Some RMG Basics

William H. Green

MIT Dept. of Chemical Engineering

RMG Study Group

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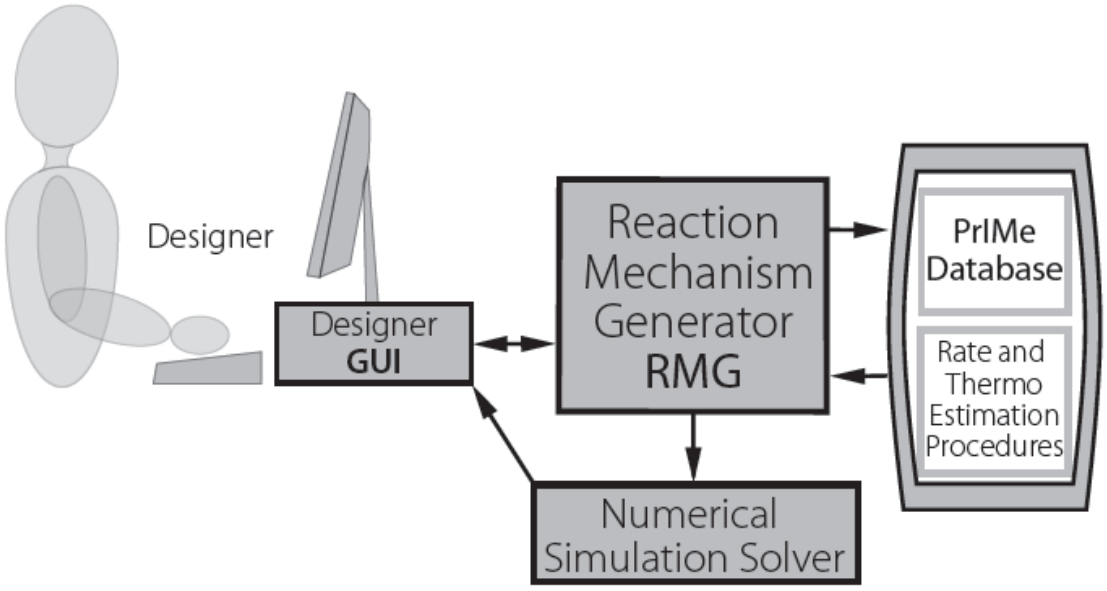
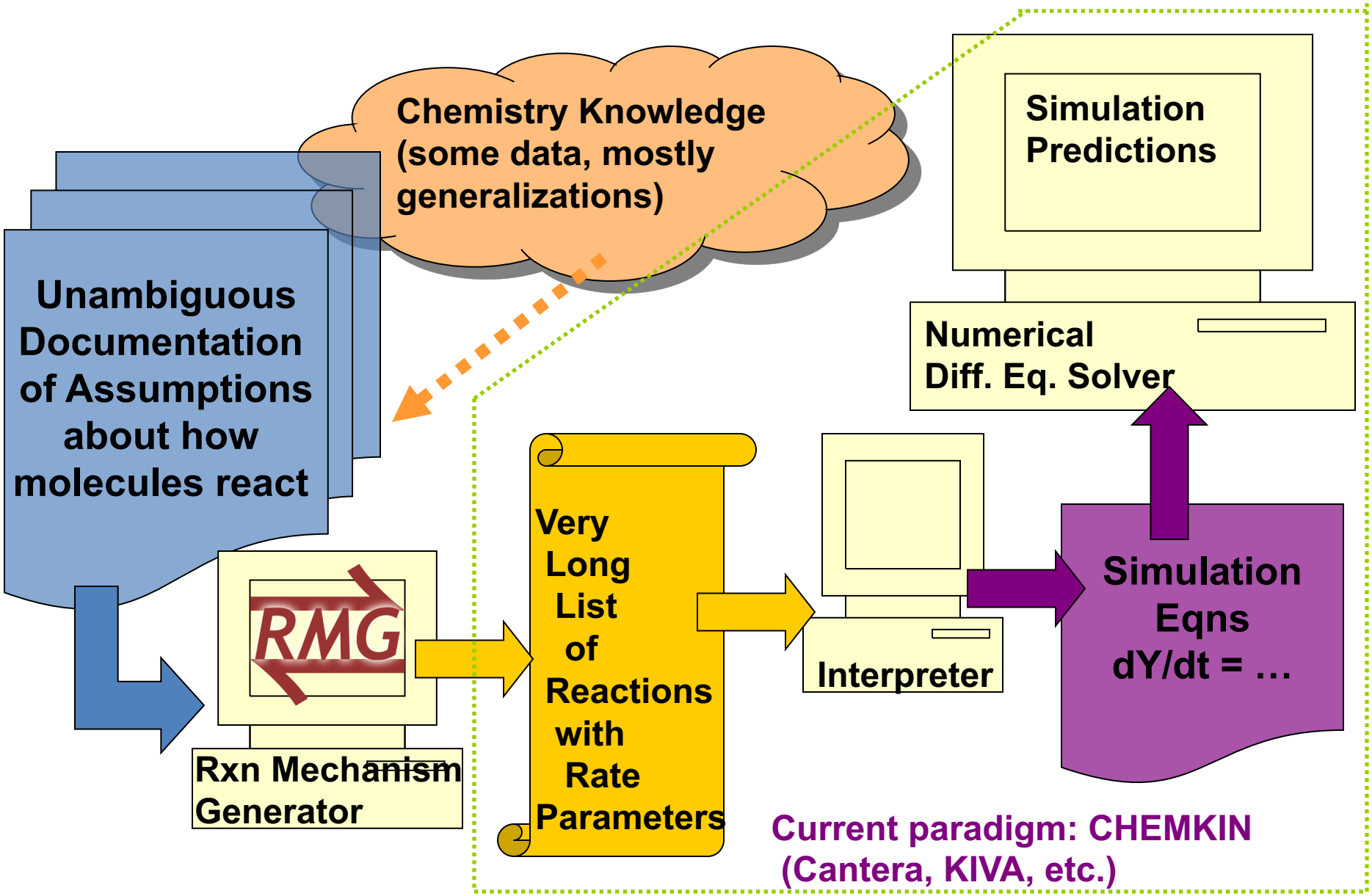
Key Components of RMG the Design Tool

