time step information (the "TimeStep" or "Conversions" field) provided in the `condition.txt` file. This data can easily be pasted into a spreadsheeting program for analysis and plotting.

   The next set of information contained in the file is a list of all reactions included in the model, along with the modified Arrhenius parameters used for each reaction. For information on where these Arrhenius parameters came from (i.e. which reaction family), consult the `chem.inp` file. This set of data may also be pasted into a spreadsheeting program easily.

   Some of the reactions listed in the `Final_Model.txt` file may not have Arrhenius rate coefficient expressions; these reactions are pressure-dependent reactions generated by RMG. The pressure-dependent rate coefficient expression for each of these reactions is located in the `chem.inp` file.

   The next set of information contains the flux of each reaction, for each time step provided in the `condition.txt` file. A negative flux means the reverse reaction (as written) was dominant.

   The last set of information is the total running time. If sensitivity information was requested, it would also appear in this file.

3. `chem.inp` (located in `$RMG/chemkin`). This file contains the CHEMKIN model and associated thermodynamic data. The file lists the elements, species, thermodynamics data (in NASA-7 polynomial form), and reactions (without N2, Ar, He, or Ne) for the model.

If a species thermochemistry came from a Primary Reaction Library, a comment will precede the NASA-7 polynomial, stating which Primary Reaction Library it came from and the name of the species as identified in the Primary Reaction Library. For example:

```
!Primary Thermo Library: GRIMech3.0 (Species ID: s00009193)
CH4(2)                  C   1H   4          G   300.000  5000.000   995.043    1
 1.20933782E+00 1.07635862E-02-3.69789759E-06 5.80285027E-10-3.41693862E-14    2
-9.79206547E+03 1.24619300E+01 3.63765769E+00-2.58941555E-03 2.18452253E-05    3
-2.01605036E-08 6.08817863E-12-1.00975312E+04 1.65214016E+00                   4
```

This comment informs the user the species thermochemistry came from the species labeled "s00009193" in the GRIMech3.0 Primary Reaction Library.

A comment follows each reaction in the `chem.inp` file. The comments are usually of the following two forms:

```
C5H7J(13)+CH3J(14)=HXD13(1) 2.4874006e+15        -0.90000        0.25000         !R_Re
C5H7J(85)=C5H7J(13) 4.0800000e+05        1.91990         7.89680         !intra_H_migr
```

The first set of characters after the "!" reflect which reaction family the modified Arrhenius parameters came from. The next set of characters is either "exact" or "estimate"; this will be explained in further detail shortly. If the numbers are an "estimate", the word "Average:" will follow. The last set of characters are the functional groups RMG classified for this reaction.

If the kinetics are "exact", this means RMG has a number in its database for the set of functional groups listed. In the previous example, RMG found kinetics in the "intra_H_migration" reaction family for the set of nodes: {R5H_DSMS, Cd_rad_out_singleH, Cs_H_out_2H}.

If the kinetics are an "estimate", RMG did not find numbers for the set of functional groups listed. Thus, RMG could not find kinetics in the "R_Recombination" reaction family for the set of nodes: {C_rad/H2/Cd, C_methyl}. So, an averaging scheme was performed to generate the reported modified Arrhenius parameters.

The previous two examples were generated by setting the "Verbose" field in the `condition.txt` file "off". If the user sets the "Verbose" field "on":

```
C5H7J(13)+CH3J(14)=HXD13(1) 2.4874006e+15        -0.90000        0.25000         !R_Re
```

If you wish to immediately run the generated `chem.inp` file in CHEMKIN, please set the "Verbose" field to off; some of the "Average of: ..." comments span too many characters for the CHEMKIN Pre-Processor to handle.

Lastly, if the reaction (and thus, kinetics) came from a Reaction Library or Seed Mechanism, the comments will reflect this. If the reaction was generated by RMG, but the kientics were taken from a Primary Kinetics Library, that information will also be reported here.

4. `RMG_Dictionary.txt`. This file lists all the species by name that are used in the model, as well as their adjacency list; if the *InChI generation feature* is turned on, the file will also contain the InChI representation for each molecule. This file allows the user to see a graphical representation of all species in the model. Typically the user will copy this file to an appropriate directory so that it can be read by the RMGVE (See Section *Viewing the Species in the RMG Viewer/Editor (RMGVE)* for further details).

5. `tran.dat` (located in `$RMG/chemkin`). This file contains the estimated transport properties for all "core" species in the mechanism. The source of each species' transport data is listed at the end of the line, for example:

```
HXD13(1)            2    356.098      5.979      0.000      0.000      1.000 ! LJ parameters
CH4(2)              2    141.400      3.746      0.000      2.600     13.000 ! Primary Trans
```

   The first species' properties were estimated by RMG. The group-additivity estimated critical properties and boiling point are listed first, followed by the node names that RMG matched in performing the group-additivity method. The complete set of transport nodes may be found in `$RMG/databases/RMG_database/transport_groups/`.

   The second species' properties were read-in from a "Primary Transport Library" supplied by the user, in this case, the library named "GRIMech3.0". The name of the species RMG matched is listed at the end of the comments, in this case, CH4.

6. `tableOfRateCoeffs.txt` (located in `$RMG/chemkin`). If pressure-dependence was turned on, an additional file will be stored in `$RMG/chemkin`. This file contains the computed k(T,P) for all reactions present in the mechanism, for each temperature and pressure requested by the user in the `condition.txt` file. These rates were used to computed the reported Chebyshev or PLOG pressure-dependent rates reported in the `chem.inp` file.

9.2 Viewing the Species in the RMG Viewer/Editor (RMGVE)

When RMG has finished, it will create a file `RMG_Dictionary.txt` in the same directory as the `condition.txt` file. This file contains a list of all the core species (usually the edge species are too numerous to be of use); the core species can be viewed easily using the RMGVE. To view the core species, rename the first part of the file (this step isn't strictly necessary, but it is convenient and a good practice). The file must still end in "`_Dictionary.txt`" (e.g. `newname_Dictionary.txt`) for the RMGVE to read it. Next, copy this file to the directory `$RMG/databases/RMG_database/thermo_groups`. Once the file is in the `thermo_groups` directory, double-click on the `RMGVE 20080101.bat` file to launch the program. Please note that you must close and relaunch the program every time you add a new file to the `thermo_groups` directory. Once the RMGVE has launched, double-click on the folder `Thermo`. Your new file should appear in this directory (e.g. newname without the "`_Dictionary.txt`"). Push the "Read family" button and a new window should appear with a list of names. Highlight any name and click "View" to see its structure.

CHAPTER

TEN

MODIFYING THE RMG DATABASES

10.1 Editing the Thermodynamic Database

As mentioned in Section *Primary Thermo Library*, it is possible to override the default thermodynamic values and substitute your own thermodynamic data.

10.1.1 Basic Structure of the Thermo Database

The thermodynamics database consists of three sections, each of which is an ASCII file that can be edited to alter the information. This description applies to non-radical groups. There are other tree/library/dictionary files for radical groups, ring corrections, and other corrections. The nomenclature is different, but they would be edited in a similar way. The files of interest are located in the directory: `$RMG/database/RMG_database/thermo_groups/`. The three files are described below.

Dictionary File

`Group_Dictionary.txt` contains the name and adjacency list (structure) for all of the nodes contained within the thermo tree. The nomenclature within all three files must be identical. The asterisk "*" denotes the central atom in the group for which the group value is defined. The format for each line in the adjacency list is: atom #, * if central atom, element, # of radicals (0, 1, 2) on element, bonding:

```
Cb-(Cd-Cdd-Cd)
1 * Cb    0  {2,S}
2   Cd    0  {1,S} {3,D}
3   Cdd   0  {2,D} {4,D}
4   C     0  {3,D}
```

Tree File

`Group_Tree.txt` defines the tree structure of the database. The nodes at any particular level are defined by including the text "`Lx:`" prior to the name of the group at that node, where "`x`" is a number corresponding to the level in the tree. A sample is given below:

```
L0: R
  L1: C
    L2: Cbf
      L3: Cbf-CbCbCbf
    L2: Cb
      L3: Cb-H
      L3: Cb-Os
      L3: Cb-C
        L4: Cb-Cs
        L4: Cb-Cd
          L5: Cb-(Cd-Od) // Cb-CO
          L5: Cb-(Cd-Cd)
            L6: Cb-(Cd-Cd) // Cb-Cd
        L4: Cb-Cb
    L2: Ct
```

Note that the indentation is not necessary because it is the "`Lx:`" that the computer reads, but is very helpful in making these files human readable.

Library File

`Group_Library.txt` is the archive of the actual data associated with a given group in the tree and dictionary. There are 15 (space or tab separated) fields in the thermo library to describe the group. The units for enthalpy are kcal/mole, and the units for entropy and heat capacity (Cp) are cal/mole-K. The columns are described in the table *"Library File Definitions"*.

Table 10.1: Table: Library File Definitions

Column	What it contains
1	A unique number; this does not correspond to any other part of the thermo database, but numbering sequentially is most logical
2	Group name; same as in tree and dictionary
3-4	Enthalpy and Entropy at 298K
5-11	Cp at T = 300, 400, 500, 600, 800, 1000, and 1500K
12-13	dH and dS: absolute uncertainties in the enthalpy/entropy estimates
14	dCp: absolute uncertainty in the Cp estimate (no temperature consideration)
15	Comments Section: usually citing the source of the data or comments on the reliability

A sample entry can be found in Section *Editing the Data for an Existing Thermo Functional Group*.

10.1.2 Thermo Database and Adjacency List Notation

In general, the thermo database uses what are known as function group elements. Function group elements serve to define the atom and its bonding environment. These definitions serve to simplify the adjacency lists of groups and allow for more general descriptions of groups. The notation used in the database is shown below. New functional group elements cannot be added to RMG in a simple way, as they must be hard-coded into the RMG software with the appropriate properties.

If you examine the file `Group_Dictionary.txt`, you will see that these groups are used extensively, even more so that the actual atoms C, H, or O. You will also see that groups can be defined using a bracketed notation, which simply means that either atom/functional group element will generate this node. For example:

```
Cb-Cd
1 * Cb        0   {2,S}
2   {Cd,CO}   0   {1,S}
```

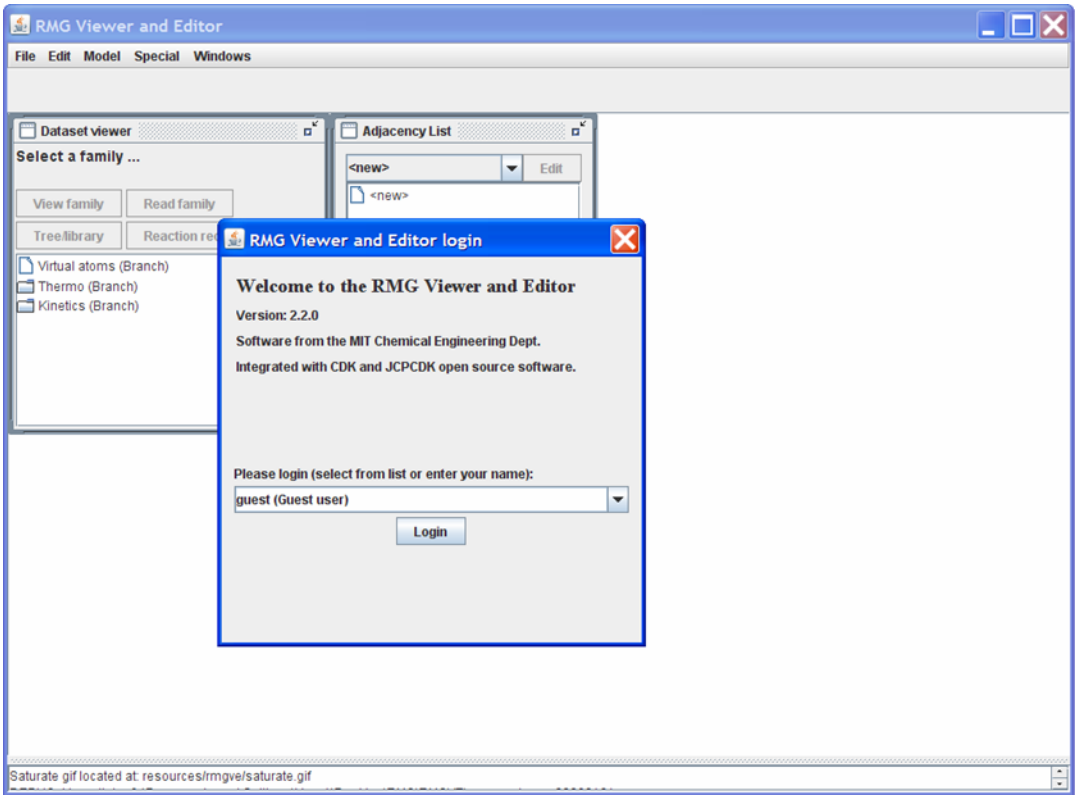
In this example, the second "element" is actually either Cd or CO. The reason that either Cd or CO will generate the same node is because both fall under the more general Cd definition, which is a carbon atom with one double and two single bonds. This can also be useful if there is a secondary effect and all that matters is that there is a π-bond present, but the fact that it is C=O or C=C does not matter. This is not used very much in the thermo database, but occurs much more in the kinetics databases where radical delocalization can play a major role in determining the rate constant of a reaction. A table of the possible functional groups can be seen in the table *"Functional Group Elements"*.

