The NIST Chemical Kinetics Database

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http://kinetics.nist.gov/
Overview

- Content
- Functionality
- Usage
- Live demo
- Future directions
- Challenges
Content

- Data on gas-phase chemical reactions abstracted from the primary literature
- Over 13,500 bibliographic references
- Over 10,000 chemical compounds
- Over 41,000 rate expressions
- Starting to gather data points
Rate expressions

- Rate data captured as fits to an Arrhenius expression (2- and 3-parameter) valid over a given temperature (and pressure) range
- Uncertainty information always captured

\[
k(T) = A \exp^{-\frac{E_a}{RT}}
\]

\[
k(T) = A \left(\frac{T}{T_{ref}}\right)^n \exp^{-\frac{E_a}{RT}}
\]
Pressure dependence

- New to database
- Capture single channels only
- Constant, Troe form, and NASA equation

\[ k_f ([M], T) = \left( \frac{k_0 (T) [M]}{1 + \frac{k_0 (T) [M]}{k_\infty (T')}} \right) 0.6 \left\{ 1 + \left[ \log_{10} \left( \frac{k_0 (T) [M]}{k_\infty (T')} \right) \right]^2 \right\}^{-1} \]

\[ k_{\text{uni}} = k_\infty \left( \frac{P_r}{1 + P_r} \right) 10^{\frac{\log F_{\text{cent}}}{1 + (\log P_r)^2}} \]

\[ F_{\text{cent}} (T) = (1 - a) \exp \left( -\frac{T}{T^{***}} \right) + a \exp \left( -\frac{T}{T^*} \right) + \exp \left( -\frac{T^{**}}{T} \right) \]
Functionality

• Search by reaction (reactants/products) and by reference (author, journal, etc.)
• Plotting of rate expressions
• Summary and detail views of data
• User selected units
• See all reactions from a given reference
• Cross-linking
• Links to NIST Chemistry WebBook
Home page

Links

Simple search interface

Chemical Kinetics Database on the Web

Chemical Kinetics Database on the Web

Welcome
About the database.
Getting Started
A quick introduction to the database.
Credits and History
Who created the present version and the earlier versions?
Targeted Evaluations
Results of more comprehensive data evaluation and estimation efforts in specific areas.
Feedback
How to report errors or obtain technical assistance.
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Search Results

User-selected units

Plot controls

Summary of search results
Plotting

Plotting of rate expressions
Detail

Full bibliography

All rate data

Data in tabular form
### Bibliographic Record

**Title:** Computational study of the kinetics of hydrogen abstraction from fluoromethanes by the hydroxyl radical

**Author(s):** Schwartz, M.; Marshall, P.; Berry, R.J.; Ehlers, C.J.; Peterson, G.A.

**Journal:** J. Phys. Chem. A.

**Volume:** 102

**Page(s):** 10074 - 10081

**Year:** 1998

**Reference type:** Journal article

**SQuID:** 1998SCH/MAR10074-10081

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### Associated entries:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Temp</th>
<th>Rate expression</th>
<th>Order</th>
<th>Detail</th>
</tr>
</thead>
<tbody>
<tr>
<td>-OH + CH3F → H2O + CH2F</td>
<td>200 - 2500</td>
<td>$3.79 \times 10^{-22} \text{ (T/298 K)}^{3.35} \cdot 6010 \text{RT}$</td>
<td>2</td>
<td>Detail</td>
</tr>
<tr>
<td>-OH + CH4 → H2O + CH3</td>
<td>200 - 2500</td>
<td>$1.22 \times 10^{-13} \text{ (T/298 K)}^{2.32} \cdot 1.6593 \text{RT}$</td>
<td>2</td>
<td>Detail</td>
</tr>
<tr>
<td>-OH + CH2F2 → H2O + CHF2</td>
<td>200 - 2500</td>
<td>$4.38 \times 10^{-22} \text{ (T/298 K)}^{3.27} \cdot 3983 \text{RT}$</td>
<td>2</td>
<td>Detail</td>
</tr>
<tr>
<td>-OH + CHF3 → H2O + CF3</td>
<td>200 - 2500</td>
<td>$1.15 \times 10^{-13} \text{ (T/298 K)}^{3.66} \cdot 8898 \text{RT}$</td>
<td>2</td>
<td>Detail</td>
</tr>
</tbody>
</table>

Use the Plot checkboxes to select data for plotting. Plot selected data using the "Create Plot" button. Click the Detail link to see extra information about a particular rate constant. Additional help is available.
Data entry tool

