Beyond A $\rightarrow$ B: Computational Approaches for Education in Reaction Engineering and Kinetics of Complex Systems

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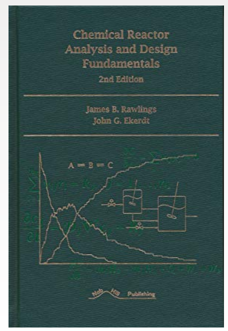
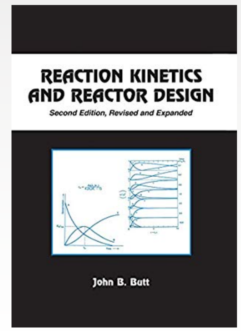
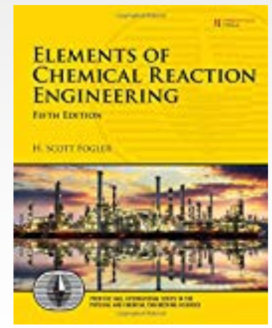
Northwestern | McCORMICK SCHOOL OF ENGINEERING

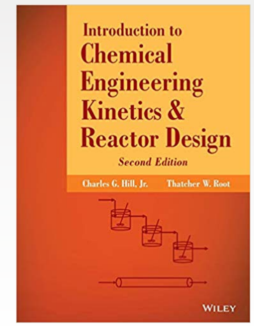
Common Elements of Undergraduate Reaction Engineering

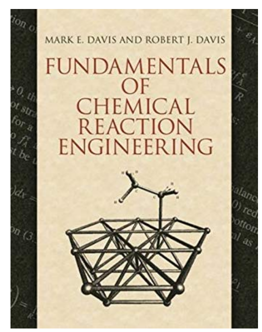
- Reaction Rate
- Reactor Sizing
- Rate Laws
- Isothermal Reactor Design
- Nonisothermal Reactor Design
- Analysis of Rate Data
- Multiple Reactions
- Reaction Mechanisms
- Catalysis and Catalytic Reactors
- External Mass Transfer
- Internal Mass Transfer
- Residence Time Distributions

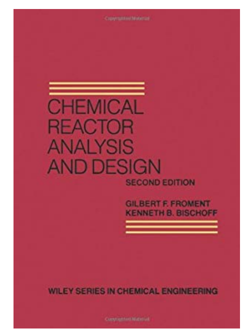


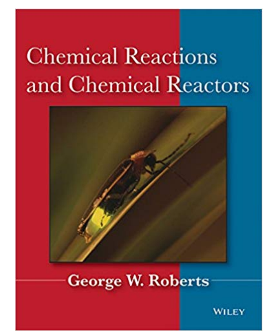












Pedagogical value of analytical solutions

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- Internal Mass Transfer

Couple reactor design equation and rate law

Express in terms of conversion

Solve analytically

$$2A \rightarrow B$$

$$X_A = \frac{N_{Ao} - N_A}{N_{Ao}}$$

$$X_A = \frac{F_{Ao} - F_A}{F_{Ao}}$$

•

•

$$V = F_{Ao} \int_0^{X_A} \frac{dX_A}{-r_A}$$

$$-r_A = kC_A^2$$

$$V = \frac{F_{Ao}}{kC_{Ao}^2}\left[2\varepsilon(1+\varepsilon)\ln(1-X_A) + \varepsilon^2 X_A + \frac{(1+\varepsilon)^2 X_A}{1-X_A}\right]$$

Assumptions leading to analytical solutions

- Reaction Rate
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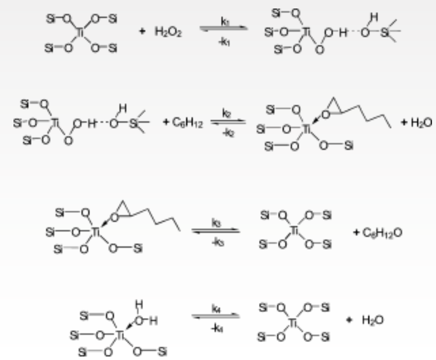
- Reaction Mechanisms
- **Catalysis and Catalytic Reactors**
- External Mass Transfer
- Internal Mass Transfer

Postulate mechanism

Assume rate-determining step and quasi-equilibrium

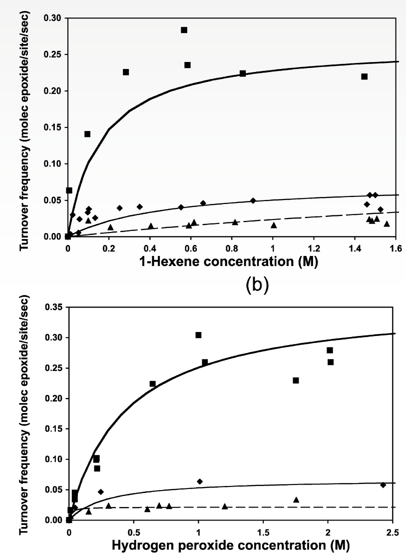
Solve analytically

Verify concentration dependence



$$r = \frac{k_2[*_{\text{total}}](K_1[O][H] - \frac{[W][E]}{K_2K_3})}{1 + K_1[O] + \frac{[E]}{K_3} + \frac{[W]}{K_4}}$$

$$r_0 = [*_{\text{total}}]\frac{k_2}{K_e}\frac{K_1 q_{\mathrm{H_2O_2}} b_{\mathrm{H_2O_2}}[O_{\text{bulk}}]\frac{q_{\text{sat}} b[H_{\text{bulk}}]}{1+b[H_{\text{bulk}}]}}{1 + b_{\mathrm{H_2O_2}}(1 + q_{\mathrm{H_2O_2}}K_1)[O_{\text{bulk}}]}$$



Ramachandran et al., *J. Catal.* **2008**, 253, 148-158.

Simple computer-aided solutions

- Reaction Rate
- Reactor Sizing
- Rate Laws
- Isothermal Reactor Design
- Nonisothermal Reactor Design
- Residence Time Distributions
- Analysis of Rate Data
- Multiple Reactions
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- External Mass Transfer
- Internal Mass Transfer

Couple rate law with reactor design equation

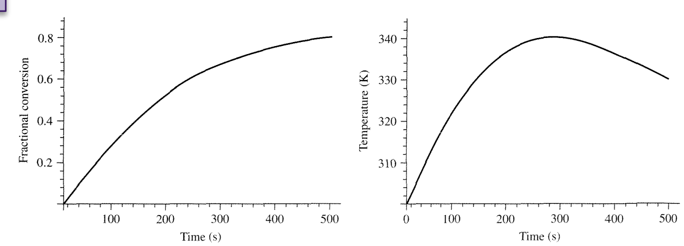
Simplify energy balance

Numerically solve (small) number of equations simultaneously

$A + B \Rightarrow C$ in a nonisothermal batch reactor

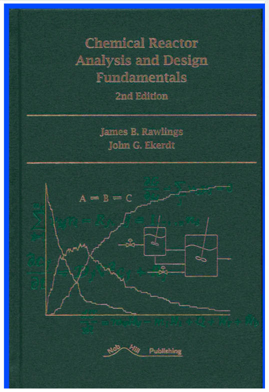
$$\frac{df_A}{dt} = g(T, f_A) = k(T)C_A^0(1 - f_A)(1.2 - f_A)$$

$$\frac{dT}{dt} = \frac{UA_H(300 - T) - \Delta H_r n_A^0 g(T, f_A)}{n_A^0(1 - f_A)C_{p_A} + n_A^0(1.2 - f_A)C_{p_B} + n_A^0 f_A C_{p_C}}$$