Table 10.2: Table: Functional Group Elements

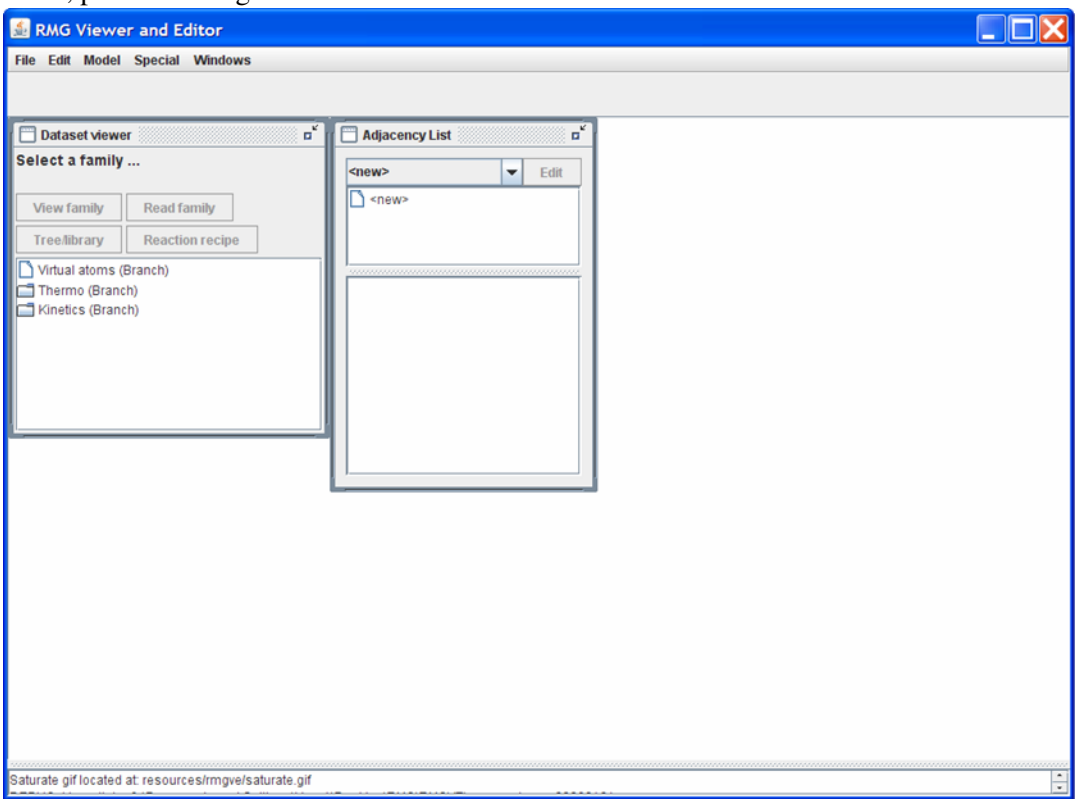
Symbol	Definition
Cs	Carbon bonded to four single bonds
Cd	Carbon bonded to a double bond and two single bonds. (The other end of the double bond is carbon)
Cdd	Carbon bonded to two double bonds
Ct	Carbon bonded to a triple bond and single bond
Cb	Carbon bonded to two benzene bonds and a single bond. (The carbon belongs to only one benzene ring)
Cbf	Carbon bonded to three benzene bonds (the carbon belongs to two or three benzene rings)
CO	Carbon bonded to a double bond and two single bonds. (The other end of the double bond is oxygen)
Os	Oxygen bonded to two single bonds
Od	Oxygen bonded to a double bond
Oa	Oxygen triplet
R	Any atom
R!H	Any non-hydrogen atom

10.1.3 Viewing a Thermo Functional Group in the RMGVE

Open the RMG Viewer & Editor (RMGVE) by running the `RMGVE 20080101.bat` file. If your RMG database is located in the `$RMGdatabaseRMG_database` folder, the following login screen should appear.



The login name is used to document who made what changes in the RMG libraries. After entering your name, press the "Login" button to reveal the RMGVE.

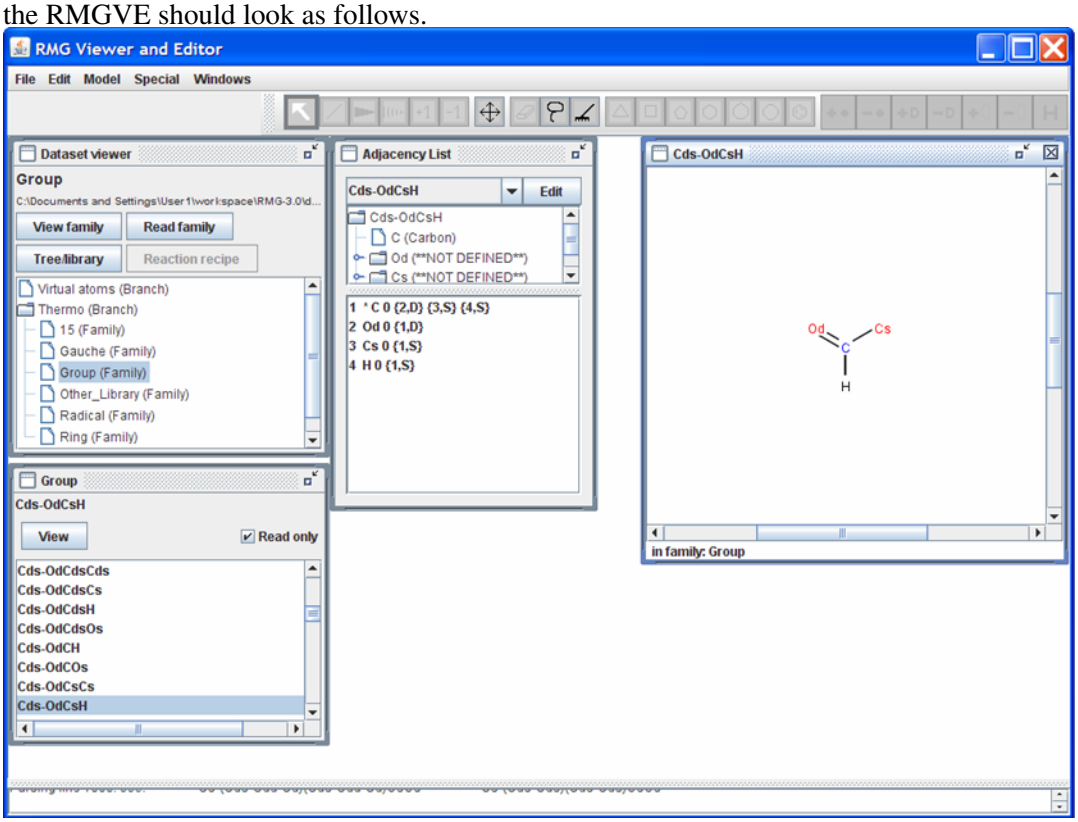


The RMGVE home screen initially has two windows open: the "Dataset viewer" and the "Adjacency List." In the "Dataset viewer" window, double-click on the "Thermo (Branch)" folder to show the different Thermo Families present in the `RMG_Dictionary` folder. To load one of the Thermo Families, either:

- double-click on one of the names OR
- highlight one of the names and then push the "Read family" button near the top of the "Dataset viewer" window

Note: Loading a family could take a few minutes, depending on how large the family is.

Once the family is loaded, a new window will pop up. The name of the window corresponds to the name of the Thermo family that was read. In the screen shot shown below, we have chosen to load the "Group" family. Use the scroll bar to see the list of functional groups contained in the "Group" family. To visualize what the different functional groups look like, highlight one of the names and then push the "View" button near the top of the "Group" window. For instance, if we select the functional group name "Cds-OdCsH," the RMGVE should look as follows.



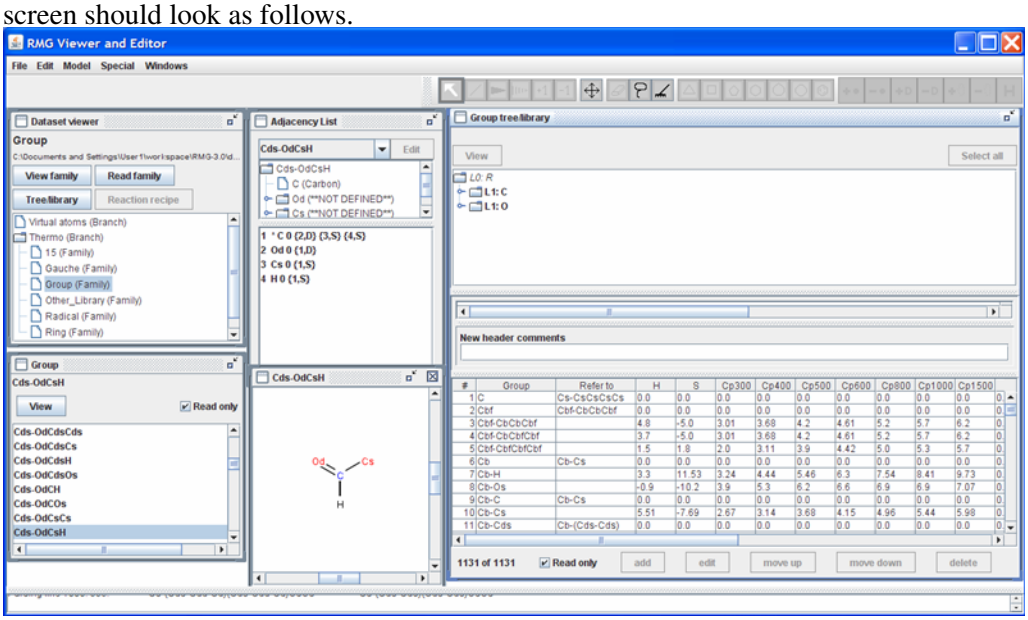
Notice that the "Adjacency List" window is no longer blank but now contains the adjacency list for the functional group "Cds-OdCsH". Furthermore, a window entitled "Cds-OdCsH" opens which contains a visualization of the functional group.

Note: Notice also that a toolbar appears above the "Dataset viewer," "Adjacency List," and "Cds-OdCsH" windows. This toolbar may be used to edit the molecule in the "Cds-OdCsH" window. For instance, click on the icon with the four arrows (pointing up, right, down, and left). Now click on one of the atoms in the "Cds-OdCsH" window and drag it to another location within the window. To restore (clean) the structure of the functional group, click on the icon containing the picture of a rake.

10.1.4 Editing the Data for an Existing Thermo Functional Group

A leaf in the thermochemistry tree may be **edited** using the RMG Viewer & Editor (RMGVE). For instructions on how to add a leaf to a thermochemistry tree, please refer to the section below entitled "Adding Additional Nodes to the Thermo Database".

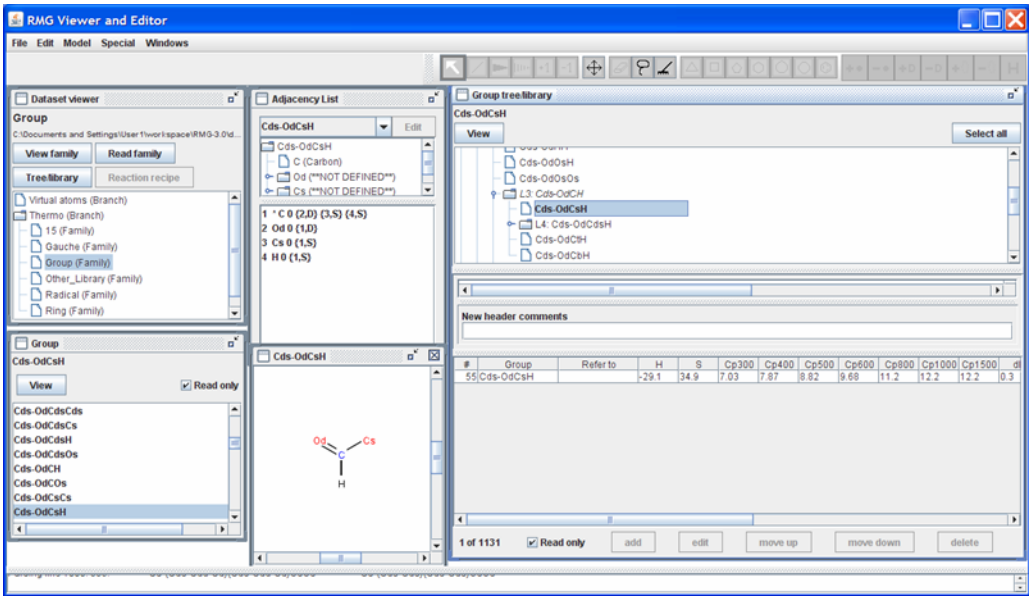
Returning to the "Dataset viewer" window, notice the "Tree/library" button has been enabled. Click on this button to show the data for the highlighted thermo family. After some re-arranging of the windows, the screen should look as follows.



The top half of the new "Group tree/library" window contains the "Group" thermo family tree; the bottom half contains the "Group" thermo family library. Suppose we want to change the thermo value for the "Cds-OdCsH" functional group. To do so, we can navigate the tree in the top half of the "Group tree/library" window by opening (double-clicking) the folders corresponding to the "Cds-OdCsH" functional group:

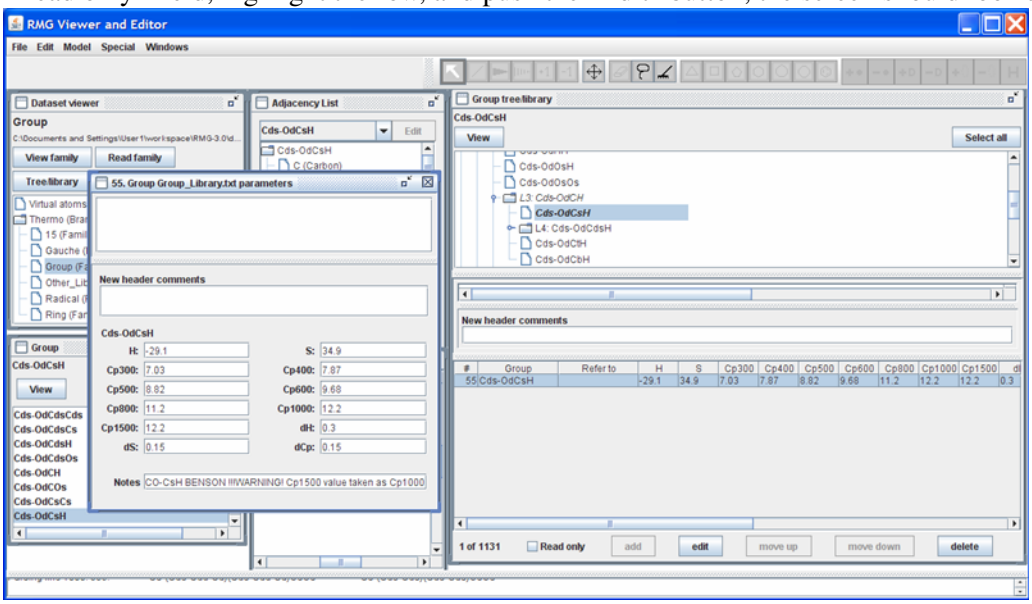
- L1: C
- L2: Cds
- L3: Cds-OdCH
- Cd-OdCsH

After navigating the tree, the RMGVE should look like the following snapshot.



Notice that RMG has thermodynamic data for this functional group. If you scroll to the right (using the scroll bar near the bottom of the "Group tree/library" window) far enough, you will see the "Notes" column. This column is used to document where the data came from. In this case, the thermodynamic data comes from the Benson defined group O=CH-Cs. Furthermore, it has been noted that the Cp1500 was assumed to be the Cp1000 value.

Suppose we had a better estimate for the Cp1500 value (e.g. 12.5 cal/mol/K). To edit this leaf, uncheck the "Read only" field, highlight the row, and push the "Edit" button; the screen should look as follows.



