NIST Standard Reference Database 17

NIST Chemical Kinetics Database

Windows™ Version 2Q98

Users' Guide

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December 1998

U.S. Department of Commerce
Technology Administration
National Institute of Standards and Technology
Standard Reference Data
Gaithersburg, MD 20899

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Introduction

An overview of the NIST Chemical Kinetics Database

The NIST Chemical Kinetics database provides the chemical kinetics community with a tool for rapidly examining experimental and theoretical studies on the rates of chemical reactions as reported in the literature. The database can find data on a specific molecular product, a particular reaction, all of the reactions of a specific species, and subsets of all of the reactions. In addition, the linear and nonlinear fits of the data available for a particular reaction, as well as the data themselves for that reaction, can be graphically compared with the fits and data from other reactions. The database was started as a long-term project to summarize completely all of the combustion kinetics literature. It has been expanded beyond that original goal to include data of interest in atmospheric modeling and in plasma chemistry. The database now covers essentially all of reported thermal gas phase kinetics results, including in excess of 37,000 separate reaction records for over 11,400 distinct reactant pairs. These data have been abstracted from over 11,000 papers with literature coverage through the second quarter of 1998.

Each rate constant record contains the following information (as available):

a. Reactants and, if defined, reaction products;
b. Rate parameters A, n, E_a/R, where $k = A^* (T/298)^{**n} *\exp[-(E_a/R)/T]$, where T is the temperature in Kelvins;
c. Uncertainty in A, n, and E_a/R, if reported;
d. Temperature range of experiment or temperature range of validity of a review or theoretical paper;
e. Pressure range and bulk gas of the experiment;
f. Data type of the record (i.e., experimental, relative rate measurement, theoretical calculation, modeling result, etc.). If the result is a relative rate measurement, then the reaction to which the rate is relative is also given;
g. Experimental procedure, including separate fields for the description of the apparatus, the time resolution of the experiment, and the excitation technique. A majority of contemporary chemical kinetics methods are represented.

System Requirements

Hardware requirements for installing and running the database

Hard disk, 7.6 MB of free space for complete installation; PC capable of running Windows 95®, Windows 98, Windows NT™ 3.51, or Windows NT 4.0; math coprocessor. A printer is optional and should be Windows compatible.

Installation

Place the CD-ROM in the CD drive. In Windows 98, 2000, NT, Me or XP

Start the installation by either double-clicking on the install file SETUP.EXE on the CD via the Windows Explorer or My Computer, or by clicking on the Start button, selecting Run and entering the appropriate location for the installation file e.g. D:\SETUP.EXE (if the CD-ROM drive is assigned the letter D:).

The Desktop

The opening screen and its menu bar, toolbar, and status bar.

The screen that is displayed when the database is run is the desktop. A menu bar containing the menu commands lies along the top of the desktop and provides access to all controls in the database. Beneath the menu bar is the toolbar which provides alternate access to many of the database controls. A status line along the bottom of the desktop displays information and error messages.

Menu Commands

Menu selections at the top of the desktop.

The program menu bar commands or "options" are listed below.

File
Open/Close files to export or import reaction data; access Print functions; Exit database

Edit
Copy to scheme; enter user Comments; Entry of user reaction data

View
Toggle on/off Toolbar and Status Bar; choose Font and Units

Search
Initiate searches by Reactant, Product, Author, or Citation

Windows
Arrange or select windows for display

Help
Enter the help system, how to contact NIST

These commands are accessed from the menu bar at the top of the desktop.

Search

The four different search methods

These commands are accessed from the Search option on the menu bar at the top of the desktop. Select a search type to display a dialog box in which the search parameters can be entered.

Reactant search

A "Reactant(s)" dialog box appears. The four primary methods for reactant entry allow searching for:

1. Two reactants
2. All reactions of a single reactant
3. Subsets of all reactions of a single reactant
4. All reactions where a specific element is present in either reactant

1. Two reactants:

Enter the two reactants in the "Reactant(s)" dialog box. Click OK to begin the search.

For the reactions of a specific molecule such as OH, CH_4, or benzene, the molecule can be entered either as a molecular formula or as a name. If the database does not understand the entry, a dialog box is displayed with an error message; click OK to reenter the reactant. For most small molecules, the semistructural formula is used as the name.

The database allows most compounds to be entered without upper case and without regard to order so that ch4 = CH_4, cf3br = CF_3Br = $CBrF_3$. In addition, ch3ch3 = C_2H_6 and (ch3)3ch = C_4H_{10}. However, it is possible to confuse the database; for example, si = Si not SI. If correct chemical symbols are used, it will always work.

If there are any references to the reactant pair that was entered, the database displays a Reactions Window showing the matching reactions that have references. Adjacent to the Reactions Window is a two-part Summary Window which shows the data and abstract information. Click on a reaction in the Reactions Window to display its data and abstract information in the Summary Window.

2. All reactions of a single reactant:

To access all reactant pairs for one reactant, enter the first reactant in the first reactant entry box and enter the wildcard '*' in the second reactant entry box. Click OK to begin the search. A Hits Window appears showing the number of retrievals and the matching reactions. Click on a matching reaction to display its Reactions Window.

3. Subsets of all reactions of a single reactant:

To limit the number of hits, a restricted search can be done using one of two techniques: a search using Boolean operators or a search by carbon number.