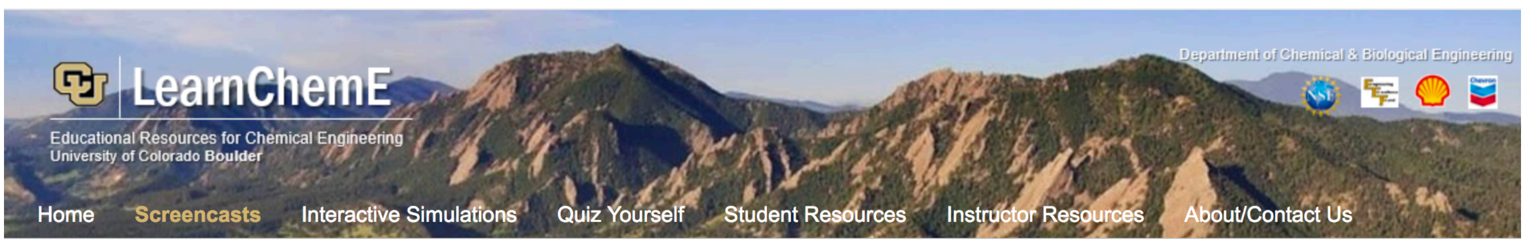
Davis and Davis, Fundamentals of Chemical Reaction Engineering, **2003**, McGraw Hill.

Going beyond simple examples



- **Seamless integration of modern computing methods.** The largest technological change of our generation is the explosion in computing and communications technology. This text takes full advantage of these advances to prepare students to use computational methods for solving reactor modeling problems. It contains 65 worked examples, 204 exercises and 278 figures. The computational software required for every example and every figure in the text is available at: https://engineering.ucsb.edu/~jbraw/chemreacfun. This information can be downloaded to check and debug calculations.

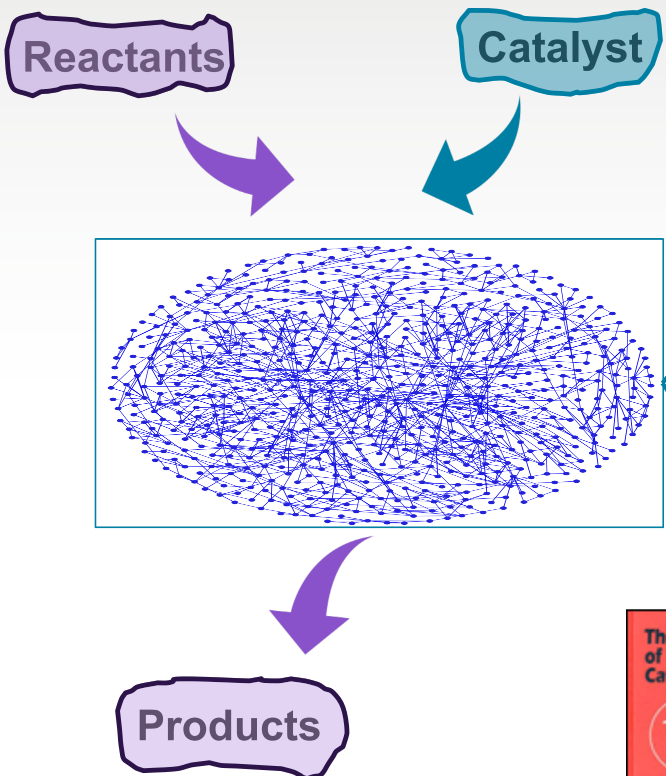
- Appendix A: Computational Methods is now available on the web. We support Matlab and Octave--a compatible, freely available language--for all calculations presented in the text. Many of the 204 exercises develop student for solving reactor problems.

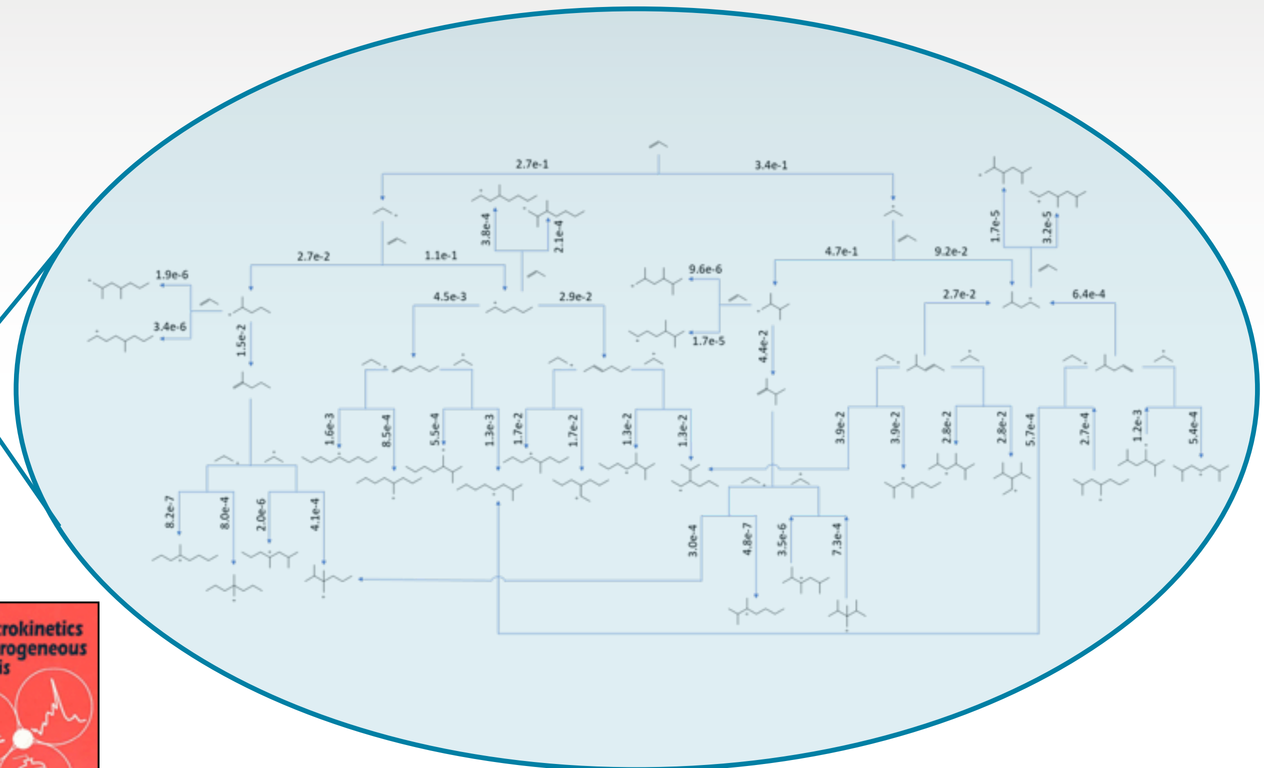


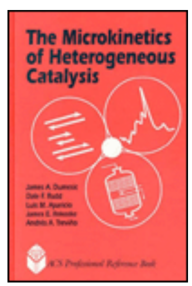
Software Tutorials

- Athena Tutorial: Batch Reactor
- Athena Tutorial: PFR
- Creating Interactive Simulations in Mathematica
- CSTR with Heat Transfer
- Multiple Regression in Excel
- Non-Linear Regression in Mathematica
- Numerically Solve ODEs with Mathematica 1
- Numerically Solve ODEs with Mathematica 2
- Plot Equations with Mathematica
- POLYMATH Excel Add-in to Solve ODEs
- Solving ODEs/POLYMATH

