

The NIST Chemical Kinetics Database

Thomas C. Allison, NIST
April 20, 2004

<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

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

$$k(T) = A \left(\frac{T}{T_{\text{ref}}} \right)^n \exp^{-\frac{E_a}{RT}}$$

Pressure dependence

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

$$k_f([M], T) = \left(\frac{k_0(T)[M]}{1 + \frac{k_0(T)[M]}{k_\infty(T)}} \right) 0.6 \left\{ 1 + \left[\log_{10} \left(\frac{k_0(T)[M]}{k_\infty(T)} \right) \right]^2 \right\}^{-1}$$

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

$$F_{\text{cent}}(T) = (1 - a)\exp(-T/T^{***}) + a\exp(-T/T^*) + \exp(-T^{**}/T)$$

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

Simple search interface

Links

The screenshot shows the NIST Chemical Kinetics Database homepage. A sidebar on the left contains links like 'Kinetics Database Resources', 'Simple Reaction Search', and 'Search Reaction Database'. The main content area features a 'Reaction Database Quick Search Form' with fields for reactants (e.g., 'ch4 + oh') and a 'Submit' button. Below the search form are sections for 'Welcome', 'Getting Started', 'Credits and History', 'Targeted Evaluations', and 'Feedback'. The top right corner includes the NIST logo and links for 'Home', '©NIST, 2000', and 'Accessibility information'. Red annotations highlight several parts of the interface: a large oval encloses the search form and its surrounding text; another large oval encloses the sidebar links; a red arrow points from the 'Links' text to the 'Accessibility information' link; and a red arrow points from the 'Simple search interface' text to the search form.

Search Results

User-selected units

Plot controls

Summary of search results

NIST Chemical Kinetics Database

http://kinetics.nist.gov/index.php?doc=ReactionSearch&type=java&r0=3352576&r1=74828&r2=

Search Results

Kinetics Database Resources

Simple Reaction Search

Search Reaction Database

Search Bibliographic Database

Targeted Evaluations

Set Unit Preferences

Feedback

Project status

Help

Other Databases

NIST Standard Reference Data Program

NIST Chemistry Web Book

NIST

Home ©NIST, 2000 Accessibility information

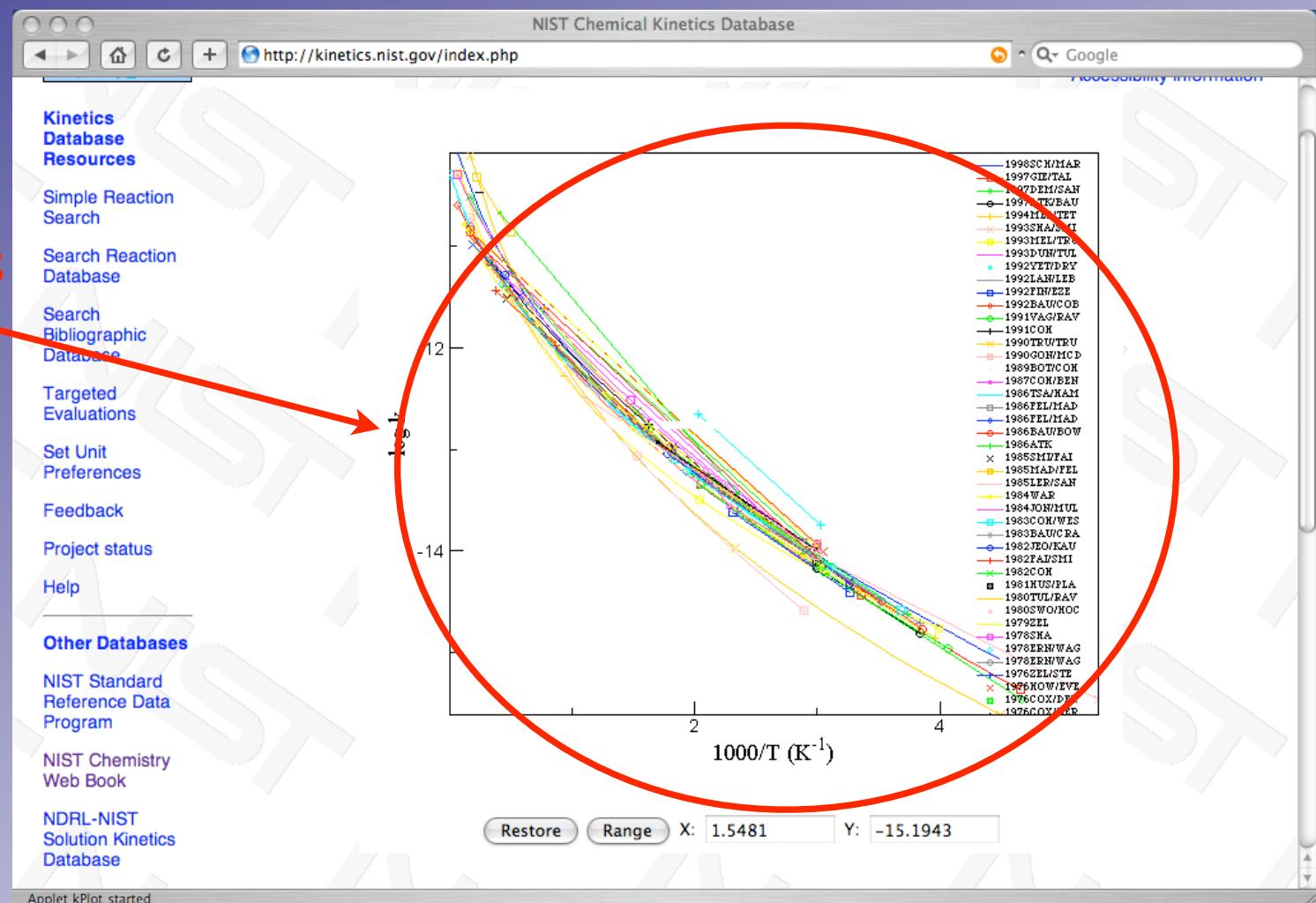
Energy Units J Molecular Units Molecule
Pressure Units bar Temperature Units K
Base Volume Unit cm Reference Temperature 298.0