Chemical Science and Technology Laboratory

NIST Kinetics Data Entry System

Kinetic Data Entry Form

Rate Expression:

\[ k(T) = A \left( \frac{T}{T_{\text{ref}}} \right)^{n} \exp\left(-\frac{E_{a}}{RT} \right) \]

- Temperature
- Pressure
- \( A (\text{or } k) \)
- \( n \)
- \( T_{\text{ref}} \)
- \( E_{a} \)

Uncertainty

Limits: \( k \)

\[ k(T, p) = k_{\infty} \left( \frac{P_{T}}{1 + P_{r}} \right)^{A} \exp^{B \frac{\log P_{r}}{T_{r}}} \]

- \( k_{\infty} \)
- \( A = 10, B = \log F_{\text{cent}} \)

Submit  Clear  Cancel  Help

Chemical Science and Technology Laboratory
Usage Statistics

- Served over 1 million pages in the last two years
- Serve more than 1,600 pages per day
- Served nearly 60,000 distinct hosts
Live demo

- Web-based database
- Data entry system
Enhancements

- Data update
- Faster
- New layout
- More search options
- Print layouts
- Standards based
- Collections
Future directions

• Ability to collect all data user select and deliver as
  • PDF report
  • ChemKin format file
  • XML file
<?xml version="1.0" encoding="UTF-8"?>
<reaction>
  <reference>1998SCH_MAR10074-10081_1</reference>
  <reactant>
    <identifier type="CASNO">593533</identifier>
    <identifier type="formula">CH3F</identifier>
    <stoichiometry>1</stoichiometry>
  </reactant>
  <reactant>
    <identifier type="CASNO">3352576</identifier>
    <identifier type="formula">HO</identifier>
    <stoichiometry>1</stoichiometry>
  </reactant>
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    <identifier type="formula">CH2F</identifier>
    <stoichiometry>-1</stoichiometry>
  </product>
  <product>
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    <identifier type="formula">H2O</identifier>
    <stoichiometry>-1</stoichiometry>
  </product>
  <arrheniusExpression>
    <reactionOrder>2</reactionOrder>
    <temperature>
      <range>
        <low>200.0</low>
        <high>2500.0</high>
      </range>
      <units>K</units>
    </temperature>
    <A>
      <value>228.0</value>
      <units>cm3/mole s</units>
    </A>
    <n>
      <value>3.35</value>
      <referenceTemperature>
        <value>1.0</value>
        <referenceTemperature>
        </referenceTemperature>
      </referenceTemperature>
    </n>
    <Ea>
      <value>368.0</value>
      <units>K</units>
    </Ea>
  </arrheniusExpression>
  <descriptors>
    <dataType>Transition state theory</dataType>
  </descriptors>
</reaction>
Future directions

• Distribute data entry tool to authors
• Work with journals to have authors submit data at publication time (a la ThermoML)
• 2-D structures
• Substructure searching
Data Usability

- Make kinetics data readily available for kinetic modeling
  - database “collection” functionality
  - NIST-PrIIMe project
  - NIST Real Fuels initiative
PrlMe

- “Process Informatics Model”
- Michael Frenklach, Berkeley
- Implemented through CMCS portal
- Recently partnered with NIST
What is PrIMe? PrIMe is a community activity aimed at the development of predictive reaction models for combustion. The primary motivation is to establish and demonstrate the community approach to kinetic-model development and, perhaps most importantly, establish a means for reaching community consensus on the models and data.
• Chemical reaction models are an ongoing challenge. The problem is that these data are scattered over different sources and are not properly evaluated.

• Chemical reaction model building is a time-consuming activity that requires expert knowledge. At present, most treat this activity as an “art” (or “religion”).

• The PrIME goal is to convert such model building into science, automate the methodology, and make the results available in a prompt and convenient form for the user.
PrlMe Warehouse/Library

NIST-PrlMe Warehouse
- All data
- User contributions
- Open
- Searchable, etc.

NIST-PrlMe Library
- Best data
- Only one number
- Dynamic
- Basis for models

Review
CMCS

• Collaboratory for Multi-Scale Chemical Science

• DOE funded project to create web-based collaborative infrastructure for doing research

• Strong emphasis on data, especially data pedigree

• A good model for future databases?
Challenges

- Need funding for data collection efforts
- Better ways to make use of existing tools
- Critical evaluation of data
- Unique species identification
- How much automation is possible? Desirable?
- Integration with thermodynamic data
Challenges...

• Need to change the way scientists work
  • reporting of data in the literature
Conclusion

- The NIST Kinetics Database is a valuable resource for gas-phase kinetics
- Future enhancements will concentrate on data updates, improved user experience and content delivery
- There are a number of hurdles to overcome
For more information...

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