Moving to more complex reaction networks





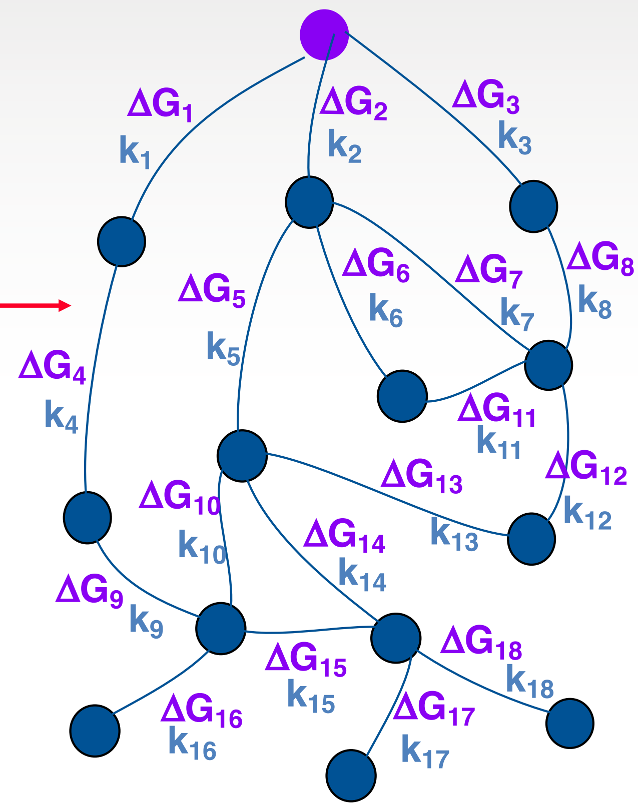


Dumesic et al., The Microkinetics of Heterogeneous Catalysis, **1994**.

Automated reaction network generation

Reactants
Reaction Types
Reaction Rules

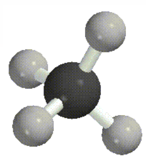
- **Graph Theory**
- **Reaction Matrix Operations**
- **Connectivity Scan**
- **Uniqueness Determination**
- **Property Calculation**
- **Termination Criteria**



Connect chemistry and mathematics

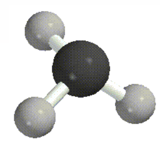
$$\begin{array}{l|ccccc} C & 0 & 1 & 1 & 1 & 1 \\ H & 1 & 0 & 0 & 0 & 0 \\ H & 1 & 0 & 0 & 0 & 0 \\ H & 1 & 0 & 0 & 0 & 0 \\ H & 1 & 0 & 0 & 0 & 0 \end{array}$$

methane



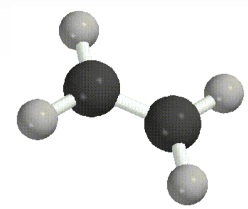
$$\begin{array}{l|cccc} C & 1 & 1 & 1 & 1 \\ H & 1 & 0 & 0 & 0 \\ H & 1 & 0 & 0 & 0 \\ H & 1 & 0 & 0 & 0 \end{array}$$

methyl radical



$$\begin{array}{l|cccccc} C & 0 & 2 & 1 & 0 & 0 & 1 \\ C & 2 & 0 & 0 & 1 & 1 & 0 \\ H & 1 & 0 & 0 & 0 & 0 & 0 \\ H & 0 & 1 & 0 & 0 & 0 & 0 \\ H & 0 & 1 & 0 & 0 & 0 & 0 \\ H & 1 & 0 & 0 & 0 & 0 & 0 \end{array}$$

ethylene



ij entries denote the bond order between atoms i and j
ii entries designate the number of nonbonded electrons associated with atom i

Chemical reaction as a matrix addition operation

$H\bullet + CH_4 \rightarrow \bullet CH_3 + H_2$

Reaction Operation

$$\begin{array}{c} H \\ C \\ H\bullet \end{array}\begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} + \begin{bmatrix} 0 & -1 & 1 \\ -1 & 1 & 0 \\ 1 & 0 & -1 \end{bmatrix} \rightarrow \begin{array}{c} H \\ C\bullet \\ H \end{array}\begin{bmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{bmatrix}$$

Reactant Matrices

$$\begin{array}{c} C \\ H \\ H \\ H \\ H \end{array}\begin{bmatrix} 0 & 1 & 1 & 1 & 1 \\ 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \end{bmatrix}$$

$$H\bullet \begin{bmatrix} 1 \end{bmatrix}$$

Reactant Matrix

$$\begin{array}{c} C \\ H \\ H \\ H \\ H \\ H\bullet \end{array}\begin{bmatrix} 0 & 1 & 1 & 1 & 1 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

Reordered Reactant Matrix

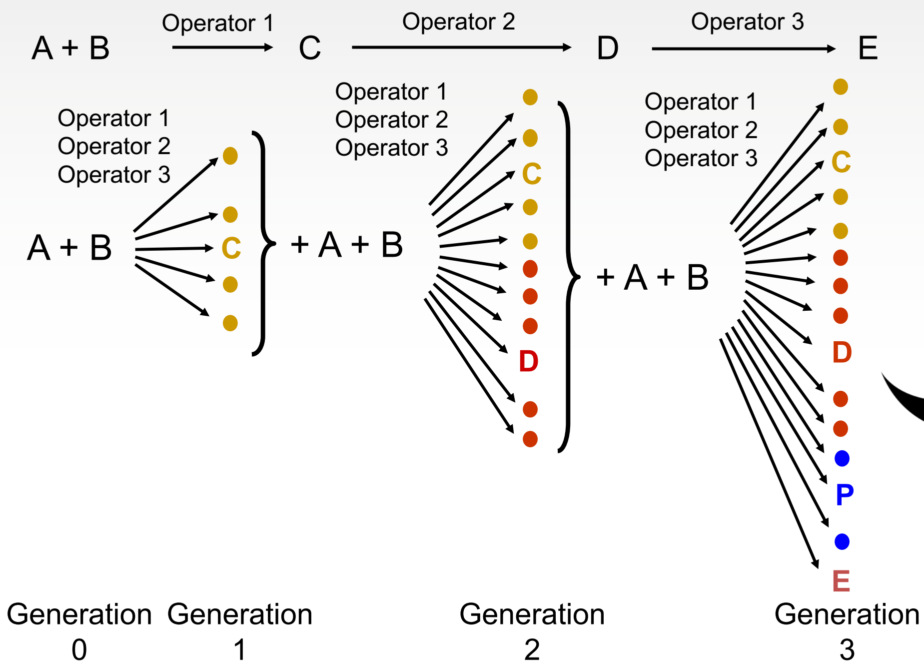
$$\begin{array}{c} H \\ C \\ H\bullet \\ H \\ H \\ H \end{array}\begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 1 & 1 & 1 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \end{bmatrix}$$

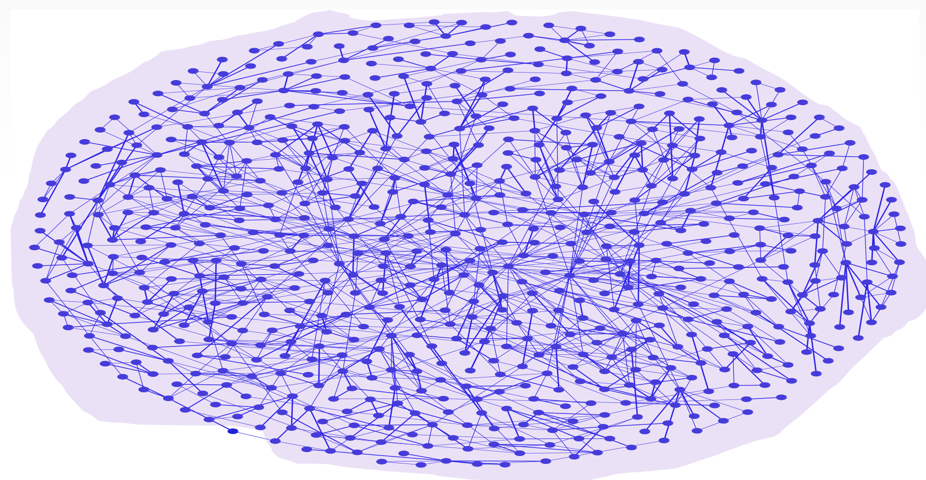
Product Matrix

$$\begin{array}{c} H \\ C\bullet \\ H \\ H \\ H \\ H \end{array}\begin{bmatrix} 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1 & 1 & 1 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \end{bmatrix}$$