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.

Plot	Reaction	Temp	Rate expression	Order	Detail
<input type="checkbox"/> 1998SCH/IVATT10071-10001	$\cdot\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \cdot\text{CH}_3$	200 - 2500	$1.22 \times 10^{-13} (\text{T}/298 \text{ K})^{3.21} e^{-6593/\text{RT}}$	2	Detail
<input type="checkbox"/> 1997GIE/TAL3125-3134	$\cdot\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \cdot\text{CH}_3$	196 - 420	$1.76 \times 10^{-13} (\text{T}/298 \text{ K})^{2.39} e^{-8206/\text{RT}}$	2	Detail
<input type="checkbox"/> 1997DEM/SAN1-266	$\cdot\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \cdot\text{CH}_3$	200 - 300	$2.46 \times 10^{-12} e^{-14800/\text{RT}}$	2	Detail
<input type="checkbox"/> 1997ATR/BAU521-1011	$\cdot\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \cdot\text{CH}_3$	240 - 300	$2.31 \times 10^{-12} e^{-14633/\text{RT}}$	2	Detail
<input type="checkbox"/> 1994MEL/TET473-487	$\cdot\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \cdot\text{CH}_3$	233 - 343	$2.56 \times 10^{-12} e^{-14633/\text{RT}}$	2	Detail
<input type="checkbox"/> 1993SHA/SMI631-638	$\cdot\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \cdot\text{CH}_3$	178 - 298	$9.65 \times 10^{-13} e^{-11807/\text{RT}}$	2	Detail
<input type="checkbox"/> 1993MEL/TRU1013-1027	$\cdot\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \cdot\text{CH}_3$	223 - 2400	$1.52 \times 10^{-14} (\text{T}/298 \text{ K})^{3.95} e^{-2286/\text{RT}}$	2	Detail
<input type="checkbox"/> 1993DUN/TUL11148-11150	$\cdot\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \cdot\text{CH}_3$	293 - 800	$2.34 \times 10^{-13} (\text{T}/298 \text{ K})^{2.58} e^{-8980/\text{RT}}$	2	Detail
<input type="checkbox"/> 1992YET/DRY757-767	$\cdot\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \cdot\text{CH}_3$	1030	2.69×10^{-12}	2	Detail
<input type="checkbox"/> 1992LAN/LEB1487-1492	$\cdot\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \cdot\text{CH}_3$	378 - 422	$2.84 \times 10^{-12} e^{-14717/\text{RT}}$	2	Detail
<input type="checkbox"/> 1992FIN/EZE1371-1374	$\cdot\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \cdot\text{CH}_3$	278 - 378	$4.0 \times 10^{-12} e^{-16130/\text{RT}}$	2	Detail
<input type="checkbox"/> 1992BAU/COB411-429	$\cdot\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \cdot\text{CH}_3$	250 - 2500	$8.77 \times 10^{-13} (\text{T}/298 \text{ K})^{1.83} e^{-11640/\text{RT}}$	2	Detail
<input type="checkbox"/> 1991MAG/RAV406-409	$\cdot\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \cdot\text{CH}_3$	223 - 420	$1.69 \times 10^{-13} (\text{T}/298 \text{ K})^{2.84} e^{-8132/\text{RT}}$	2	Detail
<input type="checkbox"/> 1991COH397-417	$\cdot\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \cdot\text{CH}_3$	298 - 1510	$1.54 \times 10^{-12} (\text{T}/298 \text{ K})^{1.60} e^{-13054/\text{RT}}$	2	Detail
<input type="checkbox"/> 1990TRU/TRU1761	$\cdot\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \cdot\text{CH}_3$	200 - 2000	$1.13 \times 10^{-14} (\text{T}/298 \text{ K})^{4.75} e^{-36827/\text{RT}}$	2	Detail

