

RMG Study Group/Meeting - Summary of the many Github issues and [hopefully] ways to resolve them. Enoch Dames, March 14 2014

Many similar issues and themes have been repeated over the last 4 years:

- 1.Symmetry and reaction path degeneracy
- 2.Aromaticity and Resonance
- 3.Pdep: failing solvers, invalid MCRCs
- 4.QM(TP)
- 5.Multiplicity
- 6.Documentation issues

Symmetry

Issue with reaction rates from rules are per site. (Libraries include all sites and are per molecule). Optical isomers of transition state may still be an issue (factor of two?)

- Not sure how to resolve this

Chirality in Cantherm not clear either. Could probably detect a chiral center in RMG.

Suggestion in a long thread

- Make symmetry perception into a separate module, rather than molecule. If it's big and complicated, may be worth its own module.

Joanna Yu's algorithm may be off by factor of 2 or sometimes 4.

Important to get symmetry number of molecules right (even if not TS)

Enoch: will check the unit tests in RMG-Py so that at least we know if/when they're wrong. Will also run all species from a big mechanism in Py and Java and see if symmetry numbers (and thermo in general, while at it!) are different.

Could set up a "thermo java estimator" module on website. (ThermoDataEstimator query) Does Java provide symmetry number output?

Aromaticity and resonance

Many issues.

Some open issues could probably be closed.

Resonance of Di-enes (in Py) mentioned last month. Someone?? is working on?

Aromaticity perception needed in Py

Pressure Dependence

Are we still seeing negative $k(T,P)$?

Proper treatment of Seed/Rxn library reactions in Pdep networks. Should they be high P?

Should be they kept as-is?

Cantherm and Measure still separate.. Measure still not deprecated hahahaha.

Connie??? Shamel?: remove all references to measure; convert to cantherm. Connie did this and it stopped working last time.

Inverse Laplace Transform problems:

if $E_a < 0$, A is adjusted so that $E_a = 0$; we think this is currently working (better than nothing).

if n is high, gives artificially low E_a (that is not a true barrier height).

Fitting problem, n values very large when fitted to large temperature ranges.

- Will affect branching of PDep channels due to artificially lowering E_a

Should we store E_0 (as well as E_a) in the database, and estimate them. (And also the negative frequency to get tunnelling etc.). Easy when our data come from quantum calcs, but what about rules coming from experiment?

Should we just try not to fit things with big n values when making rate rules for unimolecular reactions?

Look for ILT of Wigner Form?

Extrapolation beyond T,P ranges, gives solver failure.

WWJD? what would java do? ... crickets answered :)

Connie also noticed that sometimes reaction system is so stiff that RMG gets stuck on solver step (due to rate rule being multiple orders of magnitude off.) Not sure if there is way to identify reactions that cause the stiffness.

Nathan: Will check we're not extrapolating outside valid ranges. Some other sanity checks on all reaction rates. If problems are when rates are many orders of magnitude off, it should be easy to spot.

QM(TP)

Use extra QM data (when available) in the PDep calculations. Big project, using this data. Would improve the PDep. Need a way to store this data.

Do QMTP input files allow changeable keywords of method type for each quantum program? (i.e. PM7 for mopac) Implement this.

QM calculations don't check correct molecule is found.

Pierre: implement, push to master, and close issue. (We have got this working)

Multiplicities

Beat has a new proposal.

Unforeseen consequences around the corner...

Right now we're not keeping singlets and triplets straight.

Intersystem crossing is not very well generalized.

Propene + $O(^3P)$

Some families RMG makes spin-forbidden reactions, but sometimes they do happen, so maybe we're right :- (though probably we just put in the rate for O singlet, and are doing it wrong).

Biradicals. Benzene + $O(^3P)$

Enoch and _____. Turn on p-dep and see what happens. Then figure out how to do the right thing. Perhaps there are some forbidden groups.

Documentation

Resolution: make documentation with every commit. Fix or add at that time.

General Reminders

Store lots of meta-data when adding rates.

Quality control. Peer review.

Commits: Make them small. Easier to review, track, and revert.

General Issues

Stable release for public? We have a stable branch. Call something a release?

Py and Java. We need to be aware of and understand differences.

Write in whatever and port to whatever. "It doesn't seem that hard to add from one language to the next" -WHG