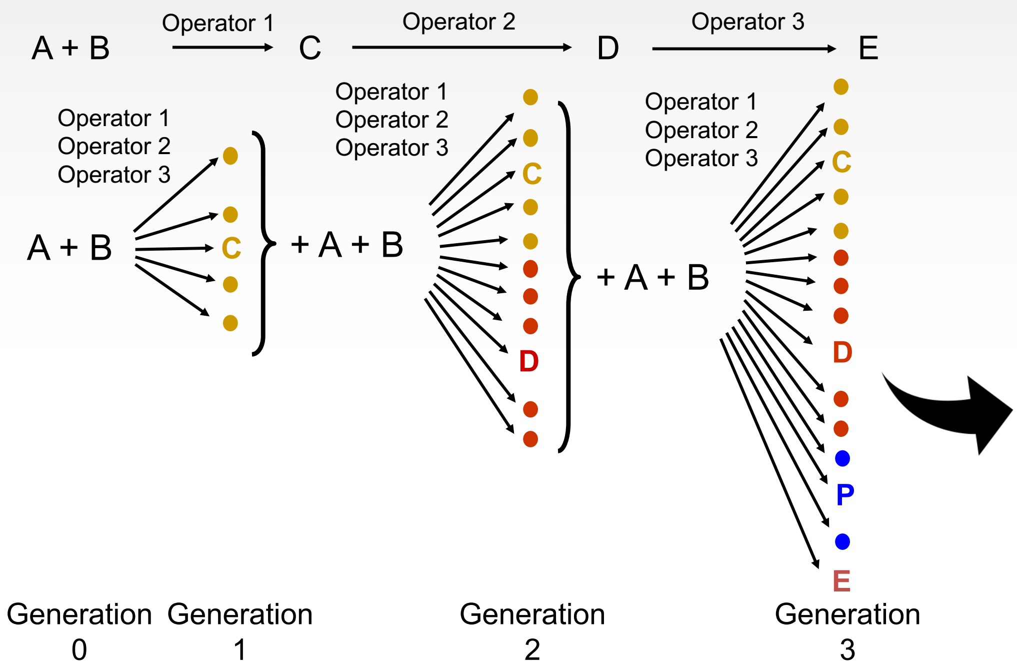
Repeated application of reaction operators…

…generates complex reaction networks automatically

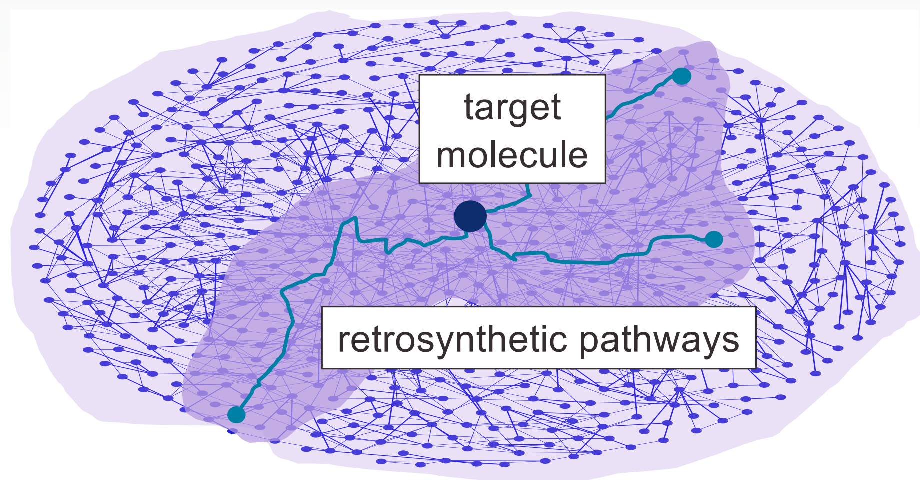




Repeated application of reaction operators…

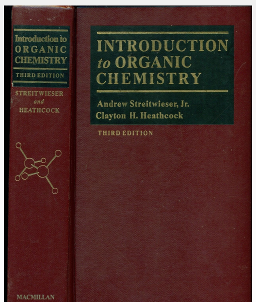


…generates complex reaction networks automatically from which retrosynthesis pathways can be mined



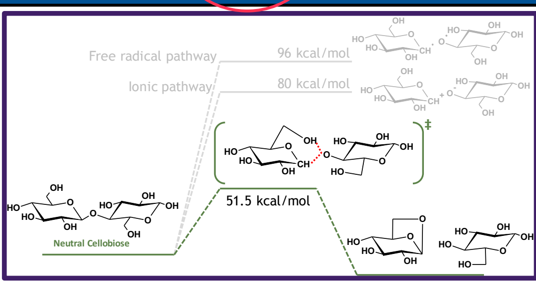
Understanding chemistry through cheminformatics

Probing mechanisms



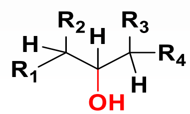
Reaction Operation

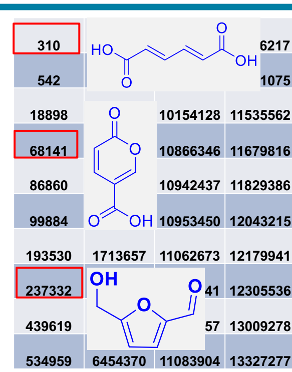
$$\begin{array}{c} H \\ C \\ H\bullet \end{array}\begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} + \begin{bmatrix} 0 & -1 & 1 \\ -1 & 1 & 0 \\ 1 & 0 & -1 \end{bmatrix} \rightarrow \begin{array}{c} H \\ C\bullet \\ H \end{array}\begin{bmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{bmatrix}$$



Querying databases

-[CH]-[CHOH]-[CH]-

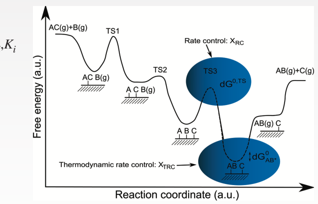


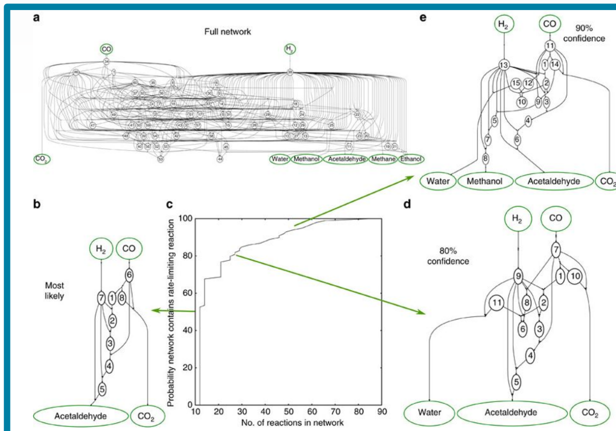


Data analytics

$$X_{RC,i} = \frac{k_i}{r}\left(\frac{\partial r}{\partial k_i}\right)_{k_{j\neq i},K_i} = \left(\frac{\partial \ln r}{\partial \ln k_i}\right)_{k_{j\neq i},K_i}$$

