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

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

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

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

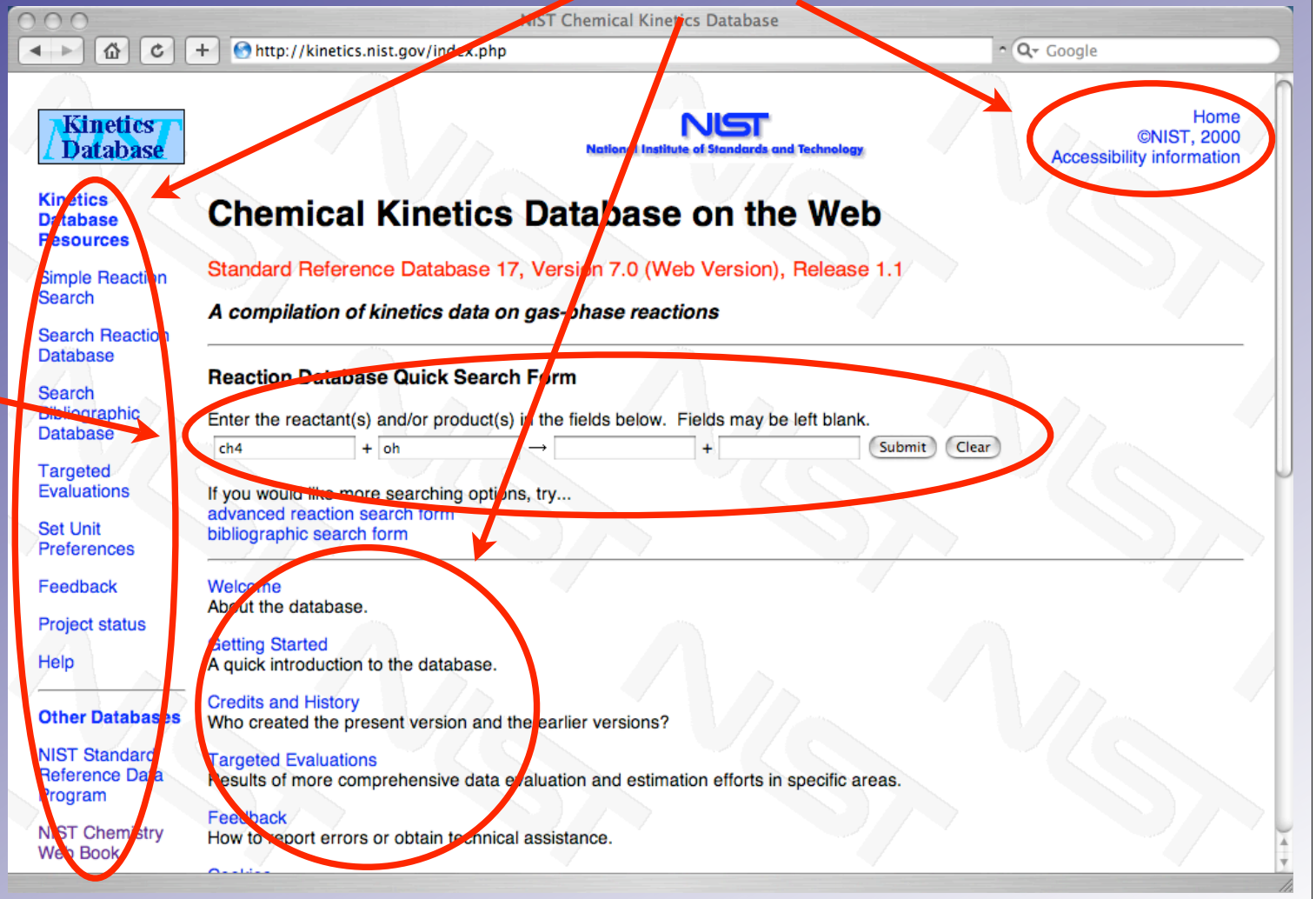
Functionality

- 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