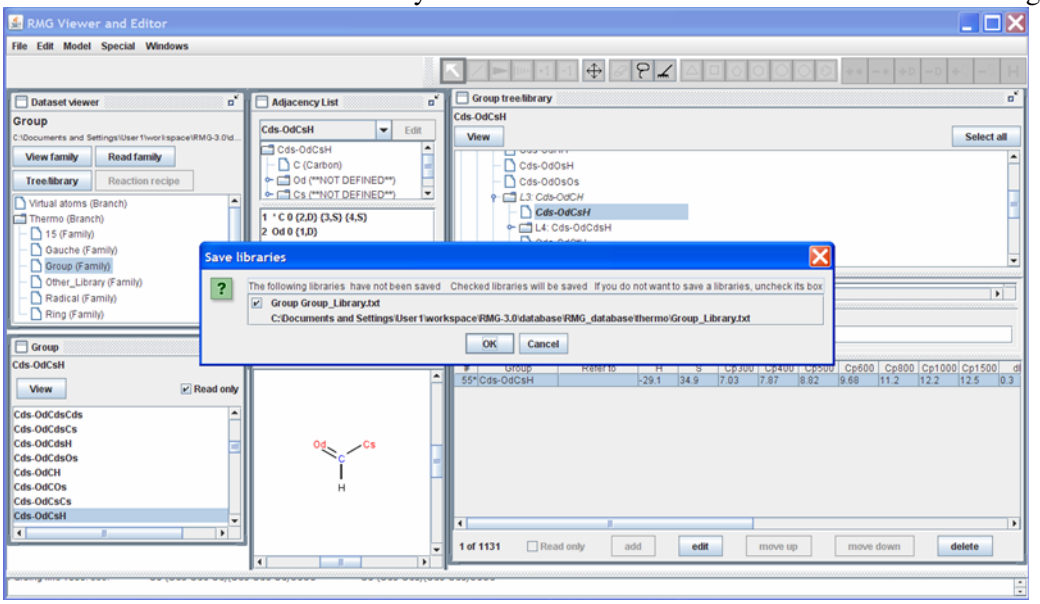
Enter the new thermochemical data (Cp1500 = 12.5) in the appropriate field. The field "Notes" will be added to the thermochemical data for the "Cds-OdCsH" functional group at the end of the line (after the 12 data entries). The field "New header comments" will be placed above the thermochemical data for the "Cds-OdCsH" functional group. Upon changing any of the thermochemical data fields, a line in the "New header comments" will automatically appear, containing your login name and the current date and time. The box immediately above the "New header comments" field shows how the RMGVE will edit the current data

in the `Group_Dictionary.txt` file. Once all data has been entered, close the window.

Returning to the "Group tree/library" window, notice the highlighted row. The thermochemical data entries have been updated and a star (*) has been placed next to the "55" value in the first column. The star (*) reflects that a change has been made.

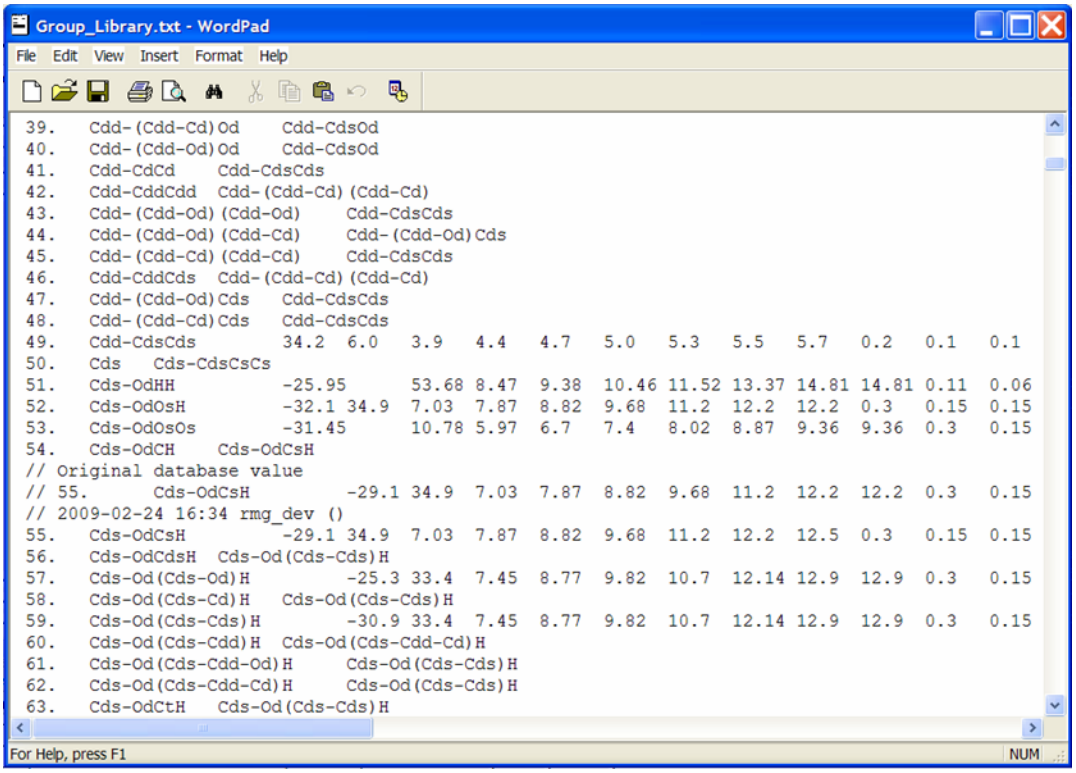
When you have completed making changes to the thermochemistry database, close the RMGVE. Upon doing so, you will be asked which changes you would like to accept and save to the `RMG_database` folder. Before pushing the "OK" button, ensure that all of the changes you want to be saved have a checkmark next to them. You will receive a message stating whether the edits were saved successfully or not. Pushing "OK" in this window will close the RMGVE.

Note: Notice the RMGVE directs you to the location of the file that is about to be changed.



Viewing the changed thermochemical data

To view the thermochemical data that was just edited, open the file from the previous screenshot: `$RMG/database/RMG_database/thermo_groups/Group_Library.txt`. Scrolling down to the entry #55, we see the old and new thermochemical data for the functional group "Cds-OdCsH".



Rather than explicitly entering data for each leaf, one may also refer one functional group to another, if you believe they should be the same. This is done by putting the name of the group that has the same thermo parameters in column 3 and leaving columns 4-15 blank. An example of this is entry #56 where we see that this leaf does not contain thermodynamic data but rather points to the functional group "Cds-Od(Cds-Cds)H," entry #59. Effectively, if RMG encounters the group and finds the name of another group instead of numerical values, it will assign the current group the same values that occur in the referred group:

```
56.     Cds-OdCdsH      Cds-Od(Cds-Cds)H
59.     Cds-Od(Cds-Cds)H                -30.9   33.4    7.45    8.77    etc.
```

The above example would assume that the group values for #56 are identical to those of #59.

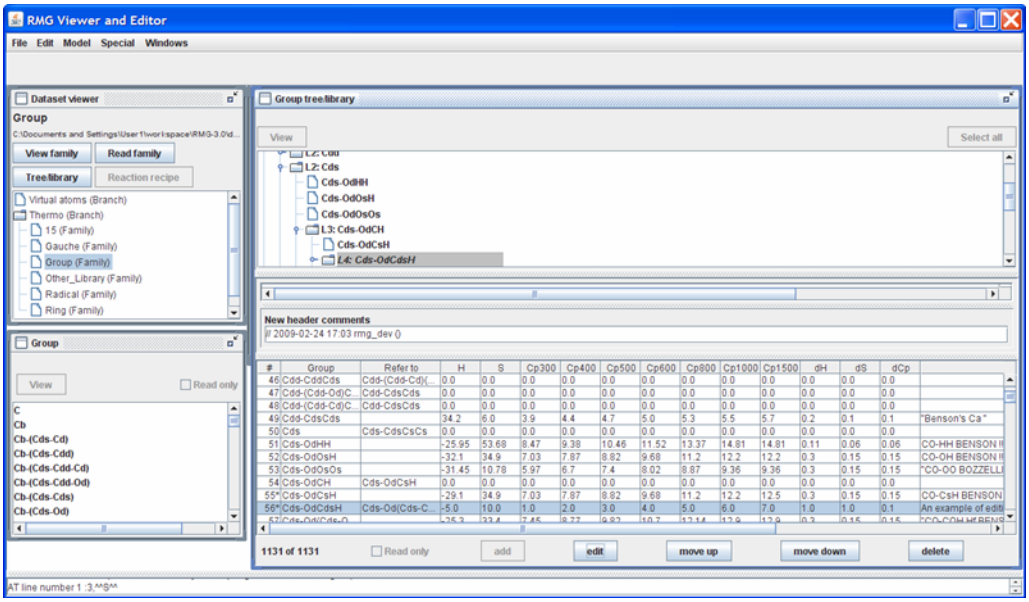
This referencing does not need to be done if the group to which you want to refer lies directly above the current group in the tree, because if the tree does not have a certain node defined it will look back up the tree to find the nearest relative and use those values:

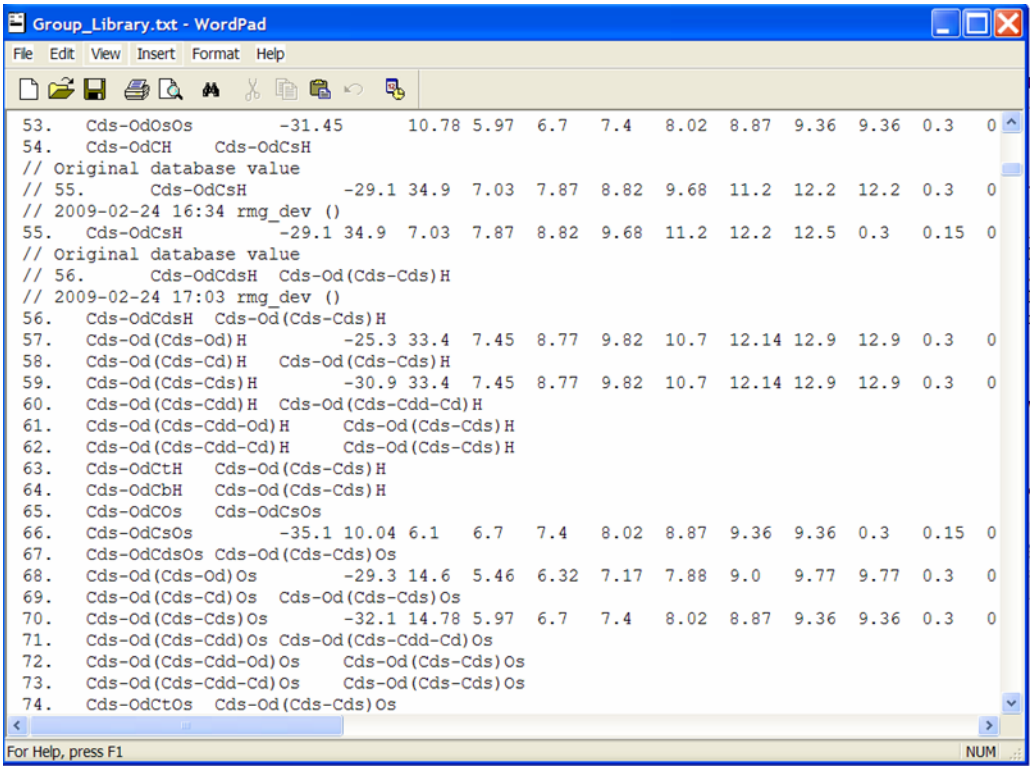
```
253   Cb-(Os-(Os-Cs))   -2.5   -8.5   etc...
254   Cb-(Os-(Os-H))    Cb-(Os-(Os-Cs))
255   Cb-(Os-(Os-(Cs-OsHH)))   Cb-(Os-(Os-Cs))
```

In this case, the referring of #255 back to #253 is unnecessary because RMG would refer back to #253 by default if it did not find any values for #255. This redundancy will not create any problems within RMG, but it is simply unnecessary.

Warning: The RMGVE can only edit leafs which already have thermochemical data stored for them. In particular:

- The RMGVE does not allow a user to change the "Refer to" field. This change must be performed manually.
- The `Group_Library.txt` file will not recognize changes made in the RMGVE to leafs that "Refer to" another species. For example, had we entered thermochemical data for entry #56, the RMGVE will show the updates to the H, S, and Cp values in the "Group tree/library" window but will also still show the "Refer to" functional group. After closing the RMGVE and confirming the change to the database, if one opened the `Group_Library.txt` file and looked at entry #56, you will notice the leaf's thermodynamic values were not updated.





Please be aware that version control may be a significant issue with the databases and should be addressed early to ensure consistency within the group.

10.1.5 Adding Additional Nodes to the Thermo Database

This task is more complicated than the previous example because it involves altering all three database files in a consistent manner, without the help of a Graphical User Interface. It is worth noting that the order in which species are added to the dictionary (`_Dictionary.txt` file) and library (`_Library.txt` file) does not matter; however, the position where the new group is added to the tree (`_Tree.txt` file) is of the utmost importance. It is useful to create the tree and dictionary with items in the same order. This ordering will facilitate cross checking and debugging if needed. Since all files must use the same nomenclature, the ability to search may make consistent ordering unnecessary. The procedure is described below.

1. Find the appropriate location to place the new group and ensure that the nomenclature is unambiguous and unique. Placing the group in the incorrect location could cause incorrect estimates to be made when the tree is being searched. Using the RMGVE to navigate the tree structure is a useful way to find the location for your new group.

2. Add the line of text to the `Group_Tree.txt` file in the following form, where "`x`" is the appropriate level. The following example is for a O-O-H off of a benzene ring.:

   ```
   Lx: Cb-(Os-(Os-H))
   ```

3. Using the same name as in the tree, append the file `Group_Dictionary.txt` to define the structure of the group and its atom center (denoted by the asterisk):

```
Cb-(Os-(Os-H))
1* Cb 0 {2,S}
2  O 0 {1,S} {3,S}
3  O 0 {2,S} {4,S}
4  H 0 {3,S}
```

4. Add the new group to the `Group_Library.txt` file using the same nomenclature and whatever thermo data you have for the group. The format was shown in the previous section.:

```
2374 Cb-(Os-(Os-H)) 3.5 10.0 ... "I added this b/c ..."
```

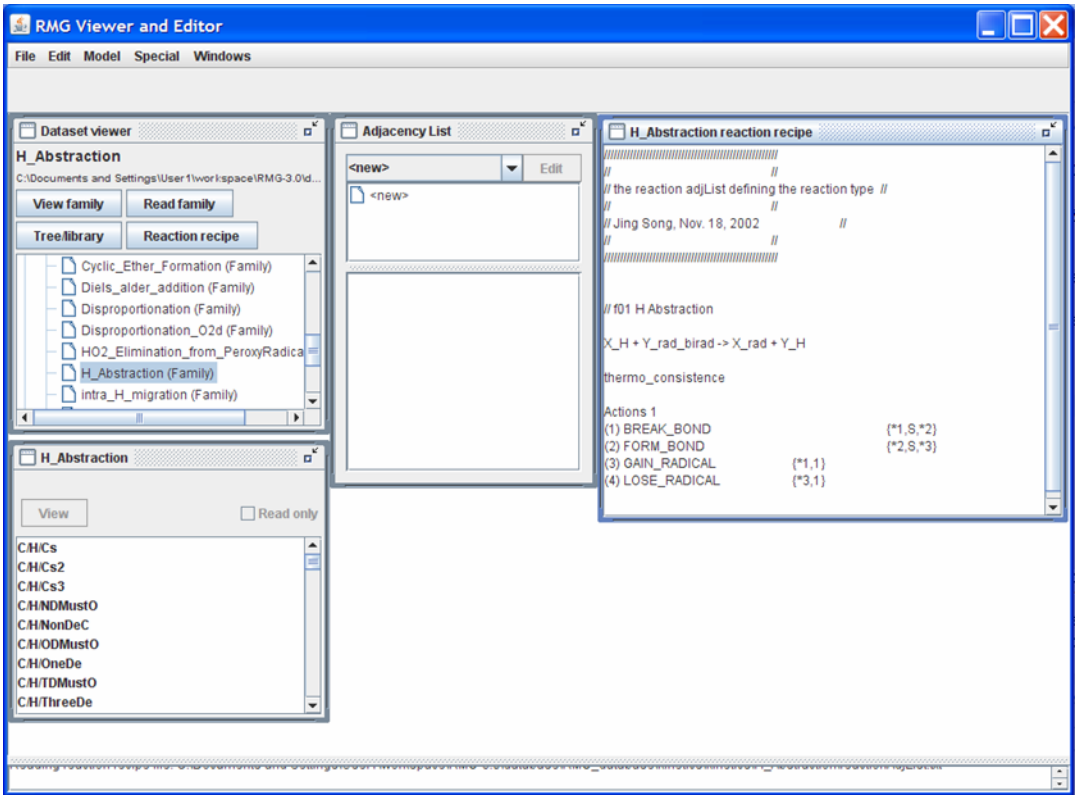
10.2 Editing the Kinetics Database

RMG's kinetics database may also be viewed and edited using the RMGVE. From the RMGVE's home screen, double-click on the "Kinetics (Branch)" folder in the "Dataset viewer" window and then double-click on the "kinetics (Family)" folder. Scroll down to the family entitled "H_Abstraction." Highlight this family and push the "Read family" button. All 4 buttons in the "Dataset viewer" window should now be active.