Plotting

Plotting
of rate
expressions



Detail

Full
bibliography

All rate
data

Data in
tabular
form

NIST Chemical Kinetics Database

Author(s): Schwartz, M.; Marshall, P.; Berry, R.J.; Ehlers, C.J.; Petersson, G.A.
Title: Computational study of the kinetics of hydrogen abstraction from fluoromethanes by the hydroxyl radical
Journal: J. Phys. Chem. A:
Volume: 102
Page(s): 10074 - 10081
Year: 1998
Reference type: Journal article
Squib: 1998SCH/MAR10074-10081

Reaction: $\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \cdot\text{CH}_3$
Reaction order: 2
Temperature: 200 - 2500 K
Rate expression: $1.22 \times 10^{-13} (\text{cm}^3/\text{molecule s}) (T/298 \text{ K})^{3.21} e^{-6593 (\text{J/mole})/RT}$
Data type: Transition state theory

[View full bibliographic record.](#)

Rate constant values calculated from the Arrhenius expression:

T (K)	k(T) [cm ³ /molecule s]
200.00	6.42×10^{-16}
300.00	8.85×10^{-15}
400.00	4.32×10^{-14}
500.00	1.31×10^{-13}
600.00	3.07×10^{-13}
700.00	6.09×10^{-13}
800.00	1.08×10^{-12}
900.00	1.75×10^{-12}
1000.00	2.69×10^{-12}

Bibliographic Record

All data
from
reference

NIST Chemical Kinetics Database

Author(s): Schwartz, M.; Marshall, P.; Berry, R.J.; Ehlers, C.J.; Petersson, G.A.
Title: Computational study of the kinetics of hydrogen abstraction from fluoromethanes by the hydroxyl radical
Journal: J. Phys. Chem. A:
Volume: 102
Page(s): 10074 - 10081
Year: 1998
Reference type: Journal article
Squib: 1998SCH/MAR10074-10081

Associated entries:

Energy Units	J	Molecular Units	Molecule
Pressure Units	bar	Temperature Units	K
Base Volume Unit	cm	Reference Temperature	298.0

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.

[Create Plot](#) | [Check all...](#) | [2nd order](#) | [Uncheck All](#)