- Mechanism Generation Algorithm
- Estimation Procedures for all the Numbers
  - Known numbers in Libraries / Databases
  - Successive refinement of sensitive numbers
- Numerical Solvers (and Sensitivity analysis)
- User GUI for variety of use cases



Where RMG fits in…

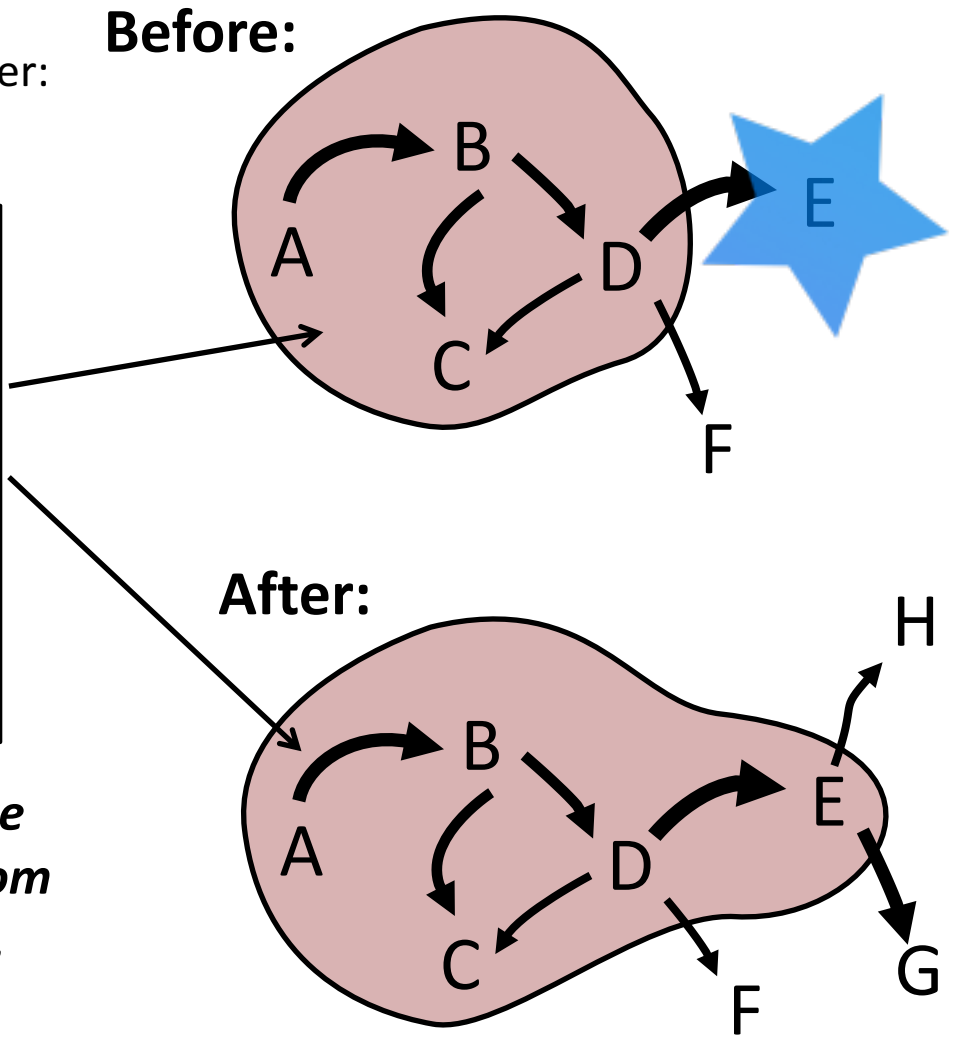


Rate-Based algorithm: Faster pathways are explored further, growing the model

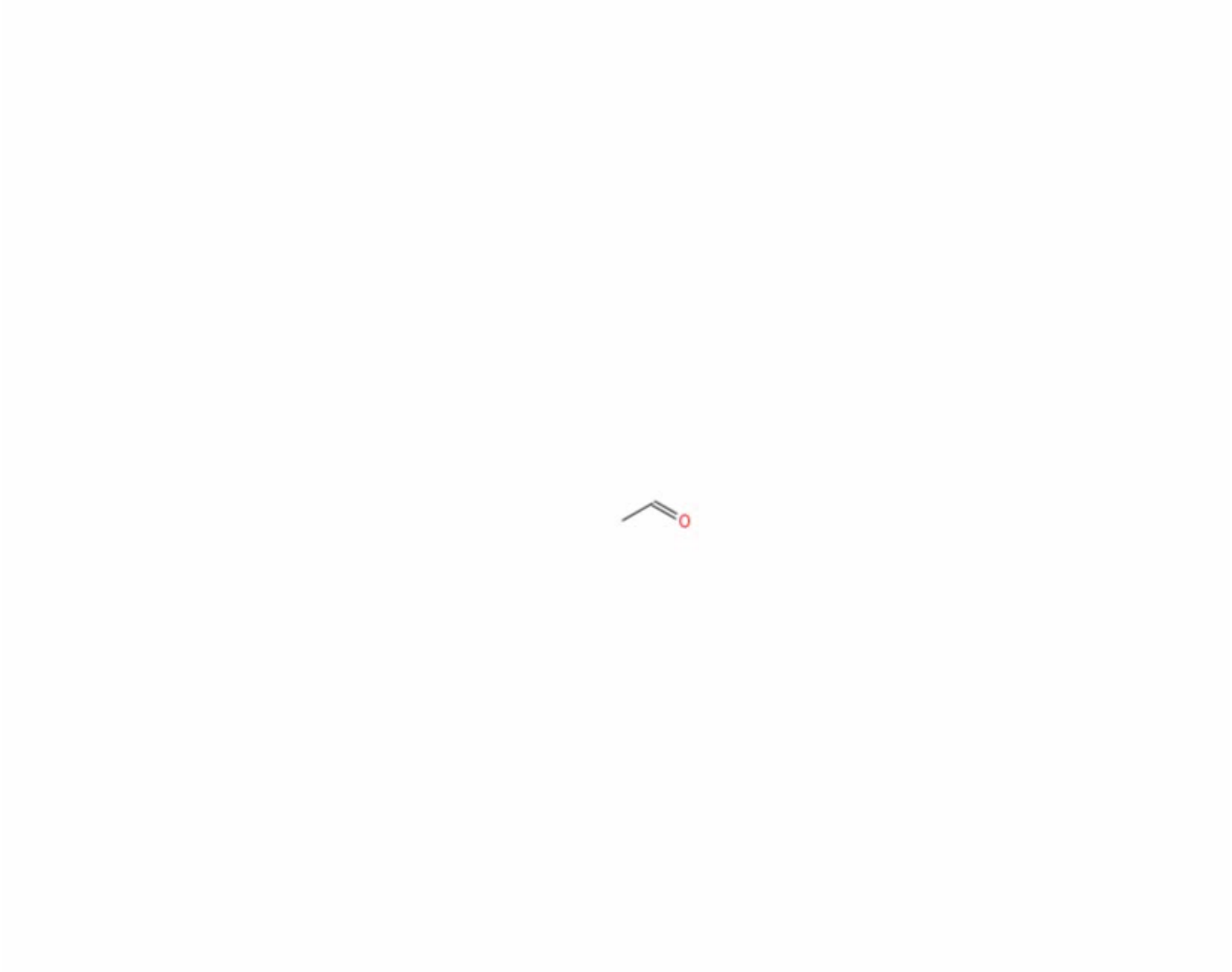
First rate-based algorithm paper:
Susnow et al. *JPCA* (1997)

