

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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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 chemical engineering**
- **...**

Introduction

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 capabilities¹

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

“Complete” simulation of a chemical reactor:

- **Global/macroscale: 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**

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

■ Hydrogen abstractions

- $\text{RH} + \text{NO}_2 \rightleftharpoons \text{R} + \text{HONO}$
- $\text{RH} + \text{NO}_2 \rightleftharpoons \text{R} + \text{HNO}_2$
- $\text{RH} + \text{NO} \rightleftharpoons \text{R} + \text{HNO}$

■ Nitrite/Nitrate/Nitro-/Nitroso-Compounds

- $\text{RONO} \rightleftharpoons \text{RO} + \text{NO}$
- $\text{RONO}_2 \rightleftharpoons \text{RO} + \text{NO}_2$
- $\text{RNO}_2 \rightleftharpoons \text{R} + \text{NO}_2$
- $\text{RNO} \rightleftharpoons \text{R} + \text{NO}$

■ Isomerizations

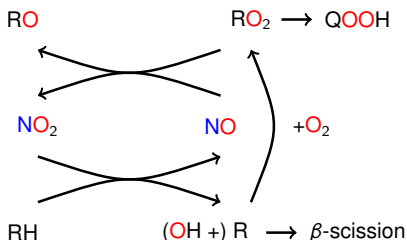
- $\text{RONO} \rightleftharpoons \text{RNO}_2$

■ HONO elimination

- $\text{RONO} \rightleftharpoons \text{alkene} + \text{HONO}$

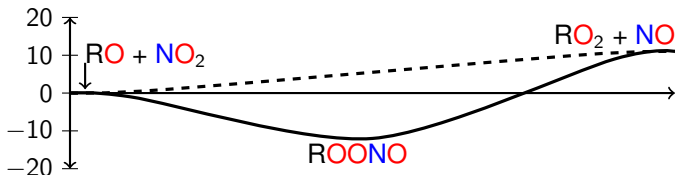
■ NO_x cycling

- $\text{RO}_2 + \text{NO} \rightleftharpoons \text{RO} + \text{NO}_2$
- $\text{R} + \text{NO}_2 \rightleftharpoons \text{RO} + \text{NO}$



Adding NO_x to a combustion process²

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



Generalized potential energy surface for alkoxy radical (RO) + NO₂ system. Energies in kcal/mol. Well-skipping occurs at virtually all combustion-relevant temperatures and pressures.

Reaction	<i>A</i>	<i>n</i>	<i>E_a</i>
CH ₃ O ₂ + NO ⇌ CH ₃ O + NO ₂	4.62E+15	-0.38	97.8
C ₂ H ₅ O ₂ + NO ⇌ C ₂ H ₅ O + NO ₂	2.11E+14	-0.12	-470.6
<i>n</i> -C ₃ H ₇ O ₂ + NO ⇌ <i>n</i> -C ₃ H ₇ O + NO ₂	1.07E+14	-0.25	-1302.0

Units: centimeters, kelvin, calories, moles

Software

- 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**)



Avogadro2



`two.avogadro.cc`

 `OpenChemistry/avogadro[app,libs]`

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





`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 Automatic Rate Calculator

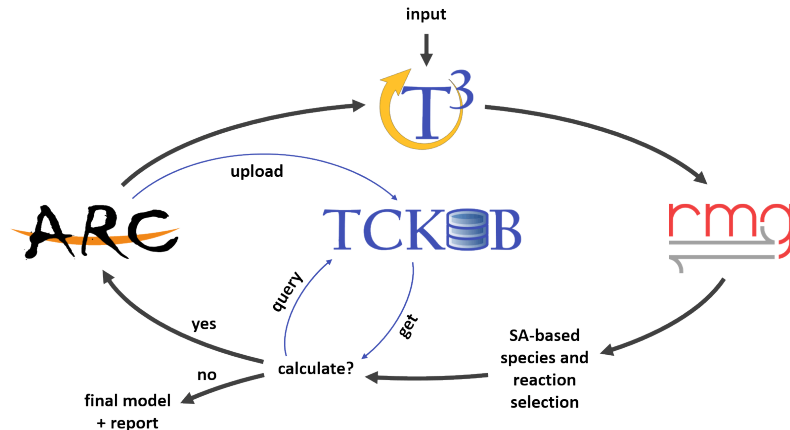
🔗 [ReactionMechanismGenerator/ARC](#)

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



The Tandem Tool

ReactionMechanismGenerator/T3



■ Written in Python 3, released under the MIT License

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](https://github.com/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**

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)**

- (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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