1. "Read family": This button reads in the functional groups pertaining to the highlighted library and displays them in a new window; the name of the new window corresponds to the thermo/kinetic family name. (Option available for both thermo and kinetics).
2. "Tree/library": This button opens a window that displays the thermochemical data for the highlighted library. (Option available for both thermo and kinetics).
3. "Reaction recipe": This button opens a window that displays the definition of the reaction family. (Option available ONLY for kinetics).
4. "View family":

10.2.1 Viewing a Reaction Recipe in the RMGVE

Push the "Reaction recipe" button. Your screen should look like the following snapshot (after rearranging and resizing the windows)

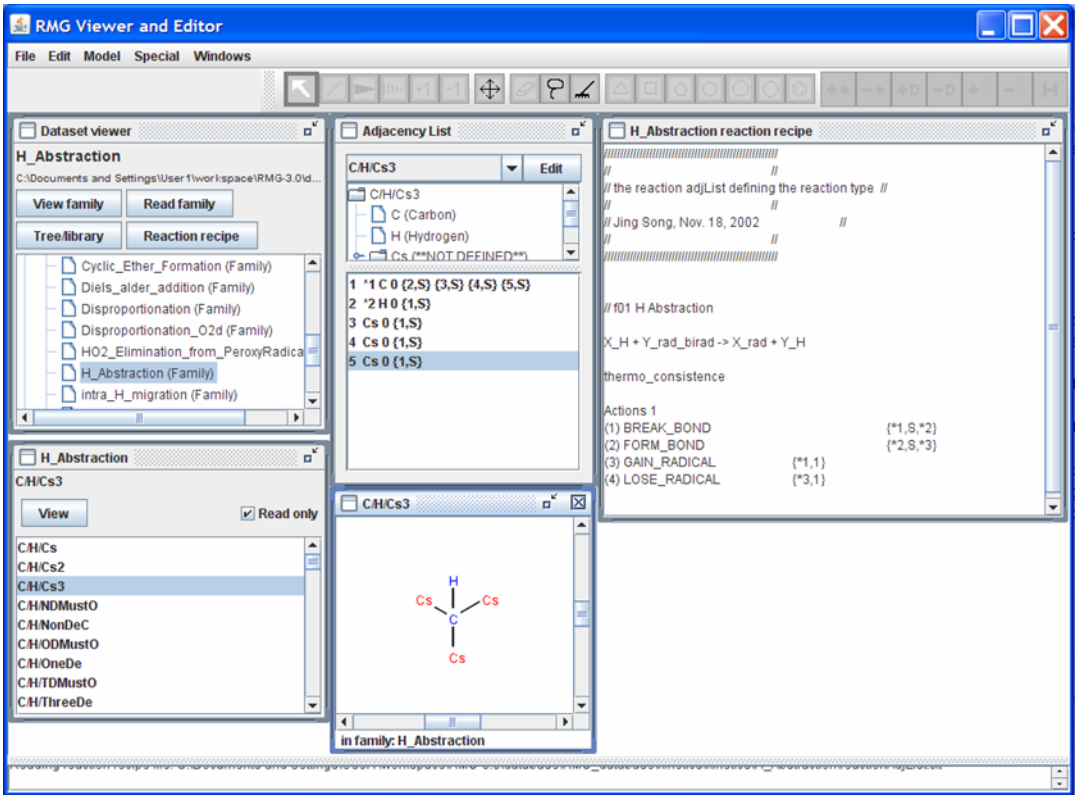


Looking at the "H_Abstraction reaction recipe" window: The first non-commented line shows the generic reaction: `X_H + Y_rad_birad -> X_rad + Y_H`. The next uncommented line informs RMG how to handle the reverse reaction. Some common occurences you will find include:

- "thermo_consistence": RMG will use the equilibrium constant to compute the reverse reaction rate
- "none": RMG assumes the reaction is irreversible
- "(f_): <rxnFamilyName>": RMG may use the forward reaction rates stored in the <rxnFamilyName> folder

The next set of uncommented lines describes the changes in the reacting molecules', "X_H" and "Y_rad_birad", connectivity graphs to form the products, "X_rad" and "Y_H". For the "H_Abstraction" reaction family, a single bond ("S") is broken between atoms "1" and "2" and a single bond ("S") is formed between atoms "2" and "3". Furthermore, atom "1" gains a radical while atom "3" loses a radical.

For a better understanding of what the atom numbering means, click on one of the species in the "H_Abstraction" window. If you click on the species "C/H/Cs3", your screen should look like the following snapshot



Looking at "C/H/Cs3" and "Adjacency List" windows reveals the identity of atoms "1" and "2". Looking at the "Adjacency List" window, notice the atoms that have the #⋆ notation between the counting index and the elemental symbol. The number before the ⋆ corresponds to the number in the reaction recipe. The atoms of interest are also shown in blue in the "C/H/Cs3" window.

10.2.2 Editing a Reaction Family using the RMGVE

Returning to the "Dataset viewer" window, click the "Tree/library" button. The bottom-half of this window contains the following kinetic information:

1. Groups: The columns entitled "Group 1", "Group 2", etc. represent the structure of the reactant(s).
2. Temp: This column contains the Temperature range (in units of Kelvin) over which the kinetic data is valid.
3. A, n, a, E0: These columns contain the modified Arrhenius parameters (A, n, E0) and the Evans-Polanyi coefficient (a). "A" has units of "mol,cm3,s" and "E" has units of "kcal/mol".:

```
The Evans-Polanyi principle states that for a series of closely-related reactions,
a linear relationship between the activation energy (Ea) and the enthalpy of
reaction (delHr) is sometimes observed and can be expressed as:

Ea = C1 + a*delHr

where C1 and a are empirically-derived constants.  For RMG, we assume C1 = 0.
```

4. dA, dn, da, dE0: These columns contain the error for the Arrhenius parameters and Evans-Polanyi coefficient. If the number is reported with a star (*) in front of it, this represents a multiplicative error; else, the error is additive.
5. Rank: This column contains the confidence the RMG developers have in the kinetic data on a scale of 1 to 5, with 1 being "very confident" and 5 being "rough estimate".
6. Notes: This column contains notes on where the kinetic data came from. The reaction library is not as well-documented as the thermo library.

Suppose we want to add a reaction rate to RMG for the following reaction:

```
H3C-CH2-CH3 + *CH3 = H3C-*CH-CH3 + CH4
```

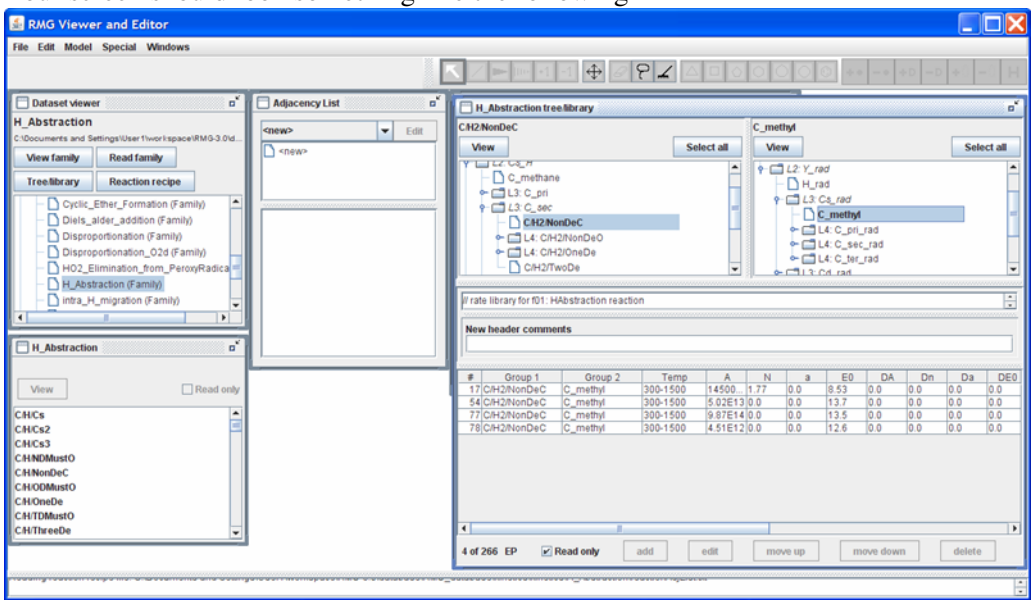
The first step would be to identify which of RMG's reaction templates the reaction of interest corresponds to. For our case, the reaction template we want is "H_Abstraction". The next step is to find the pair of nodes in the tree that correspond to the reaction of interest. Looking at the tree, we need to identify a "X_H" and "Y_rad_birad". For the example, "X" is the central carbon of propane and "Y" is the methyl radical. Traversing down the "X_H" tree leads us to the following node:

```
L1: X_H
L2: Cs_H
L3: C_sec
C/H2/NonDeC
```

If you are ever uncertain of the structure of one of the nodes, highlight it and push the "View" button to open a window with a 2-d graphical depiction of the species. Traversing the "Y_rad_birad" tree leads us to:

```
L1: Y_rad_birad
L2: Y_rad
L3: Cs_rad
C_methyl
```

Your screen should look something like the following

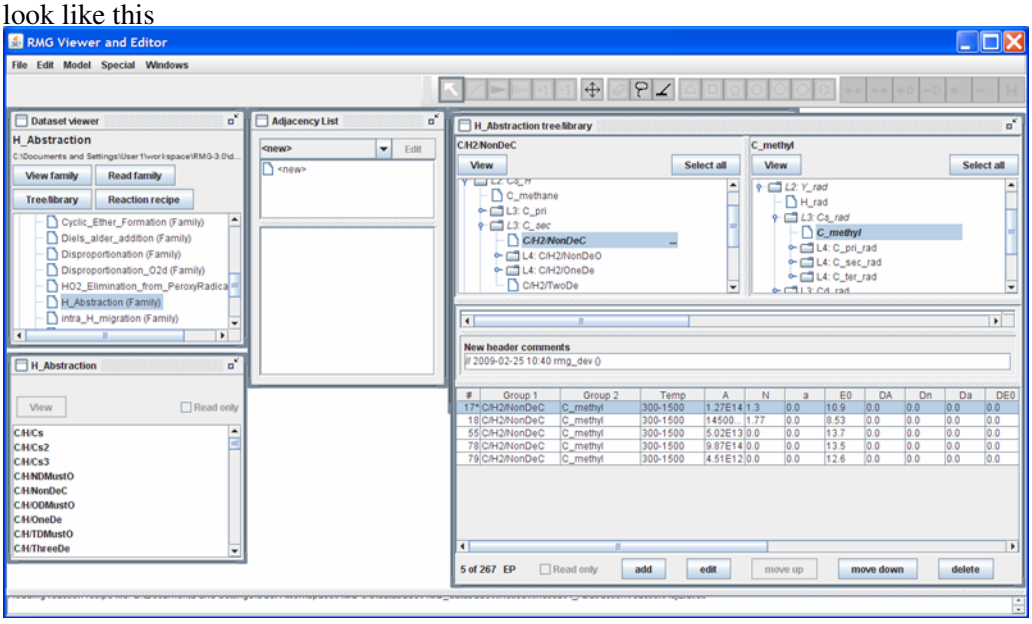


Notice that RMG contains 4 different sets of kinetic data for this reaction. There are two explanation for this:

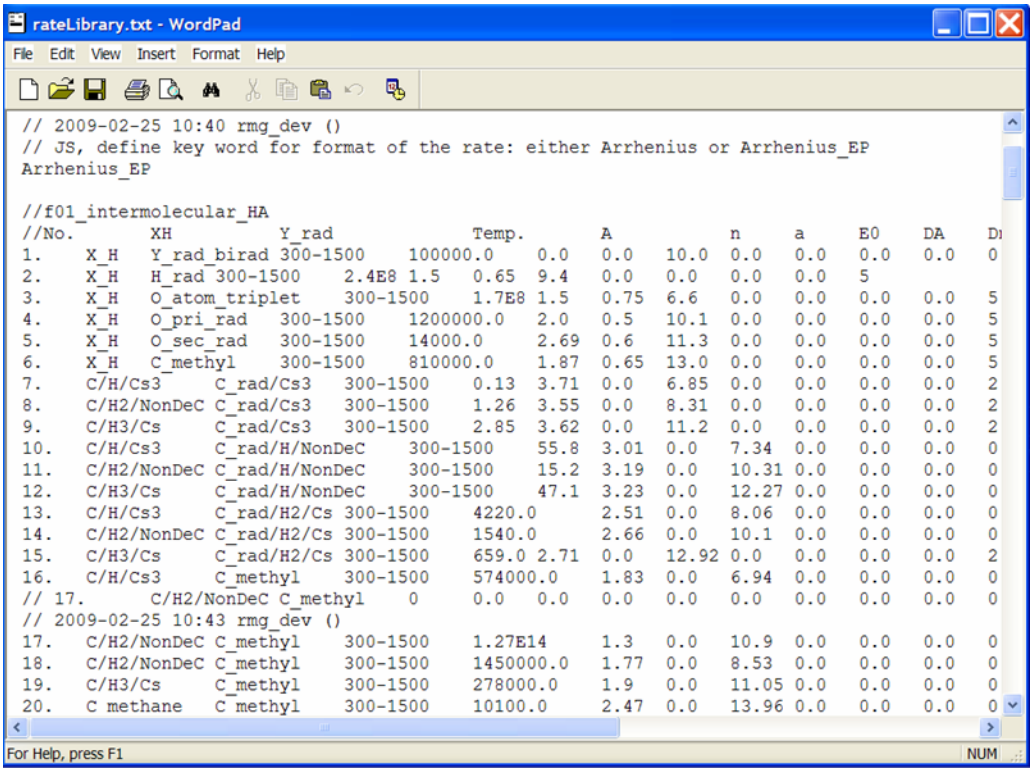
1. The reaction rates all pertain to the same reaction: The different values could pertain to experimental vs. theoretical values or differing basis sets in the theoretical calculations (e.g. using an ab initio quantum chemistry sofware package)
2. The reaction rates pertain to different reactions: Notice that the "X_H" leaf is only defined as "C/H2/NonDeC". Thus, one of the reaction rates could correspond to the methyl radical abstracting a Hydrogen atom from:
   - propane to form the iso-propyl radical
   - butane to form the sec-butyl radical
   - ...