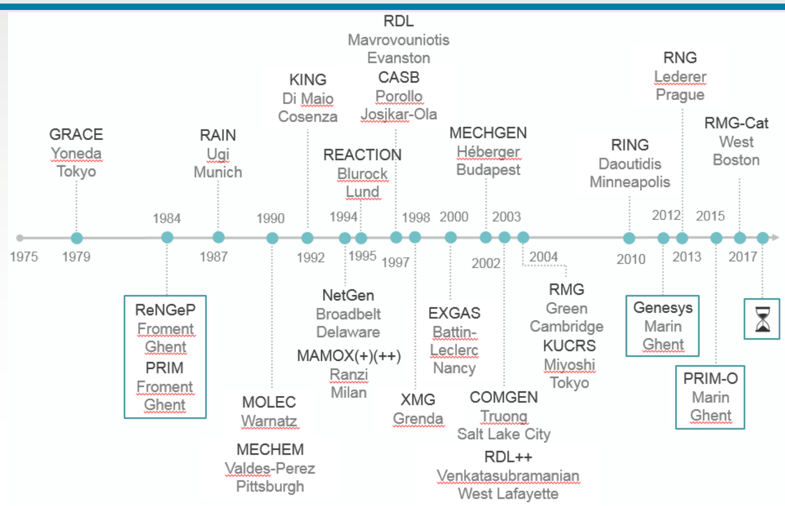
Stegelmann et al., *JACS*, **2009**, 131, 8077-8082





Ulissi et al., *Nature Communications*, **2017**, Volume 8, Article number: 14621

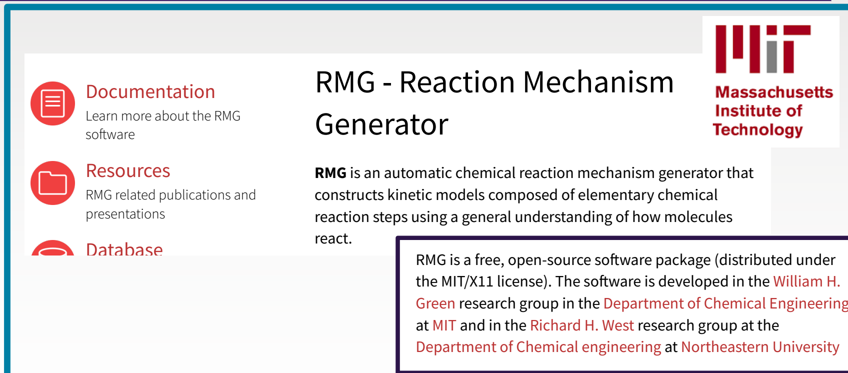
Availability of automated network generators



Vandewiele, N.M. et al., *Chem. Eng. J.*, **2012**, 207-208, 526-538.

synthesis.8 It can even be argued that a software package for performing automated network generation is as essential to kinetic model development as a stiff differential-algebraic equation solver is to model solution or a graphing program is to visualizing results.

AIChE J., **2005**, 51(8), 526-538, 2112.



RDKit
Open-Source Cheminformatics and Machine Learning

CDK

OpenBabel

LCT

GENESYS : GENEration of reacting SYStems

GHENT UNIVERSITY

Beyond continuum approaches

THE JOURNAL OF CHEMICAL PHYSICS 147, 024105 (2017)

Beyond mean-field approximations for accurate and computationally efficient models of on-lattice chemical kinetics

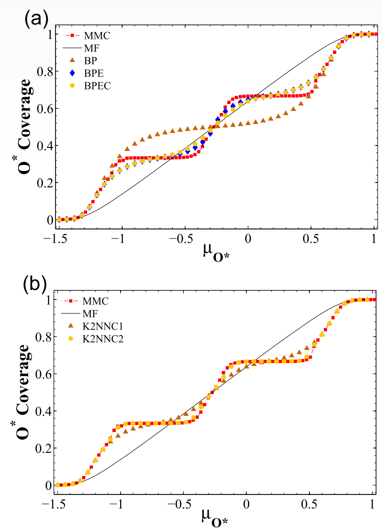
M. Pineda and M. Stamatakis[a)]
Department of Chemical Engineering, University College London, Roberts Building, Torrington Place, London WC1E 7JE, United Kingdom

(Received 7 February 2017; accepted 20 June 2017; published online 12 July 2017)

$$NO_{(gas)} + O^* \underset{k^{red}}{\overset{k^{oxi}}{\rightleftharpoons}} NO_{2(gas)} + *,$$

$$O_{2(gas)} + 2* \underset{k^{des}}{\overset{k^{ads}}{\rightleftharpoons}} 2O^*,$$

$$O^* + * \underset{k^{diff}}{\overset{k^{diff}}{\rightleftharpoons}} * + O^*,$$



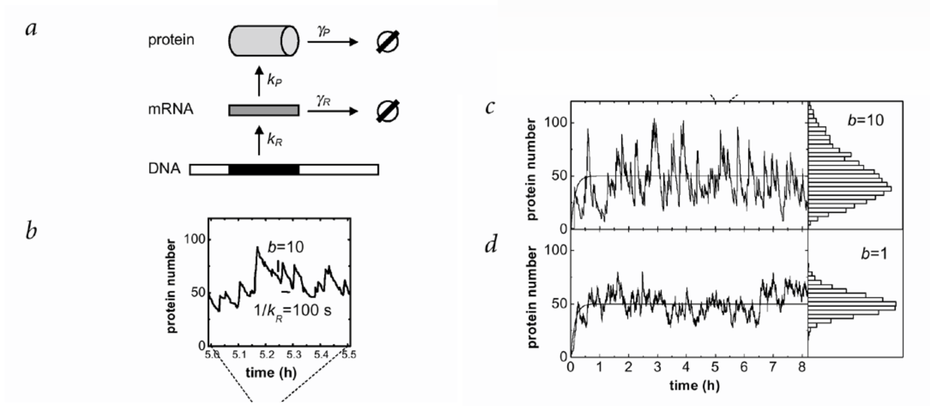
Pineda and Stamatakis, *J. Chem. Phys.*, **2017**, 024105

letter

Regulation of noise in the expression of a single gene

Ertugrul M. Ozbudak[1], Mukund Thattai[1], Iren Kurtser[2], Alan D. Grossman[2] & Alexander van Oudenaarden[1]

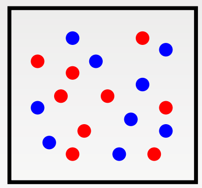
Published online: 22 April 2002, DOI: 10.1038/ng869



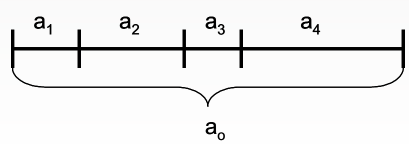
Ozbudak et al, *Nature Genetics.*, **2002**, DOI: 10.1038/ng869

Stochastic simulations: Kinetic Monte Carlo

Initialize concentrations, time, and counter



Calculate individual and total rates, a_ν and a_o



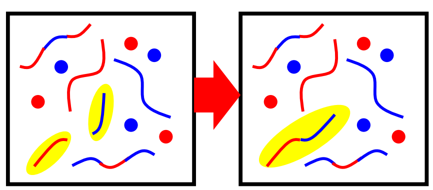
Determine reaction channel (μ) and timestep (τ) stochastically

$$\tau = (1/a_0)\ln(1/r_1)$$

$$\sum_{\nu=1}^{\mu-1} a_\nu < r_2 a_0 \le \sum_{\nu=1}^{\mu} a_\nu$$

Chain lengths vectorized, reacting chains randomly selected

Increment counter and t by τ and update concentrations based on occurrence of reaction μ