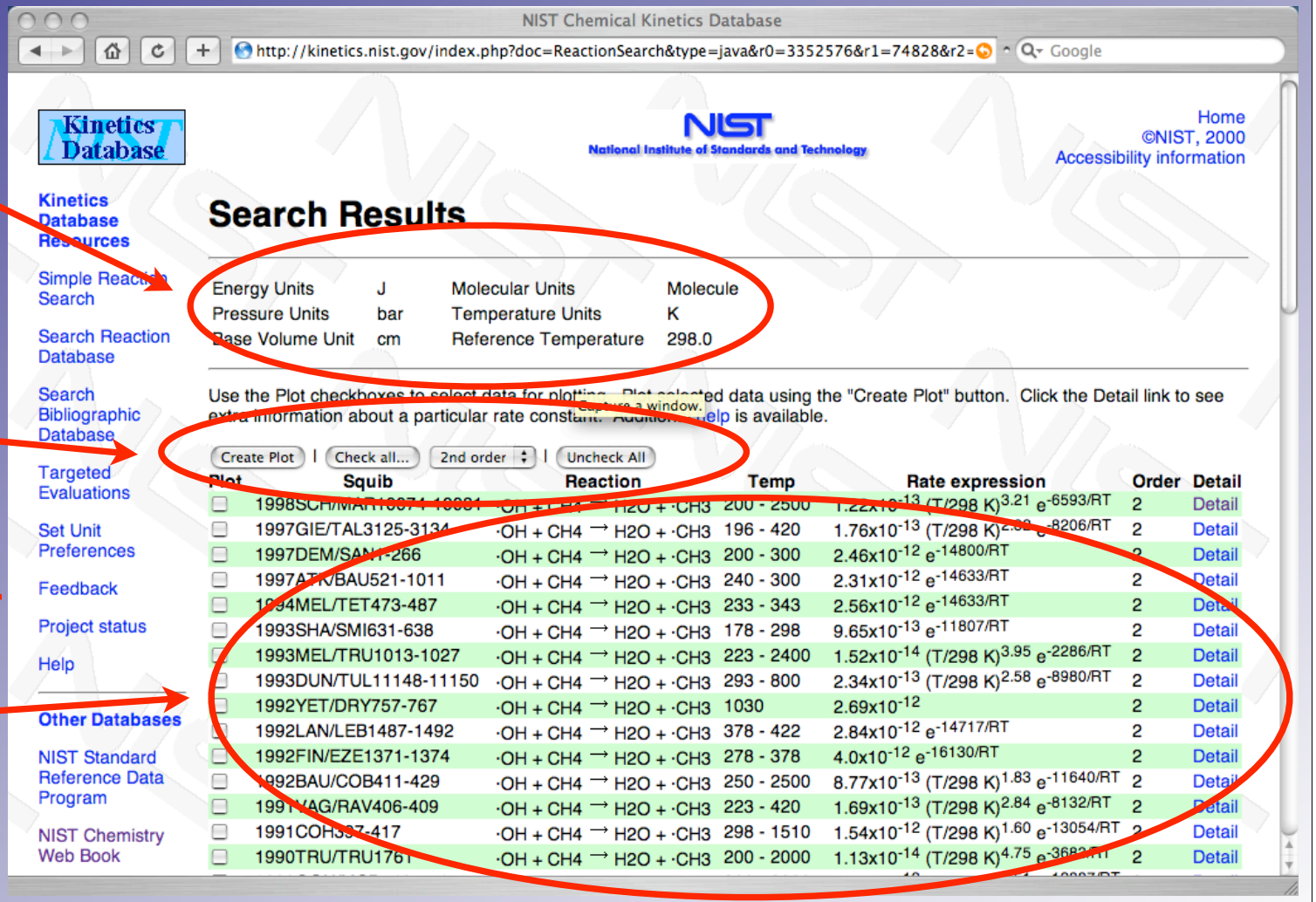


Search Results

User-selected units

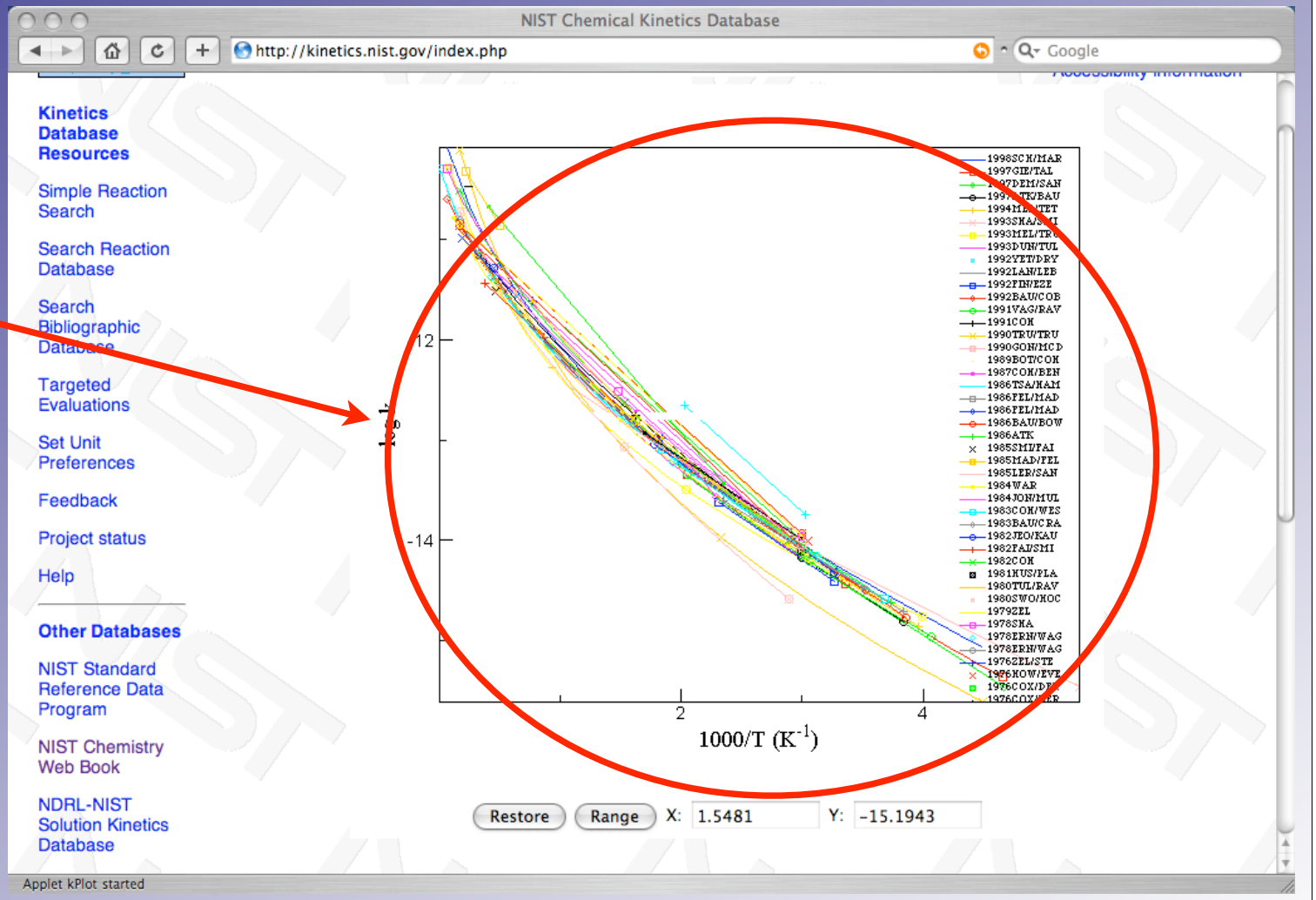
Plot controls

Summary of search results



Plotting

Plotting of rate expressions