For RMG's reaction library, the order in which the reactions appear in the `rateLibrary.txt` file is significant. RMG will use the kinetic data for the first instance of the reaction of interest that it finds. If you click on one of the 4 reaction rates, you'll notice that the RMGVE gives you the option of "edit"ing or "delete"ing the entry (as it did for the Thermo library) but it also gives you the option to "move up" or "move down" the reaction rate.

We can also add a new entry, by pushing the "add" button. For example, let's suppose we have the following modified Arrhenius parameters for the reaction mentioned above: A = 1.27E14 cm3/mol/s, n = 1.3, E = 10.9 kcal/mol over the temperature range 300-1500K. Push the "add" button, then push the "edit" button, and then fill in the popup window with the kinetic data. After closing the popup window, your screen should look like this



Close the RMGVE. A popup window will ask if you want to save the changes you have made. If you leave the box checked and then open the `$RMG/database/RMG_database/kinetics_groups/H_Abstraction/rateLibrary.txt` file, you should see that the file has been updated.



10.3 Creating a Primary Reaction Library / Seed Mechanism

Primary reaction libraries and seed mechanisms are all stored in `$RMG/databases/RMG_Database/kinetics_libraries/`

A primary reaction library / seed mechanism may consist of five files:

- `species.txt`
- `reactions.txt`
- `3rdBodyReactions.txt`
- `lindemannReactions.txt`
- `troeReactions.txt`

The `species.txt` file is **required**. All other files are optional, and if present, must include the Unit declaration and Reaction headings.

1. The `species.txt` file is a series of molecular names and connectivity lists, analogous to the formats used in the input file `condition.txt`. All species present in the four remaining files must be given a structure in `species.txt`. The structure should have the same format as the adjacency list shown in *Creating a condition file*. Please note that the names that are used in the reaction library will be those used throughout the mechanism. In this manner, the user can adopt a preferred nomenclature for individual species.

2. The `reactions.txt` file defines the standard non pressure-dependent reaction. The file has the structure shown in the following sample. Comments are denoted with "//" and are ignored by the RMG parser.:

```
// Define the units
// Units allowed for A are: "mol/liter/s" or "mol/cm3/s"
// Units allowed for E are: "kcal/mol", "cal/mol", "kJ/mol", or "J/mol"

Unit:
A: mol/cm3/s
E: kcal/mol

Reactions:
// The format is:
// R1 + R2 + R3 <=> P1 + P2 + P3        A       n       E       dA      dn      dE
//      where R1, R2, R3, P1, P2, P3 are species; A, n, and E are the Arrhenius
//      parameters, and dA, dn, dE are the errors in those parameter (normally
//      additive, but can also be multiplicative if a * comes before the number).
//      A "<=>" or "=" represents a reversible reaction and a
//      "=>" or "->" represents an irreversible reaction.
O2 + CO = CO2 + O 1.26E13 0.00 196.90 *1.7 0 0
```

3. The `3rdBodyReaction.txt` file lists reactions involving a third body (bath gas). A sample file, with a 3rd-body reaction, is listed below. The first line defines the reaction using the same format as in `reactions.txt`. The next line lists collision efficiencies for various bath-gas species that scale the concentrations of particular species when calculating the total bath gas concentration. In the example below, CH4 is particularly effective as a 3rd body, and its effective concentration is tripled.:

```
// Define the units
// Units allowed for A are: "mol/liter/s" or "mol/cm3/s"
// Units allowed for E are: "kcal/mol", "cal/mol", "kJ/mol", or "J/mol"

Unit:
A: mol/cm3/s
E: kJ/mol

Reactions:
CO + O + M = CO2 + M 1.54E15 0.00 12.56 *1.2 0 0
N2/0.4/ O2/0.4/ CO/0.75/ CO2/1.5/ H2O/6.5/ CH4/3.0/ C2H6/3.0/ AR/0.35/
//      the first line defines the reaction and Arrhenius parameters,
//      while the second gives the scaling factors for different bath gas species
//      which contribute to [M].
```

4. The `lindemannReaction.txt` file allows specifying pressure-dependent reactions, according to the Lindemann expression. The format of each reaction is the same as is used by CHEMKIN. For example:

```
Unit:
A: mol/cm3/s
E: cal/mol

Reactions:
```

```
O + CO (+M) <=> CO2 (+M)        1.800E+10     .000    2385.00   0.0     0.0     0.0
H2/2.00/ O2/6.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/3.50/ C2H6/3.00/ Ar/ .50/
LOW/ 6.020E+14     .000    3000.00/

//      the first two lines are similar to the 3rdBodyReaction.txt format
//      the next line specifies the low pressure limit Arrhenius parameters
```

5. The `troeReactions.txt` file allows specifying pressure-dependent reactions according to the Troe expression. The format of each reaction is the same as is used by CHEMKIN. For example:

```
Unit:
A: mol/cm3/s
E: kJ/mol

Reactions:
C2H2 + H (+M) = C2H3 (+M) 8.43E12 0.00 10.81 *1.2 0 0
N2/0.4/ O2/0.4/ CO/0.75/ CO2/1.5/ H2O/6.5/ CH4/3.0/ C2H6/3.0/ AR/0.35/
LOW / 3.43E18 0.0 6.15 /
TROE / 1 1 1 1231 /

//      the first three lines are similar to the lindemannReaction.txt format
//      the next line specifies the 3 or 4 Troe parameters
//      in the order: a, T***, T*, T** (the last parameter is optional).
```

CHAPTER

ELEVEN

REPRESENTING OXYGEN

Special care should be taken when constructing a mechanism that involves molecular oxygen. The ground electronic state of molecular oxygen, $^3\Sigma_g^-$, does *not* contain a double bond, but instead a single bond and two lone electrons. In RMG's adjaceny list notation the ground state of oxygen is represented as

```
(1) O2 0.1 (mol/cm3)
1 O 1 {2,S}
2 O 1 {1,S}
```

You should use the above adjacency list to represent molecular oxygen in your condition files, seed mechanisms, etc. The triplet form is 22 kcal/mol more stable than the first singlet excited state, $^1\Delta_g$, which does contain a double bond. The adjacency list for singlet oxygen is

```
(1) O2 0.1 (mol/cm3)
1 O 0 {2,D}
2 O 0 {1,D}
```

Selecting the correct structure for oxygen is important, as the reactions generated from a double bond are significantly different than those generated from a radical or diradical. For example, the reaction

$$CH_4 + O_2 \rightarrow CH_3 + HO_2$$

would occur for both triplet and singlet oxygen, but in entirely different families. For triplet oxygen the above represents a hydrogen abstraction, while for singlet oxygen it represents the reverse of a disproportionation reaction.

Previous versions of RMG databases were ambiguous as to the treatment of oxygen, with both ChemGraphs above representing ground-state oxygen. The database provided with RMG 3.2 has been modified to make all of the oxygen-related chemistry that was present in RMG databases consistent with the single-bonded biradical representation.

Conversion between triplet and singlet forms is possible through the primary reaction library `OxygenSingTrip`; the reactions involved are very slow, however, and are likely to be absent from any mechanisms generated. At this point, no other reactions of singlet oxygen have been included in RMG.

CHAPTER

TWELVE

ESTIMATING SPECIES THERMOCHEMISTRY

The `ThermoDataEstimator` utility produces group additivity-based thermochemistry estimates without running RMG. As with the thermochemistry estimates used by RMG, the `ThermoDataEstimator` utility bases its estimates on group values located in the RMG database.

12.1 Instructions for Use

1. Create a text file named `thermo_input.txt` (or some other name of your choice) in any directory that you like. If a `GATPFit` folder does not already exist in this directory, make it using the following command:

   ```
   mkdir GATPFit
   ```

The text file should begin with a block to specify a PrimaryThermoLibrary, which may be left empty if desired:

```
PrimaryThermoLibrary:
END
```

Next, in the text file, create the adjacency list(s) corresponding to the molecule(s) of interest using the same syntax used to define a species in the `condition.txt` input file (see RMG manual). Hydrogens can be omitted for simplicity. For example, the adjacency list for 2,2,4,4-tetramethylpentane could be written as:

```
1 C 0 {2,S}
2 C 0 {1,S} {3,S} {4,S} {5,S}
3 C 0 {2,S}
4 C 0 {2,S}
5 C 0 {2,S} {6,S}
6 C 0 {5,S} {7,S} {8,S} {9,S}
7 C 0 {6,S}
8 C 0 {6,S}
9 C 0 {6,S}
```

1. At the command prompt, change directory to the location of the `thermo_input.txt` file and `GATPFit` folder and then execute the command

   ```
   $ java -classpath "%rmg%"\bin\RMG.jar ThermoDataEstimator thermo_input.txt
   ```

   To have output written to file instead of to the screen, use the syntax

   ```
   $ java -classpath "%rmg%"\bin\RMG.jar ThermoDataEstimator thermo_input.txt > thermo_ou
   ```

   where `thermo_output.txt` is the name of the file to be written.

1. The program will read RMG's thermodynamics database, count groups, and output the NASA polynomials in CHEMKIN format, as well as another set of values labeled ThermoData. The format for ThermoData is

   $\Delta H_{f,298}$ S_{298} $C_{p,300}$ $C_{p,300}$ $C_{p,400}$ $C_{p,600}$ $C_{p,800}$ $C_{p,1000}$ $C_{p,1500}$

   Units are kcal/mol for $\Delta H_{f,298}$ and cal/mol*K for the other quantities (entropy and heat capacity). The symmetry number (including contributions from internal rotations) will also be displayed.

CHAPTER

THIRTEEN

THEORY AND IMPLEMENTATION DETAILS

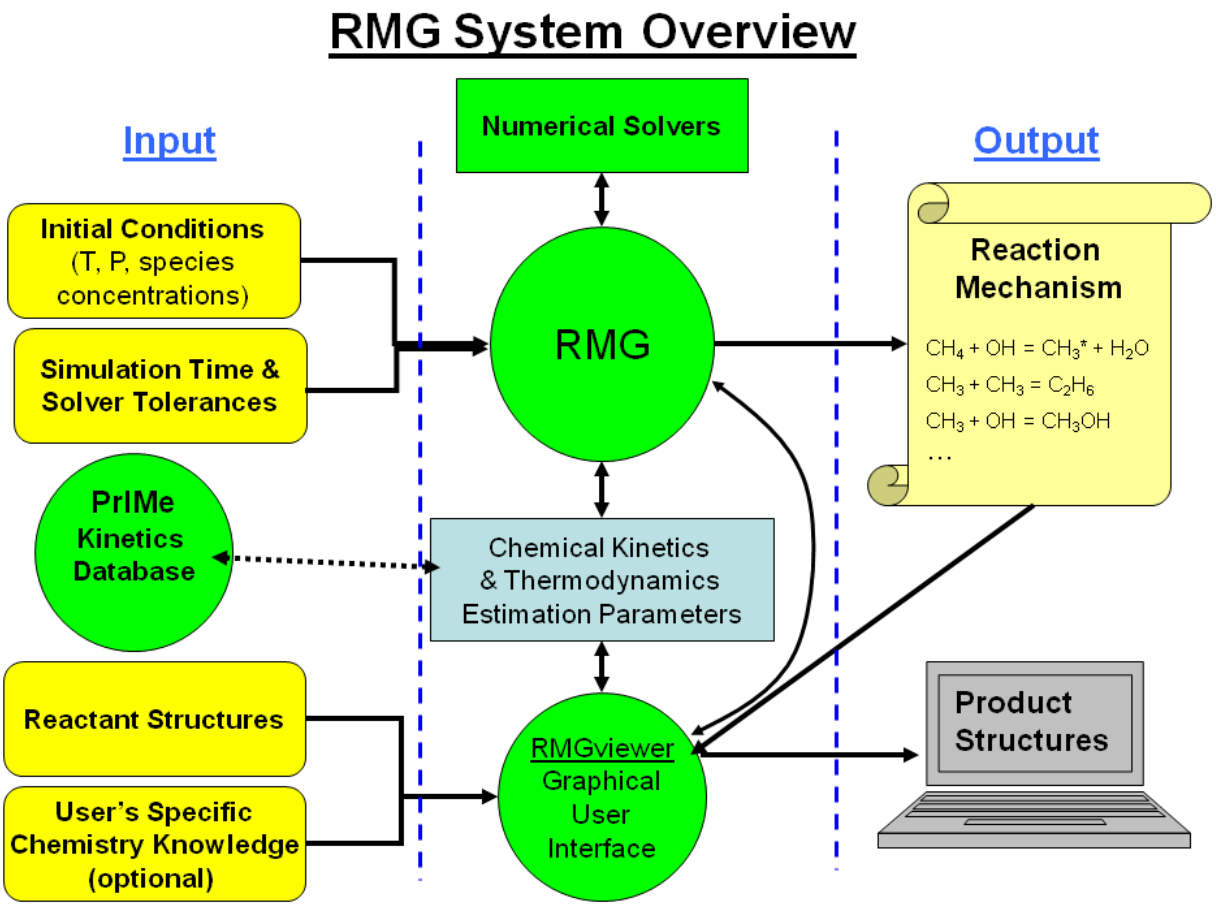


Figure 13.1: A schematic overview of RMG

A schematic overview of RMG is presented below.

Many of the details of RMG's original implementation (Version 1) are described in [JingThesis]. For a more recent discussion of RMG, see [GreenChapter].

Details of certain aspects of RMG are discussed in greater detail below.

13.1 Rate-Based Model Enlarger

To construct a mechanism, the user must specify an initial set of species and the initial conditions (temperature, pressure, species concentrations, etc.). RMG reacts the initial species in all possible ways according to its known reaction families, and it integrates the model in time. RMG tracks the rate (flux) at which each new "edge" species is produced, and species (and the reactions producing them) that are produced with significant fluxes are incorporated into the model (the "core"). These new core species are reacted with all other core species in the model, to generate a new set of edge species and reactions. The time-integration restarts, and the expanded list of edge species is monitored for significant species to be included in the core. The process continues until all significant species and reactions have been included in the model. The user is free to vary the definition of a "significant" rate to refine the mechanism as desired. For a more detailed description on rate-based model enlargement, please see [Susnow1997].