"Current Model" inside. RMG decides whether or not to add edge species to this model. Currently:
$r_E(t_n) > tol*R_{char}(t_n)$?
This algorithm always converges in finite steps, but not always efficient.

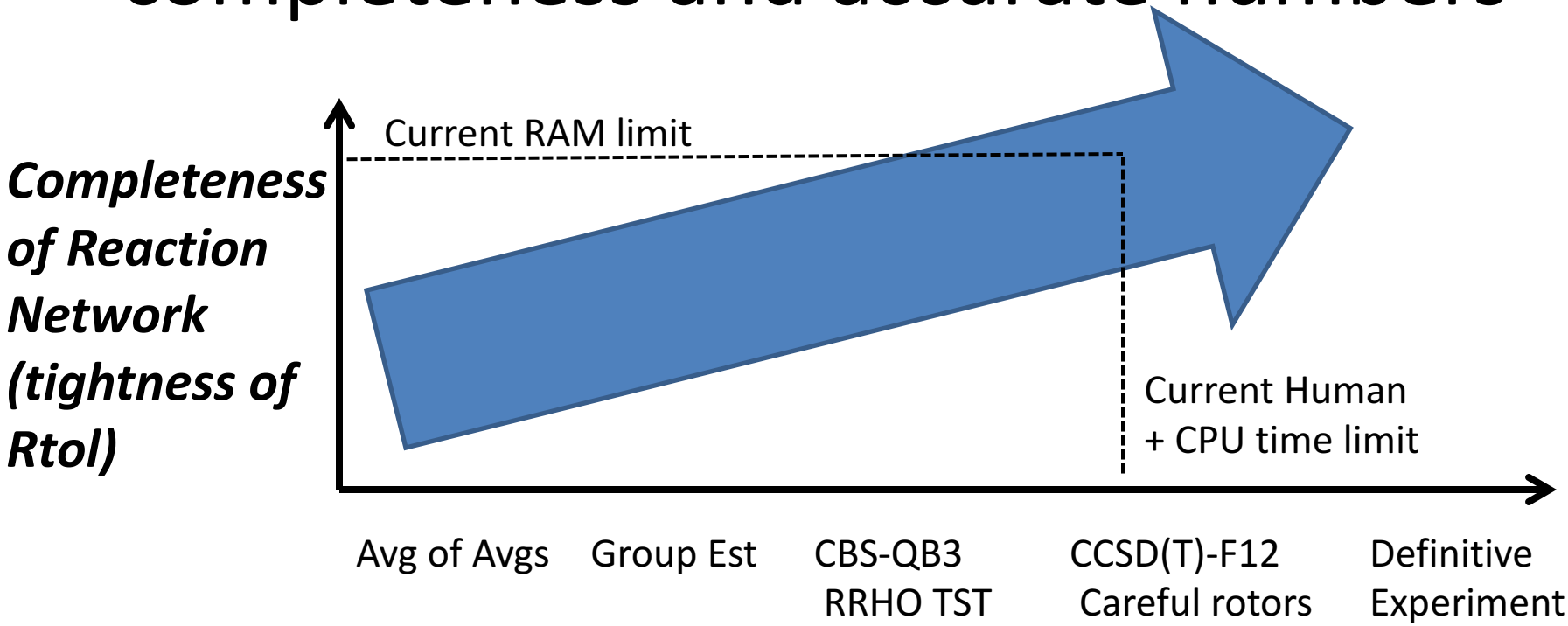
Open-Source RMG software developed with funding from DOE Basic Energy Sciences. Download from rmg.sourceforge.net