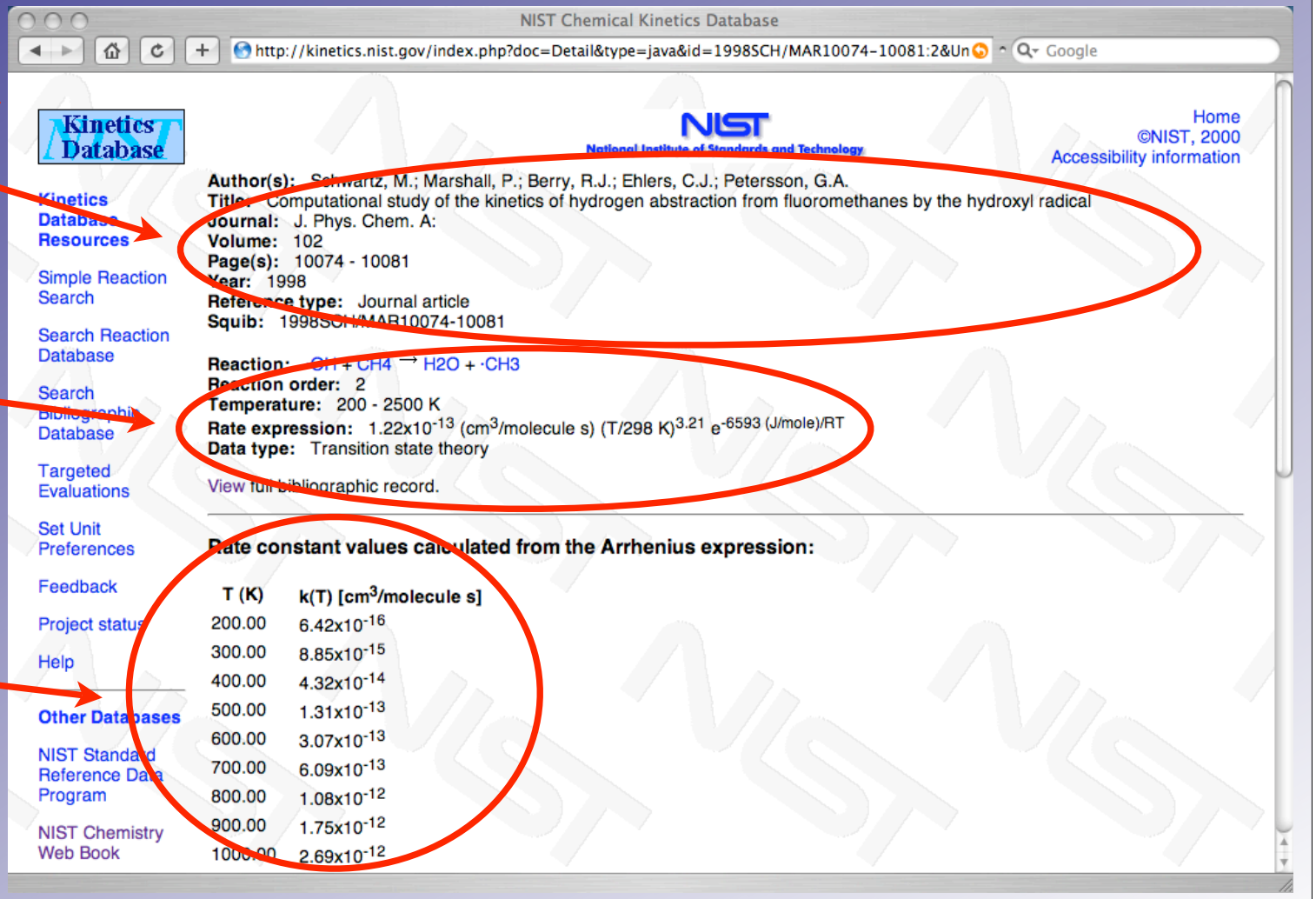


Detail

Full bibliography

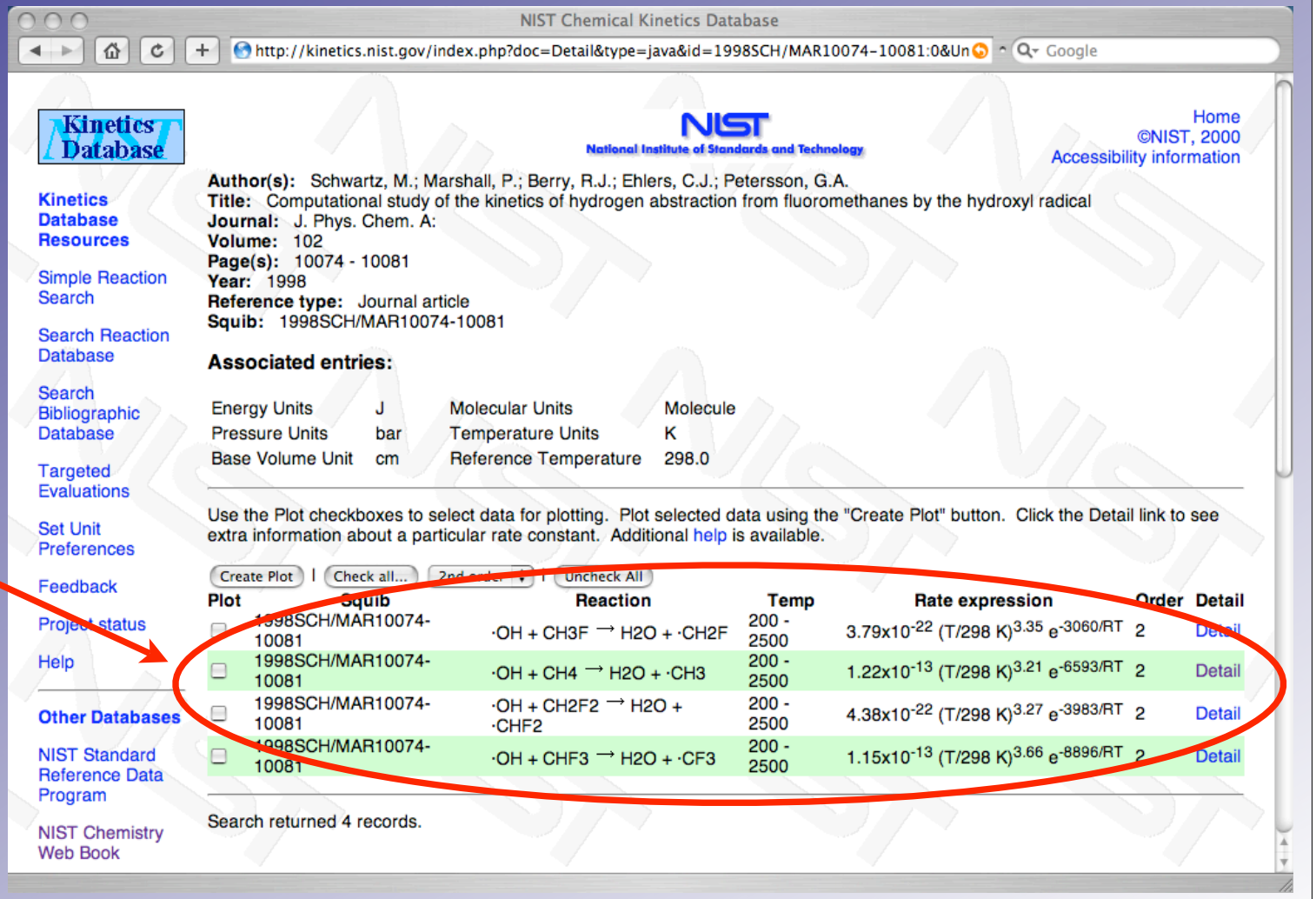
All rate data

Data in tabular form