13.2 Thermodynamics Estimation Using Group Additivity

Benson's Group Additivity approach, used by RMG, divides a molecule into functional groups, and the contribution of each functional group to the overall thermodynamics is included. RMG's kinetic rate rules use a similar strategy: the reaction rate depends on the two functional groups involved in the reaction. The rate rule database uses an innovative tree structure that allows users to include ever-more specific defintions of the functional groups and the kinetics involving them. In both cases, users can easily modify and expand these databases to suit their needs. In principle, the trees could be expanded until all possible molecules and data for the reactions between all possible pairs of molecules have been included (of course, in practice, the database is much more limited). The kinetics database includes 19 reaction types ("families"), including hydrogen abstractions, cycloadditions, disproportionation reactions, radical recombination reactions, intramolecular rearrangements, etc.

Each reaction family includes data on many possible functional group pairings involved in the reaction, for a total of roughly 1000 rate rules. When a perfect match for a given reaction is not found in the database, RMG estimates the rate parameters based on "nearby" rate rules that are similar to the desired one. In addition to modifying the RMG databases, the user may also enter thermodynamic or kinetic information for specific molecules/reactions into Primary Reaction Libraries which supersede the estimated values. In this manner, precise data for well-studied reactions/species can be included.

13.3 Pressure Dependence in RMG

One of the new features in RMG is the ability to calculate pressure-dependent rate constants. This appendix provides a brief background on the subject, followed by an explanation of how RMG calculates these rate constants. For a more detailed description on pressure-dependent rate constants, please consult the excellent texts on unimolecular reaction theory by Gilbert and Smith [Gilbert1990]; Holbrook, Pilling, & Robertson [Holbrook1996] ; and Forst [Forst2003].

Consider a molecule in a vibrationally excited state. Under non-pressure dependent conditions, the excess vibrational energy is removed via non-elastic collisions with other molecules, and the rate at which this

collisional relaxation occurs is significantly faster than any competing chemical reactions. Under certain circumstances, however, this is not the case: The vibrationally excited molecule can either isomerize or dissociate on a time scale competitive with or even faster than the time scale of collisions. When that occurs, the phenomenological rate constant from the initial molecule to the possible product channels will depend on both temperature and pressure.

Two conditions can cause pressure dependence: low pressures and high temperatures. The first condition is the simplest, and historically most discussions on the subject of pressure dependence focus on unimolecular reactions at low pressures. The collision frequency is directly proportional to the pressure, so as the pressure is decreased, the rate of collisional energy transfer decreases. Eventually the pressure becomes low enough that the rate of chemical reaction becomes faster than the collision rate.

Chemical activation is not limited to these low-pressure cases, however. Indeed, under the high temperatures of combustion-relevant conditions, many bimolecular reactions at atmospheric pressure will have multiple product channels with pressure-dependent branching ratios. When two molecules collide, the initial adduct contains excess energy that is rapidly redistributed among the vibrational modes. As the temperature is increased, a greater percentage of the adduct population is located at higher vibrational energy levels. As more of the population shifts to higher energy levels, a greater percentage of the population can undergo the isomerization and/or dissociation reactions. If the temperature is high enough, most of the population will be lost to chemical reaction before it can be collisionally stabilized.

The difficulty, of course, is knowing (i) when a reaction becomes pressure dependent, and (ii) how to quantify the pressure dependence if it occurs. To answer these questions, we need to solve the master equation.

13.3.1 Formulation of the Master Equation

Begin with the number density of species i with energy between E and $E + dE$, $n_i(E)dE$. In a chemically activated or pressure-dependent system, the energy-dependent population can undergo the following possibilities: it can gain or lose energy by colliding with other molecules, it can be formed by the association reaction of the reactants, it can decompose back to the reactants, it can isomerize to form other well species, or it can decompose to form bimolecular products. Thus,

$$
\begin{aligned}
\frac{dn_i\left(E\right)}{dt} &= \text{Gain to } n_i\left(E\right) \text{ via collisional energy transfer from } n_i\left(E'\right) \\
&- \text{loss from } n_i\left(E\right) \text{ via collisional energy transfer to all other } n_i\left(E'\right) \\
&+ \text{gain to } n_i\left(E\right) \text{ via association of reactants } n_R, n_m \\
&- \text{loss from } n_i\left(E\right) \text{ via decomposition back to reactants } n_R, n_m \\
&+ \text{gain to } n_i\left(E\right) \text{ via isomerization from } n_j\left(E\right) \\
&- \text{loss from } n_i\left(E\right) \text{ via isomerization to } n_j\left(E\right) \\
&- \text{loss from } n_i\left(E\right) \text{ via decomposition to bimolecular products } p_i
\end{aligned}
$$

Mathematically, we have

$$\begin{aligned}\frac{dn_i(E)}{dt} &= \omega\int_0^\infty P_i\left(E,E'\right)n_i\left(E'\right)dE' - \omega n_i(E)\\ &+ n_R n_m K_{eq}k_{dis}(E)F_i(E)\delta_{Rmi} - k_{dis}(E)n_i(E)\delta_{Rmi}\\ &+ \sum_{j\neq i}^{N_{wells}} k_{ij}(E)n_j(E) - \sum_{j\neq i}^{N_{wells}} k_{ji}(E)n_i(E)\\ &- \sum_{p_j}^{N_{prod}} k_{p_j i}(E)n_i(E)\end{aligned} \tag{13.1}$$

The corresponding equations for the reactants are:

$$\begin{aligned}\frac{dn_R}{dt} = \frac{dn_m}{dt} &= \sum_{i=1}^{N_{wells}}\delta_{Rmi}\int_{E_{i0}}^\infty k_{dis}(E)n_i(E)dE\\ &- \sum_{i=1}^{N_{wells}}\delta_{Rmi}\int_{E_{i0}}^\infty K_{eq}k_{dis}(E)F_i(E)n_R n_m dE\end{aligned} \tag{13.2}$$

The units of the number density $n_i(E)\,dE$ are [particle/volume]. ω is the collision frequency [s^{-1}], $P_i(E,E')\,dE$ is the probability that a particle with energy E' will have energy E after collision [unitless], $k_{ij}(E)$ is the microcanonical rate constant for the isomerization from well j to well i [s^{-1}], K_{eq} is the equilibrium constant between the reactants R and m and the i^{th} well [volume/particle], $k_{dis}(E)$ is the microcanonical rate constant for the dissociation back to the reactants [s^{-1}], $\rho_i(E)$ is the density of states [$energy^{-1}$], $Q_i(T)$ is the partition function for the active degrees of freedom [unitless], n_R and n_m are the number density of the reactants [particle/volume], and $k_{p_j i}(E)$ is the microcanonical rate constant for the dissociation from well i to the j^{th} product channel [s^{-1}]. The delta function δ_{Rmi} is there to ensure that only wells with direct access to the reactants can be formed from or dissociate back to the reactants. In principle, the energy-dependent populations are a series of delta peaks and not a continuous function; in practice, however, at energy levels relevant for our calculations, the spacing between delta functions is so small that the populations can be approximated by a continuous function.

13.3.2 Simplifying Assumptions and Solution

At this point we have $N_{wells}+2$ coupled, non-linear integro-differential equations. We would prefer a system of linear ODEs. To simply the system of equations, we start with two assumptions:

1. Energy is discretized
2. n_m is constant

The first assumption makes the system of equations numerically tractable; by discretizing the energy, we replace the integrals with summations, which yields $N_{\text{energy levels}} \times N_{\text{wells}} + 2$ coupled, non-linear ordinary differential equations. The second assumption assumes that one of the reactants is in great excess over the other (e.g. a stable species rather than a radical). This assumption linearizes the system of equations, yielding $N_{\text{energy levels}} \times N_{\text{wells}} + 1$ coupled linear ODEs. Two methods are commonly employed to solve this system of ODEs: eigenvalue decomposition, and a stochastic method. For eigenvalue decomposition, the code VariFlex [VariFlex] is recommended; for stochastic simulations, the code MultiWell [MultiWell] [Barker2001] is recommended.

Next, we make two additional assumptions:

1. The d/dt is equal to zero
2. n_R is constant

The third assumption assumes that the lifetime of the vibrationally excited intermediates is significantly less than the phenomenologically relevant time scale of the reaction. This assumption converts the system of ODEs into a single matrix equation of rank $N_{\text{energy levels}} \times N_{\text{wells}} + 1$. The fourth assumption reduces the order of the rank by one, and more importantly it ensures that the matrix equation has a non-zero solution. Conceptually, it suggests that the reaction could be modeled as a perfectly stirred reactor with a constant inlet stream, rather than as a batch reactor. With these two additional assumptions, we now have a steady-state master equation.

In the current implementation we must make one last assumption:

1. The collisional energy transfer, $\omega \int_0^\infty P_i\left(E, E'\right) n_i\left(E'\right) dE'$, is replaced by a modified strong collision, $\omega\beta$

This final assumption is the most drastic. It assumes that a certain fraction, $beta$, of all collisions will quench the vibrationally excited adducts. This assumption decouples all the energy levels for a given well, thereby reducing the large matrix equation into $N_{\text{energy levels}}$ individual matrix equations of rank N_{wells}. This approach is similar to the modified-strong collision used in CHEMDIS [CHEMDIS]. With these five assumptions, the individual equations simply to:

$$\begin{aligned} S_i\left(E\right) &= \left[\beta\omega + \sum_{j\neq i}^{N_{wells}} k_{ji}\left(E\right) + \delta_{Rmi} k_{dis}\left(E\right) + \sum_{p_j}^{N_{prod}} k_{p_j i}\left(E\right)\right] n_i\left(E\right) \\ &- \sum_{j\neq i}^{N_{wells}} k_{ij}\left(E\right) n_j\left(E\right) \end{aligned} \tag{13.3}$$

where $S_i\left(E\right) \equiv K_{eq} k_{dis}\left(E\right) n_R n_m \delta_{Rmi} \frac{\rho_i(E) e^{-\beta E}}{Q_i(T)}$ is the source term, which is the product of the association rate, $K_{eq} k_{dis}\left(E\right) n_R n_m \delta_{Rmi}$, and the equilibrium energy distribution $\frac{\rho_i(E) e^{-\beta E}}{Q_i(T)}$.

The terms in square brackets on the right-hand side are the loss channels; these terms appear in the diagonal of the matrix. The other term on the right-hand side is the gain to a well from the other wells; these rates appear in the off-diagonal positions. To calculate the phenomenological rate constants, the above equation is solved for each energy level. The phenomenological rate constant for a particular channel is the dot product of the steady-state population vector and the vector containing the microcanonical rate constant for that channel.

13.3.3 Supporting Equations

Collision Frequency

The collision frequency, ω, is the product of the second-order energy-transfer rate constant and the bath gas concentration. To simply calculations, it is assumed that the energy transfer rate constant is independent of

energy and is equal to the product of the hard-sphere collision limit and the collision integral for a Lennard-Jones potential [Forst2003]:

$$\begin{aligned} \omega &= \pi d^2 \sqrt{\frac{8k_BT}{\pi\mu}} \Omega\left(T\right) \frac{P}{k_BT} \\ \Omega\left(T\right) &= \frac{1.16145}{\left(T^*\right)^{0.14874}} + \frac{0.52487}{\exp\left[0.7732T^*\right]} + \frac{2.16178}{\exp\left[2.437887\right]} \\ T^* &= \frac{k_BT}{\epsilon} \end{aligned}$$

where d is the collision diameter, μ is the reduced mass, $\Omega\left(T\right)$ is the collision integral, and ϵ is the Lennard-Jones parameter for the depth of the potential. Note that it is through the collision frequency that the pressure enters the system of equations.

Collision Efficiency

Currently RMG uses a constant collision efficiency of $\beta = 0.38$. In the future a more rigorous formula will be introduced to more accurately capture the temperature dependence of β.

Microcanonical Rate Constants

RMG currently does not have data for individual transition states. Consequently, it is not possible to calculate the microcanonical rate constants using RRKM theory. Instead, RMG uses its database of Arrhenius parameters to calculate the microcanonical rate constant using the inverse Laplace transform method. For more details on the inverse Laplace transform method, please read Forst cite{Forst} and further references therein. One benefit of using the inverse Laplace transform method is that all the multiplicative constants will cancel. Thus, as we will see below in Section ref{density_of_states}, we do not need to know the rotational constants and symmetry numbers for a molecule.

Given an Arrhenius expression for the high-pressure limit rate constant, the microcanonical rate constant is:

$$\begin{aligned} k\left(T\right) &= Ae^{-E_a/RT} \\ k\left(E\right) &= \begin{cases} A\dfrac{\rho\left(E-E_a\right)}{\rho\left(E\right)} & E > E_a \\ 0 & E \leq E_a \end{cases} \end{aligned} \tag{13.4}$$

where A is the Arrhenius pre-exponential factor, E_a is the Arrhenius activation energy, and R is the ideal gas constant.