JOURNAL OF COMPUTATIONAL PHYSICS 22, 403–434 (1976)

A General Method for Numerically Simulating the Stochastic Time Evolution of Coupled Chemical Reactions

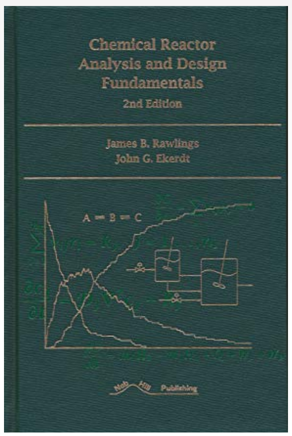
DANIEL T. GILLESPIE

Theoretical foundations of dynamical Monte Carlo simulations

Kristen A. Fichthorn
Department of Chemical Engineering, Pennsylvania State University, University Park, Pennsylvania 16802
W. H. Weinberg
Department of Chemical Engineering, University of California, Santa Barbara, California 93106

(Received 12 December 1990; accepted 10 April 1991)

Teaching kMC to undergraduates



Most Visited Getting Started

```
% along with this program; see the file COPYING.  If not, write to
% the Free Software Foundation, 59 Temple Place - Suite 330, Boston,
% MA 02111-1307, USA.

global ca0 cb0 cc0 k1det k2det
%
% add a stochastic simulation using Gillespie's algorithm
%
% example 1: A + B  --> C
%            C      --> A + B
%
nmolec = 400;
k1 = 1;
k2 = 1;
k(1) = k1/(nmolec);
k(2) = k2;
stoi = [-1 -1 1; 1 1 -1];
[nrxs,nspec]=size(stoi);
clear x
x(1,1)= nmolec;
x(2,1)= 0.9*nmolec;
x(3,1)= 0*nmolec;
stoiT = stoi';
nsim = nmolec*4;
clear time;
time = zeros(nsim+1,1);
time(1) = 0;
rng(0);
for n=1:nsim
  r(1) = k(1)*x(1,n)*x(2,n);
  r(2) = k(2)*x(3,n);
  rtot = sum(r);
  p=rand(2,1);
  tau = -log(p(1))/rtot;
  time(n+1)=time(n)+tau;
  % determine which reaction (mth) is likely to occur
  m = sum (cumsum (r) <= p(2)*rtot) + 1;
  x(:,n+1) = x(:,n) + stoiT(:,m);
end
%
```

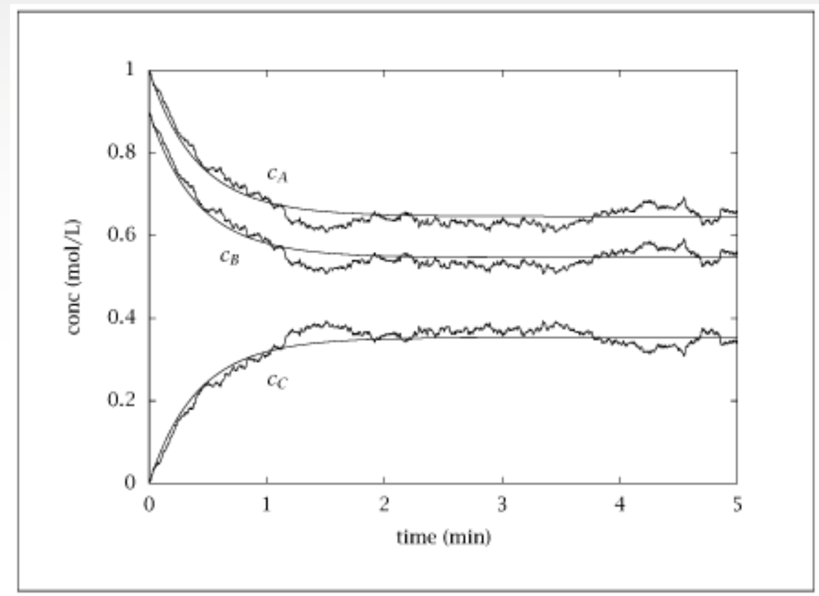


Figure 4.37: Deterministic simulation of reaction A + B <-> C compared to stochastic simulation

Software for kinetic Monte Carlo

SPPARKS Kinetic Monte Carlo Simulator

Anyone who considers arithmetical methods of producing random digits is, of course, in a state of sin. -- John von Neumann
God does not play dice -- Albert Einstein

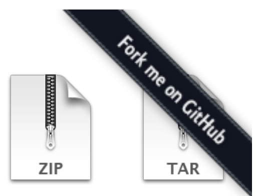
This is the home page for the kinetic Monte Carlo code SPPARKS, an acronym for Stochastic Parallel PARticle Kinetic Simulator.

Features	Documentation	Commands	Pictures & Movies
Download	Latest features & bug fixes	Performance	Open source
Pizza.py Toolkit	Publications	Thanks	Tutorial

SPPARKS is a parallel Monte Carlo code for on-lattice and off-lattice models that includes algorithms for kinetic Monte Carlo (KMC), rejection kinetic Monte Carlo (rKMC), and Metropolis Monte Carlo (MMC). It implements several KMC solvers whose serial computational complexity ranges from O(N) to O(NlogN) to O(1) in the number of events N owned by a processor. In a generic sense the solvers catalog a list of "events", each with an associated probability, choose a single event to perform, and advance time by the correct amount. Events may be chosen individually at random, or by sweeping over sites in a more ordered fashion.

https://sparks.sandia.gov

kmos



kMC on steroids: A vigorous attempt to make lattice kinetic Monte Carlo modeling as fast as possible.
kmos is being developed in the context of heterogeneous catalysis but might be of use in other applications as well. kmos wants to enable you to create first-principles kinetic Monte Carlo models faster and with less pain.
Some projects are using kmos already.