Plot	Squib	Reaction	Temp	Rate expression	Order	Detail
<input type="checkbox"/>	1998SCH/MAR10074-10081	$\cdot\text{OH} + \text{CH}_3\text{F} \rightarrow \text{H}_2\text{O} + \cdot\text{CH}_2\text{F}$	200 - 2500	$3.79 \times 10^{-22} (T/298 \text{ K})^{3.35} e^{-3060/RT}$	2	Detail
<input checked="" type="checkbox"/>	1998SCH/MAR10074-10081	$\cdot\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \cdot\text{CH}_3$	200 - 2500	$1.22 \times 10^{-13} (T/298 \text{ K})^{3.21} e^{-6593/RT}$	2	Detail
<input type="checkbox"/>	1998SCH/MAR10074-10081	$\cdot\text{OH} + \text{CH}_2\text{F}_2 \rightarrow \text{H}_2\text{O} + \cdot\text{CHF}_2$	200 - 2500	$4.38 \times 10^{-22} (T/298 \text{ K})^{3.27} e^{-3983/RT}$	2	Detail
<input type="checkbox"/>	1998SCH/MAR10074-10081	$\cdot\text{OH} + \text{CHF}_3 \rightarrow \text{H}_2\text{O} + \cdot\text{CF}_3$	200 - 2500	$1.15 \times 10^{-13} (T/298 \text{ K})^{3.66} e^{-8896/RT}$	2	Detail

Search returned 4 records.

Data entry tool

NIST Kinetics Data Entry System

File Edit Search Help

B **P** **k(T)** **?**

Kinetic Data Entry Form

Reaction Rate Data Descriptors Comments

Rate Expression

Temperature - Units
Pressure - Units
$$k(T) = A(T/T_{ref})^n \exp(-E_a/RT)$$

A (or k) \pm err Units
n \pm err
T_{ref} Units
E_a \pm err Units
Uncertainty
Limits: k
E_a

Submit Clear Cancel Help

$$k(T, p) = k_\infty \left(\frac{P_r}{1 + P_r} \right) A^{\frac{B}{1 + (\log P_r)^2}}, P_r = \frac{k_0[M]}{k_\infty}$$

$$A = 10, B = \log F_{cent}$$

F_{cent}

Submit Clear Cancel Help

Form

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

NIST Chemical Kinetics Database Home Page

<http://localhost/kinetics/index.jsp>

Google

NIST Chemical Kinetics Database

A compilation of kinetics data on gas-phase reactions

Resources

- Reaction Search
- Bibliography Search
- Targeted Evaluations
- Unit Preferences
- Feedback
- News
- Help

Links

- NIST Standard Reference Data Program
- NIST Chemistry Web Book
- NIST Computational Chemistry Comparison and Benchmark Database
- NIST Reference on Constants, Units, and Uncertainty
- More...

Administrative Links

- NIST home page
- CSTL home page
- Physical and Chemical Properties Division

Quick Search Form

Enter the reactant(s) and/or product(s) in the fields below. Fields may be left blank.

ch4 + oh → +

Submit **Clear**

If you would like more searching options, click the links for the reaction or bibliography search to the left. [Help](#) on searching is available.

Preferences Information

Show the current user preferences.

Database Information

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.

Cookies
How we use information about your preferences.

Disclaimer and Copyright Statement

Accessibility Information

Future directions

- Ability to collect all data user select and deliver as
 - PDF report
 - ChemKin format file
 - XML file

XML

```
<?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>
  <product>
    <identifier type="CASNO">3744294</identifier>
    <identifier type="formula">CH2F</identifier>
    <stoichiometry>-1</stoichiometry>
  </product>
  <product>
    <identifier type="CASNO">7732185</identifier>
    <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>
    </n>
    <Ea>
      <value>368.0</value>
      <units>K</units>
    </Ea>
  </arrheniusExpression>
  <descriptors>
    <dataType>Transition state theory</dataType>
  </descriptors>
  <copyright>&copy; 2004 copyright by the U.S. Secretary of
  Commerce on behalf of the United States of America. All rights
  reserved.</copyright>
</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-PrIMe project
 - NIST Real Fuels initiative

PrI Me

- “Process Informatics Model”
- Michael Frenklach, Berkeley
- Implemented through CMCS portal
- Recently partnered with NIST

NIST-PrIMe

- 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.

NIST-PrIMe

- 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.

PrIMe Warehouse/Library

NIST-PrIMe Warehouse

- All data
- User contributions
- Open
- Searchable, etc.

Review

NIST-PrIMe Library

- Best data
- Only one number
- Dynamic
- Basis for models

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...

- Tom Allison, NIST
 - thomas.allison@nist.gov
- Michael Frenklach, Berkeley
 - myf@me.berkeley.edu
- Larry Rahn, CMCS
 - <http://cmcs.org/>
 - rahn@sandia.gov