For modified-Arrhenius equations, the equation above requires some modification. Specifically, the temperature dependence of the A-factor must be convoluted with the density of states. This convolution is possible only when the temperature exponent is positive. For negative temperature exponents, the inverse Laplace transform is not possible. Instead, the only option is to use an effective A-factor, $A_{eff} = AT^n$. Thus for

$n > 0$, we have:

$$\begin{aligned} k(T) &= AT^n e^{-E_a/RT} \\ \phi(E) &= \frac{1}{k_B^n \Gamma(n)} \int_0^E (E-x)^{n-1} \rho(x)\, dx \\ k(E) &= \begin{cases} A\dfrac{\phi(E-E_a)}{\rho(E)} & E > E_a \\ 0 & E \leq E_a \end{cases} \end{aligned}$$

and for $n < 0$, we have:

$$\begin{aligned} k(T) &= AT^n e^{-E_a/RT} \\ k(E) &= \begin{cases} A_{eff}\dfrac{\rho(E-E_a)}{\rho(E)} & E > E_a \\ 0 & E \leq E_a \end{cases} \end{aligned}$$

For barrierless reactions, such as radical-radical reactions and radical + O_2 reactions, the activation energy in the Arrhenius expression is often negative. For these types of reactions, variational transition state theory is required to calculate the microcanonical rate constant; unfortunately, it is impossible for RMG to implement a VTST approach. Furthermore, because there is no inverse Laplace transform for a positive exponential, The Inverse Laplace method described in the previous two sections must be altered. At best, RMG has one of two approaches. In the simplest approach RMG can calculate an effective A-factor from the product of the A-factor and the exponential term: $A_{eff} = Ae^{|E_a|/RT}$. Applying the inverse Laplace transform as before, the microcanonical rate constant will be constant with respect to energy for a standard Arrhenius equation, and it will increase slightly with energy for a modified-Arrhenius equation:

$$\begin{aligned} k(E) &= A_{eff} && \text{standard Arrhenius} \\ k(E) &= A_{eff}\frac{\phi(E)}{\rho(E)} && \text{modified Arrhenius} \end{aligned}$$

The second method makes use of the fact that the Arrhenius activation energy is relatively small for barrierless reactions (often less than 1 kcal/mol), so it performs a truncated series expansion of the exponential: $e^{|E_a|\beta} \approx 1 + |E_a|\,\beta$. This approach guarantees that the rate constant will increase with energy. However, it requires the derivative of the density of states, which must be done numerically. Applying the inverse Laplace transform to this approach yields:

$$\begin{aligned} k(E) &= A\frac{\rho(E) + |E_a|\,\frac{d\rho(E)}{dE}}{\rho(E)} && \text{standard Arrhenius} \\ k(E) &= A\frac{\phi(E) + |E_a|\,\frac{d\phi(E)}{dE}}{\rho(E)} && \text{modified Arrhenius} \end{aligned}$$

Density of States Estimation

An important quantity to the pressure dependence calculation is the density of states: the number of quantum states per unit energy. In the master equation, we are interested in the density of states for the active degrees of freedom. The active degrees of freedom are those degrees of freedom in which the energy of the excited species can be randomized; within RMG, they include the rigid-rotor harmonic-oscillator (RRHO)

vibrational frequencies, hindered internal rotors (HR), and the unique one-dimensional external rotation of the molecule (i.e. the K-rotor for a symmetric top approximation). The translational degrees of freedom and the two degenerate external rotational degrees of freedom are inactive. Furthermore, RMG assumes that each of these modes is independent. Thus, just as the partition function for two independent modes is the product of the individual partition functions, the density of states for two independent modes is the convolution integral of the respective density of states:

$$\begin{aligned} Q_{AB}(T) &= Q_A(T)\,Q_B(T) \\ \rho_{AB}(E) &= \mathcal{L}^{-1}\{Q_1 Q_2\} \\ &= \int_0^E \rho_A(E-x)\,\rho_B(x)\,dx \end{aligned} \tag{13.5}$$

To calculate the density of states, RMG assumes that each molecule may be approximated as a symmetric top, which implies that the non-degenerate rotational mode is an active degree of freedom. The density of states for this one-dimensional rotor is:

$$\rho_r(E) = \frac{1}{\sigma}\left(\frac{1}{BE}\right)^{1/2} \tag{13.6}$$

where σ is the rotational symmetry number, and B is the rotational constant. As noted above in the section on microcanonical rate constants, these parameters do not matter, since they will cancel in the inverse Laplace transform method. For internal rotors, the density of states is more complicated, and the calculation method is described as follows. For simplicity, it is assumed that the potential for internal rotation may be approximated by a single cosine:

$$V(\theta;\sigma) = \frac{1}{2}V_0\left[1-\cos(\sigma\theta)\right]$$

where V_0 is the barrier height, θ is the dihedral angle, and σ is the number of potential minima (e.g. 3 for a methyl group). The classical partition function for a hindered rotor is:

$$\begin{aligned} Q_{\text{HR}_{\text{classical}}} &= \frac{1}{h^2}\int\int e^{-H/k_BT}dqdp \\ &= \left(\frac{\pi k_B T}{\sigma^2 B_r}\right)^2 e^{-V_0/2k_BT} I_0\left(\frac{V_0}{2k_BT}\right) \end{aligned}$$

where $B_r \equiv 8\pi^2 h^2/I_r$, h is Planck's constant, I_r is the reduced moment of inertia, and I_0 is the modified Bessel function of the first kind. The semi-classical approximation for the hindered rotor partition function is classical hindered-rotor partition function multiplied by the ratio of the quantum partition function and the classical partition function for a harmonic oscillator:

$$\begin{aligned} Q_{\text{HR}_{\text{semi}}} &= Q_{\text{HR}_{\text{classical}}}\frac{Q_{\text{RRHO}_{\text{quantum}}}}{Q_{\text{RRHO}_{\text{classical}}}} \\ &= \left(\frac{\pi k_B T}{\sigma^2 B}\right)^2 e^{-V_0/2k_BT} I_0\left(\frac{V_0}{2k_BT}\right)\frac{\frac{e^{-\nu/2k_BT}}{1-e^{-\nu/k_BT}}}{\frac{k_BT}{\nu}} \end{aligned} \tag{13.7}$$

where the frequency ν is the harmonic oscillator frequency approximation to the bottom of the potential well, and k_B is Boltzmann's constant. According to Knyazev [Knyazev1994], the inverse Laplace transform for

the hindered rotor partition function is:

$$\rho_{\mathrm{HR}_{\mathrm{semi}}}(E) = \begin{cases} \dfrac{2\mathbf{K}\left(\sqrt{E/V_0}\right)}{\pi\sigma\sqrt{B_r V_0}} & \text{for } E < V_0 \\ \dfrac{2\mathbf{K}\left(\sqrt{V_0/E}\right)}{\pi\sigma\sqrt{B_r E}} & \text{for } E > V_0 \end{cases}$$

where $\mathbf{K}$ is the complete elliptical integral of the first kind. The equation above is calculated for each hindered rotor. If a molecule has more than one hindered rotor, then the total density of states for hindered rotors is obtained by successively applying the convolution integral. The density of states for internal rotors and active external rotation is calculated by convoluting the density of states for the active K-rotor with the density of states for all the hindered rotors:

$$\rho_{r,HR_{\mathrm{total}}}(E) = \int_0^E \rho_r(E-x)\,\rho_{\mathrm{HR}_{\mathrm{total}}}(x)\,dx \tag{13.8}$$

Finally, following the method of Astholz [Astholz1979] [Gilbert1996], we initialize the Beyer-Swinehart algorithm [Beyer1973] with the K-rotor/hindered-rotor density of states. This algorithm convolutes this with the vibrational modes. The result is the density of states for all the active degrees of freedom, $\rho(E)$.

13.3.4 Frequencies and Barrier Heights

To summarize everything up to this point: Our objective is to calculate pressure dependent rate constants for chemically-activated reactions. To calculate these rate constants, we must solve the master equation. In order to solve this system of equations, we need the micro-canonical rate constants for the association, isomerization, and dissociation channels. These rate constants, in turn, require the density of states for the adducts. Last but not least, the density of states requires detailed information about the rigid-rotor harmonic-oscillator frequencies as well as hindered rotors parameters. Normally, these physical parameters would be determined from a 3D model of the molecule.

Unfortunately, RMG does not have access to 3D structure models at this time (although we are working on it). The current version of RMG represents each molecule solely by its connectivity. The connectivity diagram for each species is used to calculate the heat capacity at seven temperatures (300, 400, 500, 600, 800, 1000, 1500 K), based upon the group additivity theories developed by Benson [Benson1976].

Since the heat capacity is a function of the vibrational and rotational modes, it is possible, in theory, to determine the frequencies and barrier heights from the heat capacity. In practice, however, this is almost never possible, since the number of unknown vibrational/torsional parameters ($3N - 6$) will most likely exceed the number of C_p values (7). Consequently, some approximations must be made. The remainder of this section describes the subroutine that RMG uses to estimate the unknown parameters.

RMG uses a two-step process to estimate the vibrational frequencies and hindered rotor barrier heights. In the first step, the subroutine will examine the structure of the molecule to determine the types of groups present; it will then use this information to predict most of the vibrational frequencies. In the second step, the subroutine examines the heat capacity as a function of temperature to determine the barriers to internal rotation and the remaining vibrational frequencies.

Estimating the vibrational frequencies based on the group type

What is meant by group type is unique to this subroutine. In principle, however, it is similar to functional groups. Thus, methyl groups are one group type, as are ethers, peroxides, branched and straight-chain alkyl backbones, etc. For each type of group, we have compiled a list of corresponding vibrational modes. To take methyl groups (R-CH3) as an example, there are nine frequencies that are common to methyl groups: 3 C-H stretches, 2 R-C-H bending modes, 2 R-C-H rocking modes, 1 R-C stretch, and 1 umbrella mode. Each of these modes has an upper and lower limit (for example, the C-H stretch in methyl groups is typically confined between 2750 and 2850 cm^{-1}).

For a non-linear molecule with N atoms and R internal rotors, there will be 3N-6-R vibrational modes. The objective of the first part of the subroutine is to determine as many of these RRHO frequencies as possible, as accurately as possible, without determining too many. If the code determines fewer than 3N-6-R modes, that is ok, because they will be estimated in the second section of the code. If, however, the code determines more than 3N-6-R modes, there is a serious problem. To avoid this complication, we have limited the number of modes attributed to each group type so that this situation can never arise.

For each group type, we count both the number of atoms in that group as well as the number of single bonds between heavy atoms in that group (since each of these bonds may contribute one internal rotor). Thus, we limit the number of modes for each group to 3 $\times$ (Number of atoms in group) - (number of single bonds between heavy atoms in group) - 6. This approach guarantees that the number of RRHO modes is less than 3N-6-R. By using this method, the first section of the code will predict almost all of the RRHO modes.

Estimating the vibrational frequencies based on the heat capacity

The second part of the subroutine uses the heat capacity to determine both the remaining unknown vibrational modes as well as the barrier heights of any hindered internal rotors. Using Benson-type group additivity formulas, RMG will calculate the heat capacity for the molecule at seven temperatures. At each temperature, the heat capacity can be separated into the contributions from external translation, external rotation, rigid-rotor harmonic-oscillator frequencies (RRHO), and hindered internal rotation (HR):

$$C_V^{\text{total}} = C_V^{\text{translation}} + C_V^{\text{rotation}} + \sum_{j=1}^{3N-6-N_{\text{rotors}}} C_V^{\text{RRHO}} + \sum_{j=1}^{N_{\text{rotors}}} C_V^{\text{HR}}$$

The first part of the subroutine should estimate some of the RRHO vibrational frequencies, call it $N_{estimated}$. The contribution of the estimated frequencies, as well as the contributions from the external translation and rotation, are subtracted from the total heat capacity. What remains is the heat capacity due to the unknown degrees of freedom (udof):

$$\begin{aligned} C_V^{\text{udof}} &= C_V^{\text{total}} - C_V^{\text{translation}} - C_V^{\text{rotation}} - \sum_{j=1}^{N_{\text{estimated}}} C_V^{\text{RRHO}} \\ &= \sum_{j=1}^{N_{\text{remaining}}} C_V^{\text{RRHO}} + \sum_{j=1}^{N_{\text{rotors}}} C_V^{\text{HR}} \end{aligned} \tag{13.9}$$

where $N_{\text{remaining}} \equiv 3N - 6 - N_{\text{rotors}} - N_{\text{estimated}}$. The formula for the heat capacity for the i^{th} rigid-rotor harmonic-oscillator frequency can be found in any text on statistical mechanics [McQuarrie1973]

[Hill1986]:

$$\frac{C_V^{\text{RRHO}}(T;\nu_i)}{R} = e^{\nu_i/k_BT}\left(\frac{\nu_i/k_BT}{e^{\nu_i/k_BT}-1}\right)^2 \tag{13.10}$$

where ν_i is the vibrational frequency for the i^{th} mode.

As we saw in the density of states section, the approximation used for the heat capacity of a hindered internal rotor is more complicated. Recall the semi-classical partition function for a hindered rotor:

$$\begin{aligned} Q_{\text{HR}_{\text{semi}}} &= \left(\frac{\pi k_BT}{\sigma^2 B}\right)^2 e^{-V_0/2k_BT} I_0\left(\frac{V_0}{2k_BT}\right)^{\frac{e^{-\nu/2k_BT}}{1-e^{-\nu/k_BT}}}_{\frac{k_BT}{\nu}} \\ &= \left(\frac{V_0\pi}{2\sigma^2 B}\right)^{1/2} u^{1/2} e^{-u} I_0(u)\frac{e^{-\alpha u}}{1-e^{-2\alpha u}} 2\alpha \end{aligned}$$

where $u \equiv V_0/2k_BT$, and $\alpha \equiv \nu/V_0$. The frequency ν is the harmonic oscillator frequency approximation to the bottom of the potential well. The heat capacity for this partition function is:

$$\begin{aligned} \frac{C_V^{\text{HR}}(T;V_0,\nu)}{R} &= \frac{d}{dT}\left(T^2\frac{d\ln Q_{\text{HR}}}{dT}\right) \\ &= u^2\frac{d^2\ln Q_{\text{HR}}}{du^2} \\ &= -\frac{1}{2} + u\left[u - \frac{I_1(u)}{I_0(u)} - u\left(\frac{I_1(u)}{I_0(u)}\right)^2\right] + \left(\frac{2u\alpha e^{-\alpha u}}{1-e^{-2\alpha u}}\right)^2 \\ &= -\frac{1}{2} + \frac{V_0}{2k_BT}\left[\frac{V_0}{2k_BT} - \frac{I_1\left(\frac{V_0}{2k_BT}\right)}{I_0\left(\frac{V_0}{2k_BT}\right)} - \frac{V_0}{2k_BT}\left(\frac{I_1\left(\frac{V_0}{2k_BT}\right)}{I_0\left(\frac{V_0}{2k_BT}\right)}\right)^2\right] + \left(\frac{\frac{\nu}{k_BT}e^{-\frac{\nu}{2k_BT}}}{1-e^{-\frac{\nu}{k_BT}}}\right)^2 \end{aligned} \tag{13.11}$$

Fortunately, both the symmetry number σ and the reduced moment of inertia I_r do no appear in the expression for the heat capacity. What remains is the barrier height, V_0, and the frequency, ν. The heat capacity for the unknown degrees of freedom may now be written as:

$$C_V^{\text{udof}}(T) = \sum_{i=1}^{N_{\text{remaining}}} C_V^{\text{RRHO}}(T;\nu_i) + \sum_{j=1}^{N_{\text{rotors}}} C_V^{\text{HR}}(T;V_{0,j},\nu_j)$$

Unfortunately, even if the first part of the subroutine is successful in determining most of the vibrational modes, it is unlikely that it will determine all of them. Furthermore, since there are only seven heat capacity data, it is unlikely that all of the remaining parameters can be determined by the second part of the subroutine. In many cases, either the rigid-rotor harmonic-oscillator frequencies or the hindered rotors (and in some cases both) must be lumped into a single pseudo-frequency or pseudo hindered rotor, respectively:

$$\begin{aligned} \sum_{i=1}^{N} C_V^{\text{RRHO}}(T;\nu_i) &\rightarrow N C_V^{\text{RRHO}}(T;\nu) \\ \sum_{j=1}^{N} C_V^{\text{HR}}(T;V_{0,j},\nu_j) &\rightarrow N C_V^{\text{HR}}(T;V_0,\nu) \end{aligned}$$

Depending upon the exact number of unknown frequencies and rotors, the code will call 26 possible fitting subroutines. In order to make the resulting parameters as realistic as possible, there must be physically meaningful constraints. Thus, the RRHO frequencies are bound between 400 and 4000 cm_{-1}. The HR parameters are less constrained: the low-temperature frequency is bound between 40 and 600 cm_{-1}, and the barrier height is bound between 10 and 10000 cm_{-1}. The fitting procedure is a bounded, constrained least squares fit for a system of highly nonlinear equations, which is a difficult problem to solve. To accomplish this fitting, we use the publicly available code DQED [DQED] [DQED90].

