An open-source toolchain from molecular vibrations to detailed combustion

how (some) physical chemists and chemical engineers have escaped proprietary software

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About Us

Mark and Kfir are both active in developing and contributing to FOSS projects within the scientific community including CANTERA, the REACTION MECHANISM GENERATOR, and the AUTOMATIC RATE CALCULATOR.

Mark:

- **Ph.D. in chemical engineering**
- **Linux/FOSS user and contributor over 15+ years**
- **Research foci are combustion chemistry, batteries, fuel cells, and heat transfer**
- **Currently employed in DevOps**

Kfir:

- **Fourth-year undergraduate student at the Technion in Biochemical Engineering**
- **Contributes to FOSS for over a year**
- **Conducts research at `dana.net.technion.ac.il`**

Introduction

Computational chemistry: an essential science

Just a few examples:

- **Alternative bio and manufactured fuels**
- **Batteries and fuel cells**
- **Drug and pharmaceutical manufacturing and degradation**
- **Proteins and organic molecules**
- **Refining and materials synthesis**

We are moving from postdictive to predictive computational capabilities[1]

[1] Green, W. H. AIChE Journal **2020**, *66*, 1–16.

Toolchain overview: macro to micro-scale

"Complete" simulation of a chemical reactor:

- **Global/macroscopic: temperature, pressure, chemical composition (TPX)**
- **Reactor/condition-specific implementation of laws of thermodynamics, conservation equations**
- **Chemical reactions for all chemical species**
- **Thermodynamic properties for all chemical species**

Toolchain overview: computing and sourcing properties

Various computational approaches:

- **“Guess” new species and thermodynamic properties from tabulated rules**
- **Estimate reaction rates by analogy to other reactions**

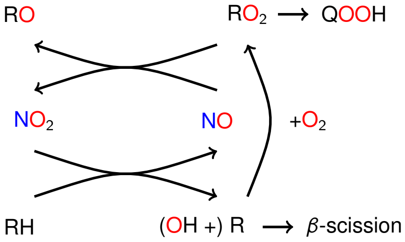
or

- **Compute molecular structures (many different methods)**
- **Calculate thermodynamic properties and reaction rates**

{Cheap and fast} versus {expensive and slow},
but we need both approaches to solve real problems

Guessing Species and Reactions

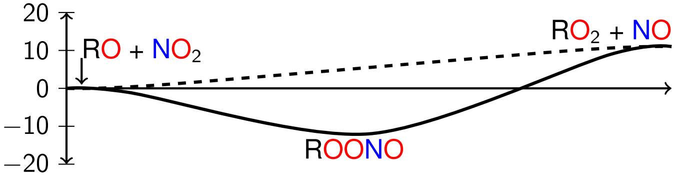
- **Hydrogen abstractions**
  - $RH + NO_2 \rightleftharpoons R + HONO$
  - $RH + NO_2 \rightleftharpoons R + HNO_2$
  - $RH + NO \rightleftharpoons R + HNO$
- **Nitrite/Nitrate/Nitro-/Nitroso-Compounds**
  - $RONO \rightleftharpoons RO + NO$
  - $RONO_2 \rightleftharpoons RO + NO_2$
  - $RNO_2 \rightleftharpoons R + NO_2$
  - $RNO \rightleftharpoons R + NO$
- **Isomerizations**
  - $RONO \rightleftharpoons RNO_2$
- **HONO elimination**
  - $RONO \rightleftharpoons \text{alkene} + HONO$
- **NO_x cycling**
  - $RO_2 + NO \rightleftharpoons RO + NO_2$
  - $R + NO_2 \rightleftharpoons RO + NO$



Adding NO_x to a combustion process[2]

[2] Fuller, M. E. et al. Reaction Chemistry & Engineering **2021**, *6*, 2191–2203.

Calculating Species and Reactions



Generalized potential energy surface for alkoxy radical (RO) + NO_2 system. Energies in kcal/mol. Well-skipping occurs at virtually all combustion-relevant temperatures and pressures.