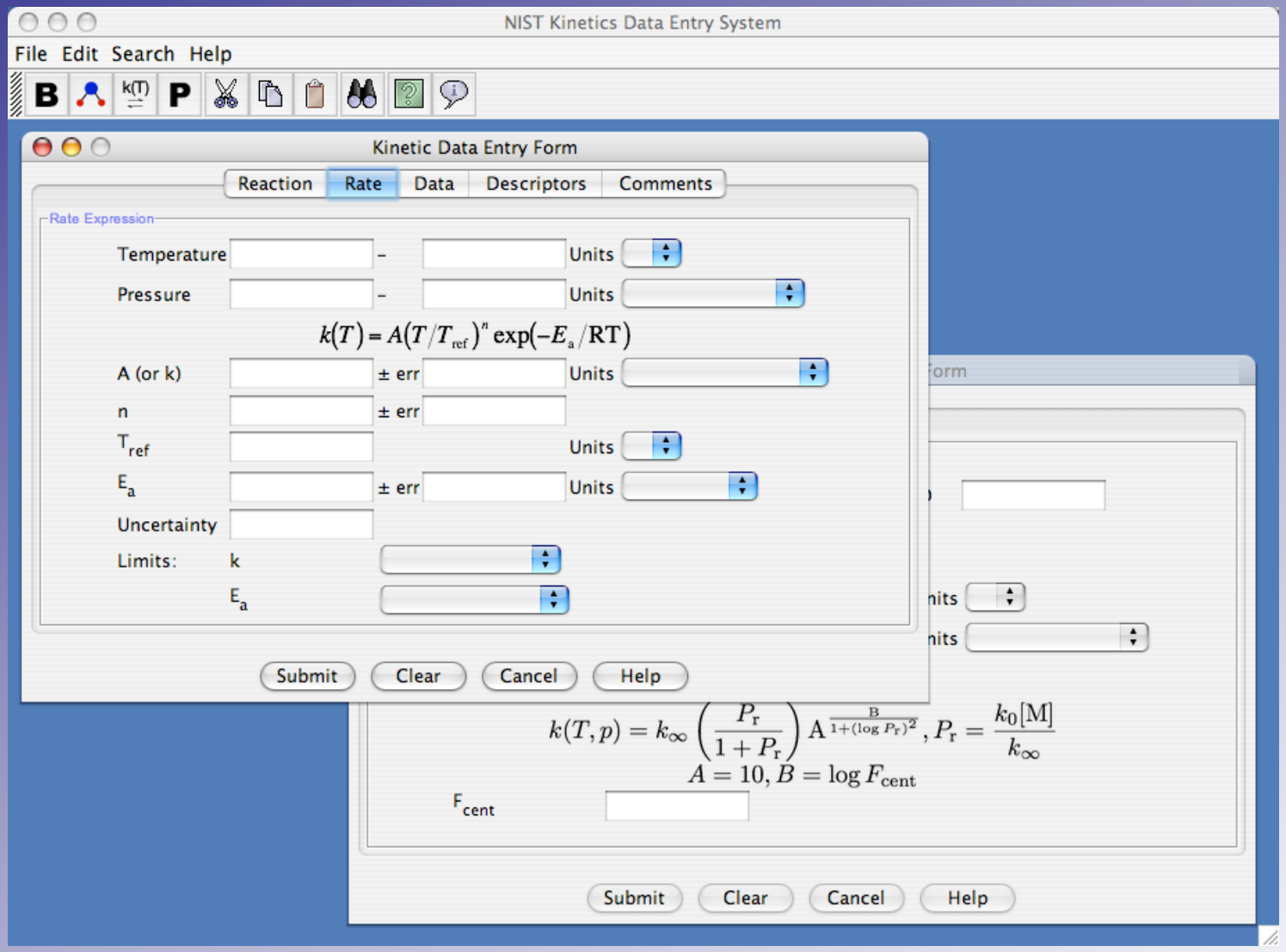


Bibliographic Record

All data from reference



Data entry tool



Usage Statistics

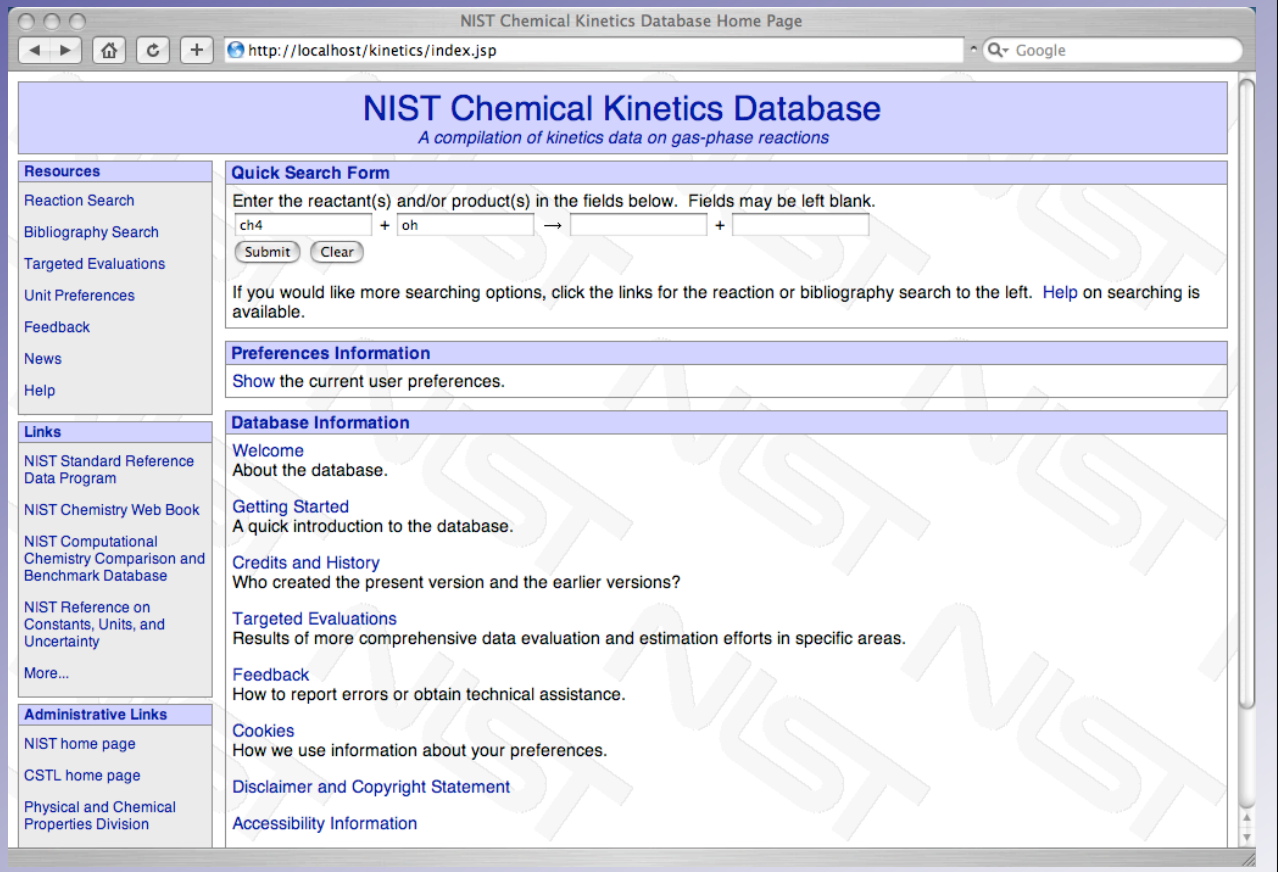
- Served over 1 million pages in the last two years
- Serve more than 1,600 pages per day
- Served nearly 60,000 distinct hosts

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

```
<?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>&amp;amp;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

PrIMe

- "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