13.4 Automated Time Stepping

A means of automated time stepping in RMG was implemented in order to eliminate the need for the user to specify times/conversions for mechanism validity testing. The AUTO option implementing this automated time stepping was successfully integrated into RMG starting in version 3.00. Several tests have been carried out with the new AUTO option. Results were promising, suggesting that the option functions as intended without being unreasonably computationally expensive. The AUTO option offers a more rigorous implementation of RMGs rate-based mechanism generation algorithm while allowing straightforward generation of reaction mechanisms that encompass chemistry at all time-scales of interest.

13.4.1 Motivation

Originally, the implementation of RMGs reaction mechanism generation algorithm required the user to specify times or conversions at which the program will estimate edge reaction fluxes and decide whether to include a new species in the core reaction model. The choice of which conversions or times to specify is, to a certain extent, arbitrary, and could have a significant impact on the model generated by the program. This arbitrariness can be effectively eliminated by keeping track of the edge reaction flux continuously within the ODE solver (analogously to how conversion is handled) and terminating ODE solver integration when the threshold reaction flux is reached (whereupon a species would be moved from the edge to the core as in the current RMG implementation). This new method is here referred to as automated time stepping. Implementation of such a method would reduce the number of adjustable parameters that the user must tweak during mechanism generation and provide a more rigorous use of the mechanism generation algorithm. At the same time, such a method would allow straightforward generation of mechanisms that encompass chemistry at all time-scales of interest.

13.4.2 Background

The reaction mechanism is divided into a core and an edge. The core is tracked by integrating the appropriate equations using an ordinary differential equation (ODE) solver. The edge includes species that are products of reactions among the core species. Periodically during the course of simulating species concentrations using the ODE solver, mechanism validity is tested. Mechanism validity criteria used by RMG are shown in the equations below.

$$\frac{dC_j}{dt} < tol \cdot R_{char} \forall j \in \text{edge species} \tag{13.12}$$

$$\text{with } R_{char} = \left[\sum_i \left(\frac{dC_i}{dt} \right)^2 \right]^{\frac{1}{2}} i \in \text{core species} \tag{13.13}$$

In these criteria, tol is a tolerance specified by the user. If any of these criteria are not valid, the edge species with the highest flux is added to the mechanism core and the ODE solver restarts simulation from t = 0. In the original implementation, the times or conversions at which model validity is tested are specified by the user. The ODE solvers used by RMG are FORTRAN programs (DASSL or DASPK), while RMG itself is written in Java.

13.4.3 Implementation

In order to achieve the desired behavior for automated time stepping, modifications of the type illustrated in Figure 1 were required.

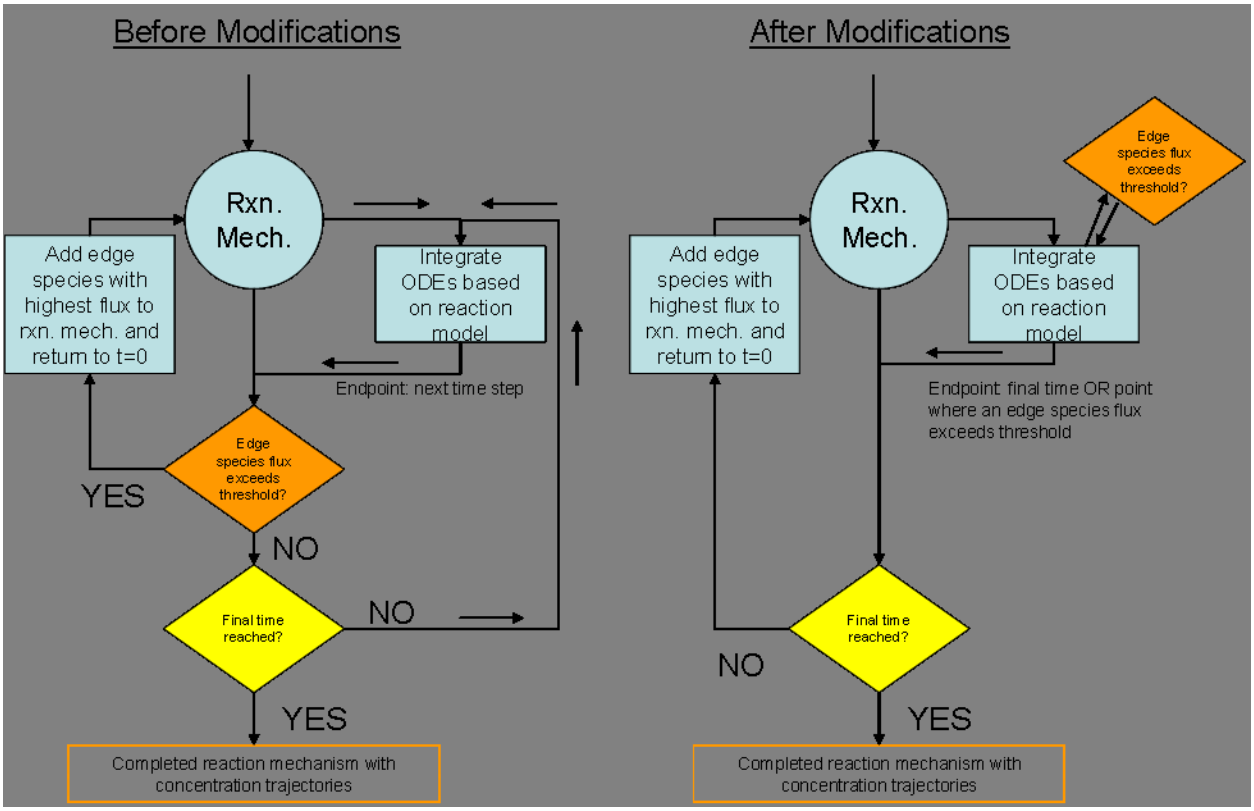


Figure 13.2: Figure 1. Modifications to implement automated time stepping.

As the figure shows, a significant required change was the modification of the ODE solver to have access to edge species flux information at each ODE solver time step. Thus, much of the modification effort involved implementing a scheme for passing edge reaction information to the ODE solver. The implementation ended up requiring changes to the Java classes ReactionModelGenerator and JDASSL and the FORTRAN file call_dassl.f (the modified version was renamed to call_dasslAUTO.f90 to distinguish from the original version). Also, a minor change to the Java class ReactionTimeTT was made. An example of an ODE solver input file for automated time stepping is shown in Figure 2, below. Differences from normal operation are highlighted with boxes.

The first box in the above figure highlights an integer flag signalling to the FORTRAN code that automated time stepping is desired (as opposed to normal operation). The next box highlights the section containing the

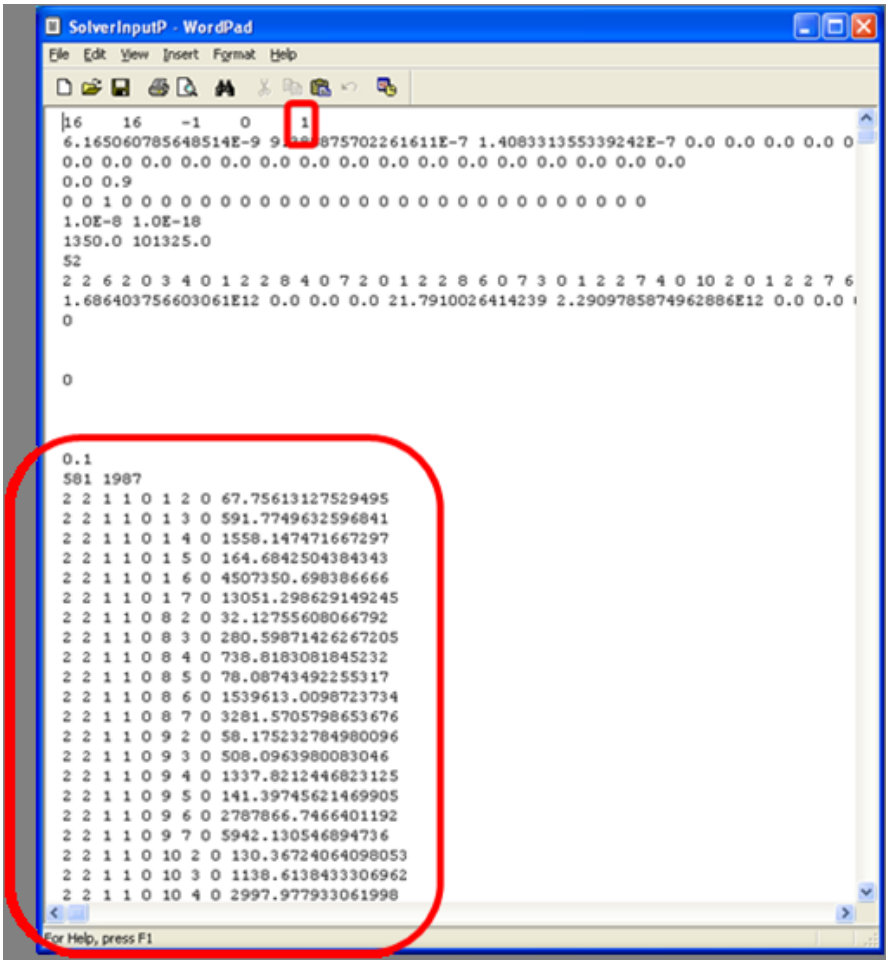


Figure 13.3: Figure 2. ODE solver input file example for automated time stepping. Boxes highlight differences from the normal version.

information needed by the ODE solver to check mechanism validity at each step. In particular, this includes the user-specified tolerance, the number of edge species/reactions, and a line for each edge reaction containing the number of reactants, the number of products, ID numbers corresponding to reactants and products, and finally the rate coefficient, k, for the reaction. It should be noted that in the current implementation, the rate coefficient is considered to be a constant, as additional information regarding temperature/pressure dependence is not passed to solver. Thus, the automated time stepping code (along with other preexisting DASSL code) would need to be modified to handle non-isothermal cases (as well as non-isobaric pressure-dependent cases). In order to reproduce existing validity testing for cases with pressure-dependence, special considerations are necessary. In particular, each pressure-dependent network is considered as a pseudo-species with an associated pseudo-reaction using the kleak associated with the network as the rate coefficient. Monitoring flux to these pseudo-species thus allows us to consider whether a pressure-dependent network needs to be enlarged, analogously to how monitoring of species flux allows us to consider whether a species needs to be added to the core reaction mechanism.

13.4.4 Usage notes

The modified code still allows for evaluating flux at user-defined time/conversion points, and the use of automated time stepping is invoked by replacing the user-defined time/conversion points with the keyword AUTO. Thus, the use of automated time stepping will be referred to as the AUTO method in subsequent discussion. The modified code has been designed to work for both pressure-dependent and non-pressure-dependent cases; also, the code allows automatic stepping with either a conversion or a reaction time as the user-specified termination criterion.

13.4.5 Results

The new option of AUTO time-stepping was tested for several cases to verify that the option was working as desired and to investigate the effects on mechanism generation time and on the resulting mechanism. Note: Throughout this section, 1,3-hexadiene refers to a system involving methane doped with 1,3-hexadiene (in particular, the system defined by the condition files distributed with RMG 2.00 (March 2007)). A brief summary of findings follows.

Effects on Generated Mechanism

One would expect that mechanisms generated using AUTO method would be more rigorously valid than those generated using arbitrary user-specified time/conversion steps. In the case of the 1,3-hexadiene system, mechanisms generated using the AUTO method were compared to mechanisms generated using evenly-spaced conversion steps. The results are shown in Table 1, below.

Table 13.1: Table 1. Size of mechanisms generated using the AUTO method and varying numbers of evenly-spaced conversion steps. In all cases, the goal conversion is 0.9 and the tolerance is 0.05.

# of conversion steps	Core reactions	Core species
1	308	31
2	56	17
3	55	16
4	55	16
6	55	16
9	48	15
Auto	48	15

It should be noted that the mechanism generated with the AUTO method and the mechanism generated using nine evenly-spaced conversion steps appear to be essentially identical for this system. Thus, in this case, we approach AUTO method behavior as we specify a finer grid for conversion steps, as one might intuitively expect. It is also interesting to note that in the test case considered, the "AUTO" method produced a smaller mechanism than cases with a small number of specified conversion steps. Thus, in this case, the mechanism generated by the AUTO method (and cases with a sufficiently fine grid of conversion steps) would not be expected to be more accurate than the mechanism generated without any conversion steps (assuming the kinetics and thermochemistry of the extra species and reactions is accurate). However, the time required to generate the AUTO mechanism is significantly shorter, due to the smaller size of the mechanism. Furthermore, one can imagine that mechanisms of similar size to the largest mechanism reported above could be generated by using tighter tolerances and the AUTO method, and one could be more confident in their validity. In summary, although it produces a larger mechanism, the use of a low number of conversion steps is not "better" than the use of a high number of conversion steps or the AUTO method.

Timing Studies

Tests suggest that the time required to generate a mechanism with the AUTO method is virtually the same as the time required to generate the same mechanism with conventional use of conversion steps. However, that the computational cost associated with tracking edge-species is significant compared to the cost of solving the ODEs, with the AUTO cases requiring a longer amount of time by a factor of two to eight (for the same number of ODE time steps). Three phenomena are proposed to explain this discrepancy. First, one would expect that in the AUTO case, the total time that we must integrate over during mechanism generation will be shorter, in general; that is, the AUTO method avoids wasted ODE time steps associated with overshooting the point where threshold flux has been reached. Second, the time associated with ODE solving is small in comparison to the total time requirement (< 10% of the total time for mechanism generation). Third, and perhaps most significant, there are fewer calls to the ODE solver when the AUTO method is used. In the case of the AUTO method, each call to the ODE solver is associated with a modification to the reaction mechanism (with the exception of the final integration). However, in the case of the normal method, there are extra calls to the ODE solver, as the integration is often stopped despite the mechanism being valid (i.e. no edge species fluxes exceed the threshold). Thus, in order to generate the same mechanism, the normal method requires a larger number of calls to the ODE solver, which, in turn is associated with greater overhead such as reading and writing ODE solver input and output files. Timing studies for the 1,3-hexadiene test case suggest that this overhead can be significant. (Note that the use of eighteen rather than nine conversions ex-

acerbates the time cost, in accord with expectations based on the aforementioned overhead considerations.) The contribution of this overhead to FORTRAN time requirements is relatively small, but noticeable, while the contribution from the overhead on the Java side appears to be more significant. In fact, in this case, the total ODE solver time-requirement is noticeably lower in the AUTO case (relative to the normal cases). Thus, in this case, it appears that the added overhead associated with extra calls to the ODE solver in the normal method has outweighed the extra cost associated with tracking the flux at each time step within the ODE solver, using the AUTO method.

13.4.6 Summary

The AUTO method was implemented and tested during development of RMG 3.00 and provides the option of automated time stepping. Even so, timing studies suggest that tracking the edge flux continuously in the ODE solver is associated with a significant time penalty. However, various mitigating factors appear to reduce the impact of this time penalty on overall mechanism generation time when the AUTO method is used. Thus, the AUTO method appears to be an appealing alternative to user-specification of time/conversion steps.

CHAPTER

FOURTEEN

CREDITS

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