Reaction	A	n	E_a
$CH_3O_2 + NO \rightleftharpoons CH_3O + NO_2$	4.62E+15	-0.38	97.8
$C_2H_5O_2 + NO \rightleftharpoons C_2H_5O + NO_2$	2.11E+14	-0.12	-470.6
n-$C_3H_7O_2 + NO \rightleftharpoons n$-$C_3H_7O + NO_2$	1.07E+14	-0.25	-1302.0

Units: centimeters, kelvin, calories, moles

Software

Our toolchain

- Graphical drawing of structures, basic, geometry, and input file generation with AVOGADRO2
- Electronic structure calculations of individual molecules with PSI4
- Conversion of individual molecule results to thermodynamic properties and reaction rates with ARC
- Automated model construction including estimating properties with RMG
- Automating decisions to refine estimates with computations using T3
- Reactor simulations with CANTERA
- Comparing to experimental data with standardized formatting (CHEMKED) and tools for validation and manipulation (PYKED)

Avogadro2

`two.avogadro.cc` OpenChemistry/avogadro[app,libs]

- **Written in C++, released under the BSD 3 Clause License**
-

Psi4

psicode.org   psi4/psi4

- **Written primarily in C++ with Python interfaces, released under the LGPL-3.0 License**

The Reaction Mechanism Generator

`rmg.mit.edu` ReactionMechanismGenerator/RMG-Py

- **Written in Python 3, released under the MIT License**
- **The goal is to define the significant reaction in the model**

ARC

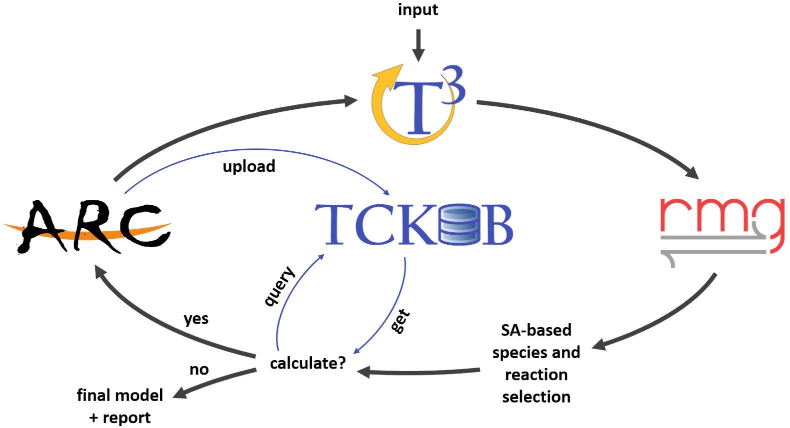
The Automatic Rate Calculator

ReactionMechanismGenerator/ARC

- **Written in Python 3, released under the MIT License**
- **The goal is to automatically calculate chemical species thermochemistry and reaction rate coefficients.**

The Tandem Tool

ReactionMechanismGenerator/T3



- **Written in Python 3, released under the MIT License**

Cantera

`cantera.org` Cantera/cantera

- **"Cantera is an open-source suite of tools for problems involving chemical kinetics, thermodynamics, and transport processes."**
- **BSD 3-Clause license**
- **Written in C++; interfaces for programming with Python, C++, Fortran, and Matlab**
- **Built-in classes to represent wide range of gas-phase and surface chemical kinetics, multiple transport models, and reactor classes to consolidate determination of governing equations**
- **Implements Eigen and SUNDIALS libraries for solving equations**
- **Binary distribution on Fedora, RHEL, Ubuntu, Gentoo, FreeBSD, Mac and Windows plus Conda installation**

PyKED and ChemKED

pr-omethe-us/PyKED

- **ChemKED is a standard human and machine-readable file format for experimental data typical in combustion (`github.com/pr-omethe-us/ChemKED-database`)**
- **PyKED is a Python interface for validating ChemKED files and implements standard interactions and routines for use with the data (`github.com/pr-omethe-us/PyKED`)**
- **Written in Python, released under BSD 3-Clause license**

Help wanted

There is a lot that can be contributed by non-experts in chemistry (actually our biggest deficit):

- **Cleanup of Conda environments and updating versions of dependencies (e.g. migrating away from NOSETESTS) in RMG and ARC**
- **Developing database for TCKDB with reactions and interfacing to T3**
- **Binary packages and distribution in mainstream repositories on Linux distributions**
- **Overhauling data validating and type-checking in PYKED (old version of CERBERUS currently)**

Q&A

References

(1) Green, W. H. AIChE Journal **2020**, *66*, 1–16.

(2) Fuller, M. E.; Morsch, P.; Goldsmith, M. P. C. F.; Heufer, K. A. Reaction Chemistry & Engineering **2021**, *6*, 2191–2203.

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