Example: pyrolysis of acetaldehyde



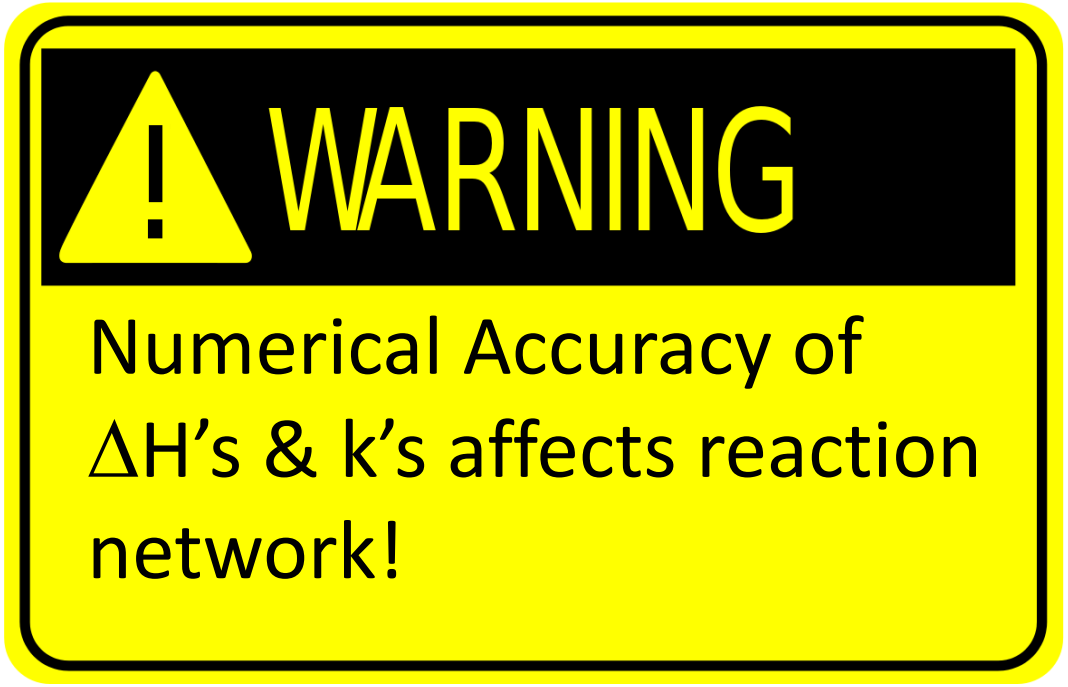
Accuracy depends on both mechanism completeness and accurate numbers



Accuracy of sensitive k's, ΔH's, ΔS's, C_p's

Often assume simulation solver errors & approximations are negligible and that we have perfect knowledge of boundary conditions; sometimes these errors are larger than errors from reaction network incompleteness and errors in k's etc.

Model can also be incomplete due to missing reaction family or forbidden species.



Rate-based algorithm is selecting species based on estimated formation rate. If rate is wildly underestimated, (e.g. too-low k, possibly from too-high H) the edge species will never be considered important at any practical Rtol, and so it will never make it into the kinetic model.

Edge Species omitted from the model are currently GONE FOREVER. No easy way to catch a mistake like this (except sometimes by Experimental validation).

Recommended Model-Construction Procedure with RMG

- RMG assembles large kinetic model for particular conditions using rough estimates of rate coefficients ***k*** to decide which species to include.
- *If sensitive* to ***k*** derived from rough estimate, recompute that ***k*** using **quantum chemistry**.
  - Unfortunately, quantum calcs for rates not fully automated.
  - Generalize from quantum to improve rate estimation rules, and ensure they get incorporated into RMG database.
- ***Iterate* until predictions you care about are not sensitive to any rough estimates.**
- *Repeat* for different conditions ($\underline{C}_o$,T,P,Δt) using current model as seed.
- Compute prediction & compare with **experiments**.
  - Called “validation”. Predictive Mode: no tweaking of k’s to force agreement with experiment.

What do we Expect from Model vs. Data Comparisons?

- At present, Thermo rarely known better than 1 kcal/mole, Ea's uncertain by ~ 2 kcal/mole, and A's often uncertain by factor of 2. So….
  - **we don't expect perfect agreement!**
  - Precise agreement means model parameters were fitted to match experiment, not predictions. Or lucky.
- However, we think our estimates are reasonable, and our software is pretty good.
- So… we **expect discrepancies to be less than an order of magnitude** for both overall reaction timescale and product distribution.