http://mhoffman.github.io/kmos/

frontiers in Chemistry

REVIEW
published: 09 April 2019
doi: 10.3389/fchem.2019.00202

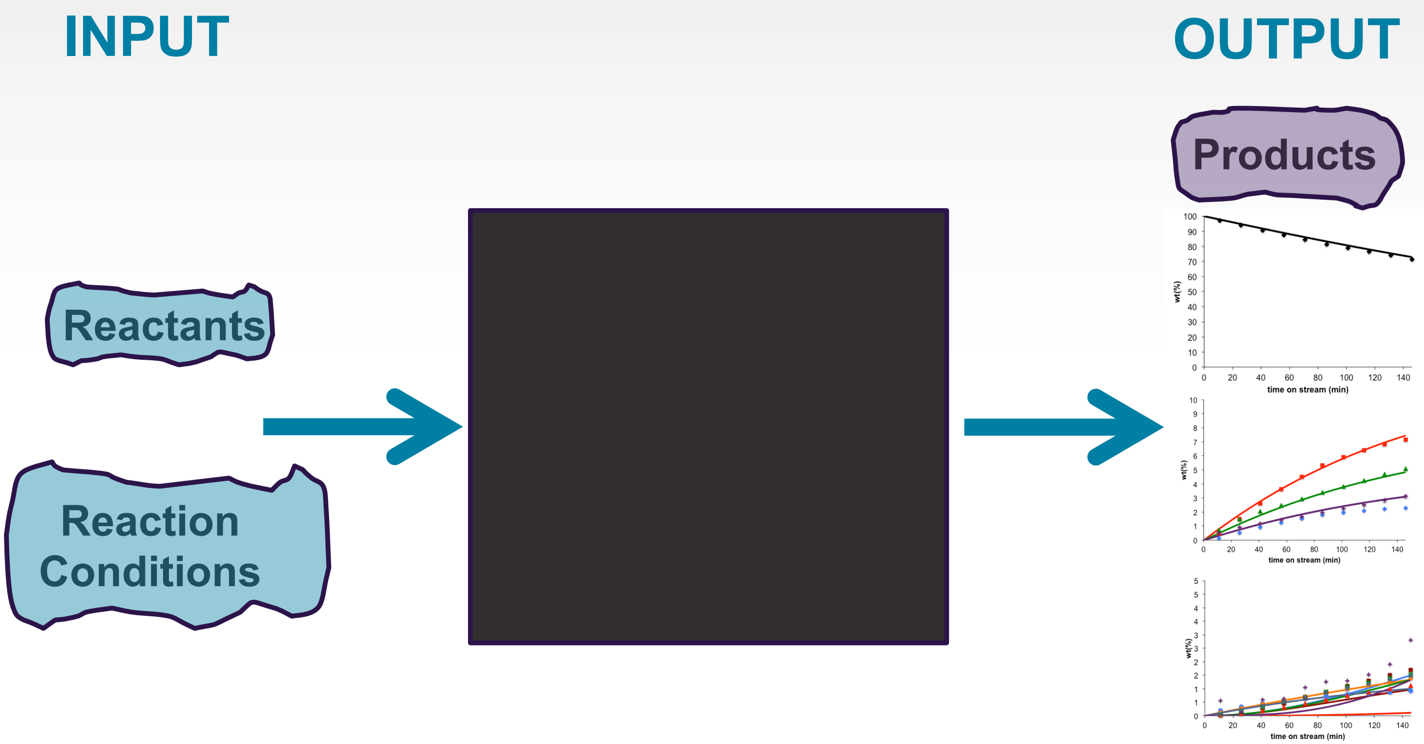
Check for updates

A Practical Guide to Surface Kinetic Monte Carlo Simulations

Mie Andersen, Chiara Panosetti and Karsten Reuter*

Example KMC models will be presented within the application areas surface diffusion, crystal growth and heterogeneous catalysis, covering both transient and steady-state kinetics as well as the preparation of various initial states of the system. We highlight the sensitivity of KMC models to the elementary processes included, as well as to possible errors in the rate constants. For catalysis models in particular, a recurrent challenge is the occurrence of processes at very different timescales, e.g., fast diffusion processes

Connecting data science with kinetics and reaction engineering

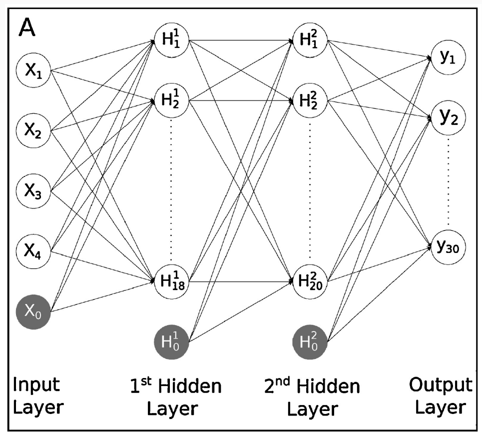


Connecting data science with kinetics and reaction engineering

INPUT

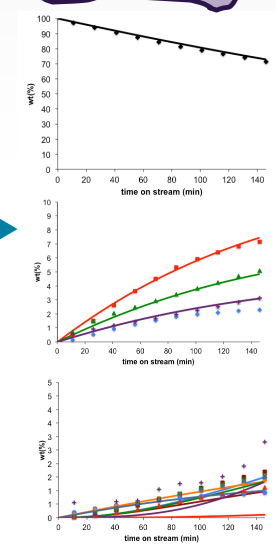
Reactants

Reaction Conditions



OUTPUT

Products



Example: artificial neural networks applied to lignin pyrolysis

- Choose relevant input and output variables for lignin pyrolysis

Black Box
Learning complex, non-linear and multivariate relationships

Inputs

T_{max}
Heating rate
Carbon mass fraction in feed
Hydrogen mass fraction in feed

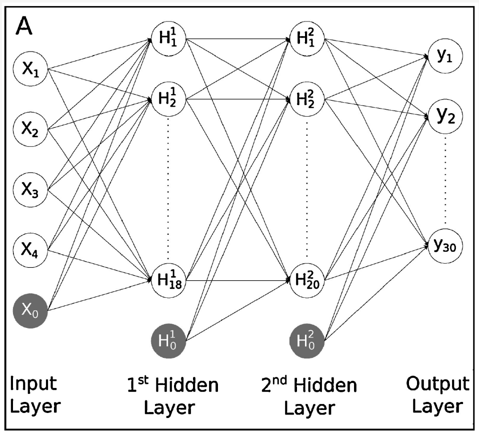
Outputs

CO
CO2
H—C
H2O
Moisture
heavy_C—O
heavy_aliphatic C—C
heavy_aliphatic_C—O
heavy_aromatic_C—C
heavy_aromatic_C—H
heavy_aromatic_C—O
heavy_aromatic_methoxyl
heavytars
light_C—O
light_aliphatic_C—C
light_aliphatic_C—O
light_aromatic_C—H
light_aromatic_C—O
lighttars
othergases
solids
tot_C—O
tot_aliphatic_C—C
tot_aliphatic_C—O
tot_aromatic_C—C
tot_aromatic_C—H
tot_aromatic_C—O
tot_aromatic_methoxyl
totalgases
totaltars

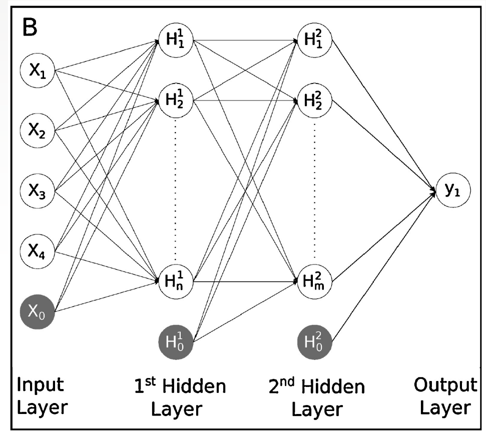
Hough et al., Computers and Chemical Engineering, **2017**, 104, 56-63.

Example: artificial neural networks applied to lignin pyrolysis

- Choose relevant input and output variables for lignin pyrolysis
- Choose neural network architecture and learning algorithms



Full net: predict all 30 output measures

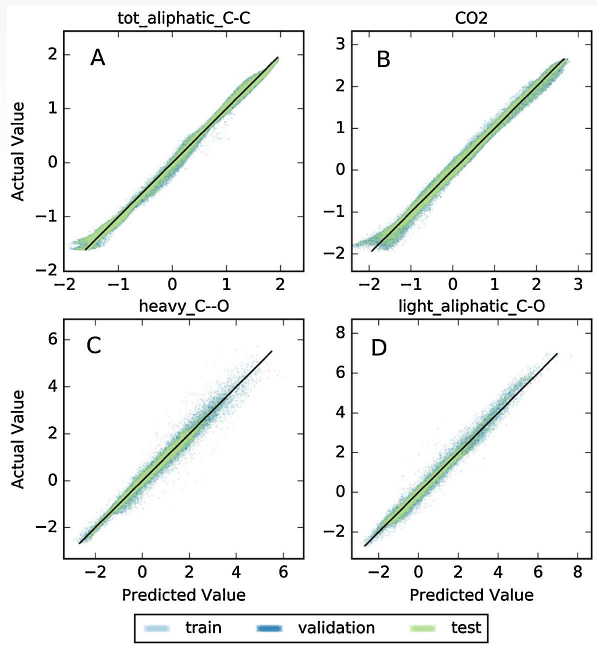


Single net: predict single output measure, repeat x 30

Hough et al., Computers and Chemical Engineering, **2017**, 104, 56-63.

Example: artificial neural networks applied to lignin pyrolysis

- Choose relevant input and output variables for lignin pyrolysis
- Choose neural network architecture and learning algorithms
- Train neural networks



Full net results

Hough et al., Computers and Chemical Engineering, **2017**, 104, 56-63.

Example: artificial neural networks applied to lignin pyrolysis

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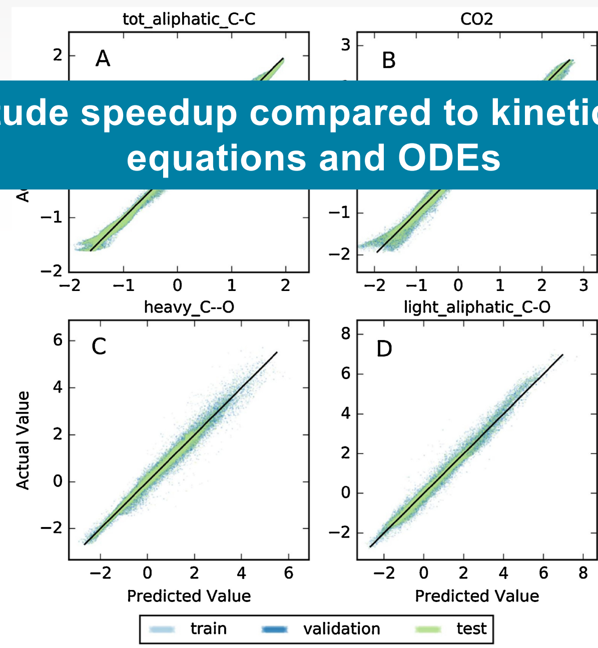


3-4 orders of magnitude speedup compared to kinetic model based on rate equations and ODEs

Full net results

Hough et al., Computers and Chemical Engineering, **2017**, 104, 56-63.

The Confluence of *Kinetic Modeling* and Data Science

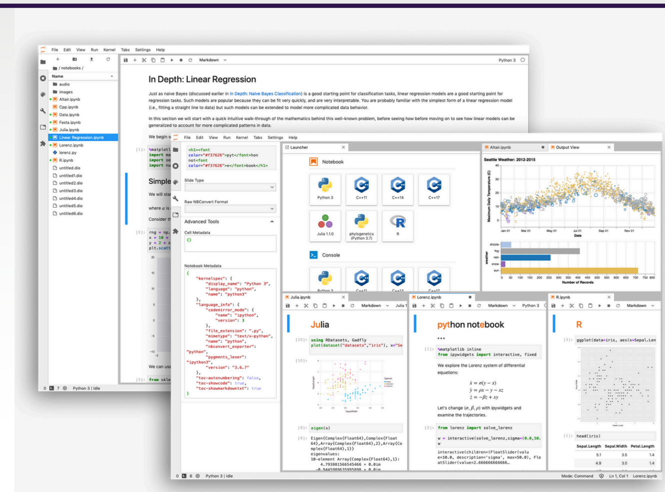
- Choose relevant input and output variables for lignin pyrolysis
- Choose neural network architecture and learning algorithms
- **Generate training and valuation data from *kinetic model***
  - 250,000 parameter combinations to cover input parameter space
    - T_{max} = 450-900 °C
    - Heating rate = 5-120,000 °C/min
    - 56-67.8 wt% carbon in feed
    - 5.4-6.6 wt% hydrogen in feed
  - Ran combinations through kinetic model to get outputs
  - Training set: 140,000 pairs
  - Validation set: 60,000 pairs
  - Test set: 50,000 pairs
- Train neural networks

Hough et al., Computers and Chemical Engineering, **2017**, 104, 56-63.
Hough et al., Ind. Eng. Chem. Res., **2016**, 55 (34), 9147–9153

Teaching data science methods: starting with Python

Introduction to data science at Northwestern

- 10-day programming bootcamp focusing on Python
- Opportunity to learn the programming skills needed to collect, process, and analyze data

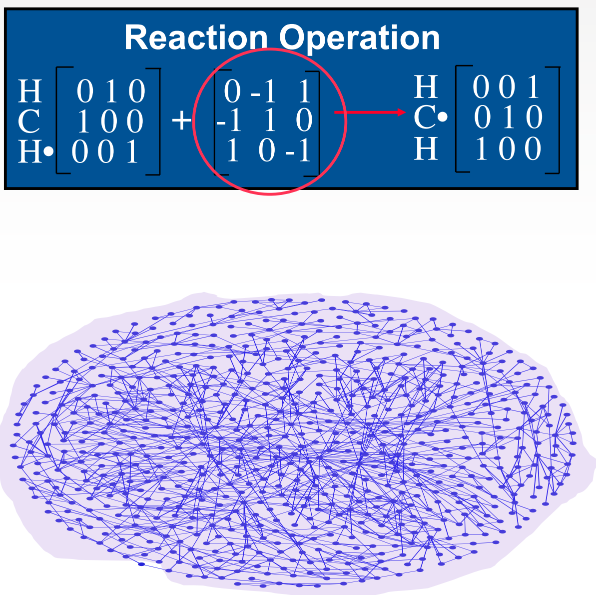


JupyterLab 1.0: Jupyter's Next-Generation Notebook Interface

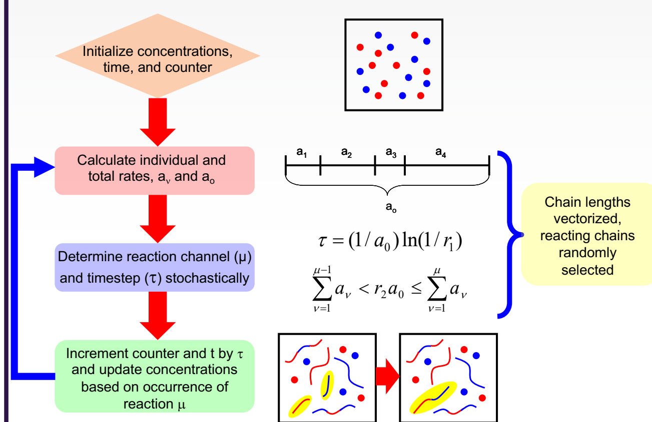
JupyterLab is a web-based interactive development environment for Jupyter notebooks, code, and data. JupyterLab is flexible: configure and arrange the user interface to support a wide range of workflows in data science, scientific computing, and machine learning. JupyterLab is extensible and modular: write plugins that add new components and integrate with existing ones.

Beyond A→B: Computational Approaches for Education in Reaction Engineering and Kinetics of Complex Systems

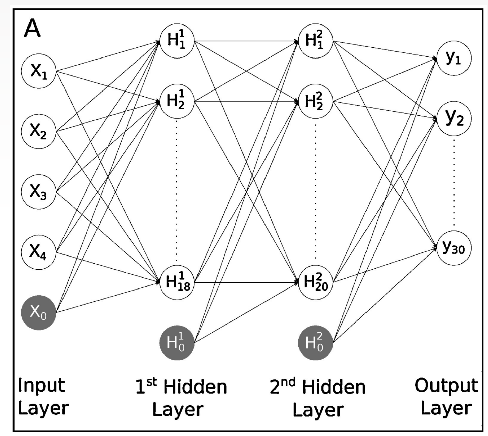
Network generation



Stochastic simulations



Machine learning



Acknowledgments

CACHE
Computer Aids for Chemical Engineering

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