To do a Boolean search, use the symbols defined in this table:

Operator	Symbol
containing	?
and	&
or	|
not	! or ~

Application of these symbols is not order dependent. The "?" is not necessary if other Boolean symbols are used. These symbols can be used alone or in combination to restrict the second reactant. For example, by entering ?Cl for the second reactant, the search finds all reactions of the first reactant with chlorine-containing compounds. By entering !Cl or ~Cl for the second reactant, only reactions of the first reactant with compounds not containing chlorine are found. By entering Cl & F, only reactions with compounds containing both chlorine and fluorine are found; whereas by entering Cl | F, only reactions with compounds containing either chlorine or fluorine are found.

To find reactions of the first reactant only with molecules having a specified number of carbon atoms, enter Cn* where n = the number of carbon atoms (n = 1 is assumed from C*, but it can be entered). For example, C2* finds the reactions of the first reactant

with all C_2 compounds. This type of search can be combined with a Boolean search. C2* & F finds all C_2 compounds with fluorine. C2* & F | Cl finds all C_2 compounds with fluorine or chlorine. Note that the search by carbon number cannot be combined with an "or" search. Thus, C2* | F is not allowed.

4. All reactions where a specific element is present in either reactant:

This option is designed to find all data for compounds containing a specified element for which there are limited data, for example, Si compounds. The results are far too numerous and therefore not reasonable for H, C, O, N. To select all reactant pairs where one or both reactants contain a certain element, type that element in the first reactant box followed by an '*'. Click OK and the search will begin.

Note: This search *excludes* reactions of single atoms since there is another method of finding those data. In the example above, no reaction would be found where one of the reactants was an Si atom. To find all reactions of the single atom, enter the atom as the first reactant and * as the second.

Unless both reactants are completely specified, the search can find several reactions which match the conditions entered. These matches are displayed in a Hits Window. Select any of these by double-clicking on the desired reaction. A Reactions Window showing all of the data for the selected reactant pair is displayed. (This same window appears if the two reactants are specified directly.)

Product search

A "Product" dialog box appears. Type a specific molecule and click OK. The matches are displayed on a Reaction Producing Window which shows all reactions in the database for which that molecule is a product. The second column gives the number of abstracted records for each reaction. Double-click a reaction to select it and display its Reactions Window.

Author search

An "Author" dialog box appears. All authors on each paper are indexed so the order of the author's name on a paper is not important. Type only the last name of the author. For common last names, this means that more than one person's work may be found. Click OK and an Author Window is displayed, showing all squibs in the database for the requested author. Highlight the squib of interest by clicking it to show the reaction data from the corresponding reference.

Note that the squib is formed from the last two digits of the year of publication followed by the first three characters of the first or only author's name. If there is a second author, a "/" separates the first three letters of that name. For example, 84WAR is for the single author Warnatz of a 1984 review and 71ADE/WAG is for the authors Aders and Wagner of a 1971 paper. If this procedure results in a duplicate squib, the second case has a number following the name (e.g., 71ADE/WAG2). The numbering continues for as many squibs as are created for the same combination.

Citation search

A "Squib" dialog box appears. To search by citation, type the squib and click OK. A Reactions Window appears displaying all the reactions abstracted for the squib. Double-click a reaction to display its Summary Window.

Display of Results

The Summary Window used to display search results.

From a Reactions Window, select a reaction by clicking it. The data and abstract information for that reaction are displayed in a two-part Summary Window. The first part is a window displaying the following information for the selected reaction: the reference squib, the temperature range of the experiment or review, A (or k), n (if given), E_a/R (if given), the order (1=unimolecular, 2=bimolecular, 3=termolecular), the rate constant at 298 K, and the uncertainty (if stated by the authors).

The second part is the abstract window which shows the authors, the title of the paper, and the journal citation. In addition, the window provides a brief summary of the experimental technique, the pressure and temperature range (if appropriate), and the type of data. If the data were reported as a rate ratio, both reactions are given here. Uncertainties in the individual rate parameters are given if provided in the original paper.

Plot

A description of options available when displaying an Arrhenius graph.

An Arrhenius graph can be displayed for any reaction in the Reactions Window. Click the desired reaction or the desired channel for that reaction if there is more than one channel, to select it. Then click the Draw plot option from the toolbar. An Arrhenius graph of all the data for the selected channel will be displayed.

Note: If the reaction data to be plotted are of more than one type, for example, if both bimolecular and termolecular data are available in the database for the reaction, a "Reaction Order" dialog box will appear before the graph is displayed. Select the desired order and click OK. Then the Arrhenius graph will be displayed containing only data for the selected order.

Once the graph is displayed, several different options are available:

Axes

Choose the menu command Plot, then Axes, to select between two choices for the axes: k vs T or Log(k) vs 1000/T and to specify the ranges for the x- and y-axes.

Properties

Choose the menu command Plot, then Properties, to select the data points and curve fits, if any, to be displayed. Click Experimental or Review to toggle off and on the display of experimental data and review data, respectively. Click Rescale Graph to change the scale of the plot back to default.

Fit data

Choose the menu command Plot, then choose Fit data to generate a curve fit of the data. There are two choices. Click k=A*exp(E/T) for a linear fit; click k=A*T**n*exp(E/T) for a nonlinear fit. A curve for the selected fit is superimposed on the graph, and the corresponding equation and symbol used are displayed in the legend on the right side of the window.

To bring up a window displaying the parameters for a curve fit, double-click the curve on the graph. A "Select reference" dialog box is displayed. Select the equation for the curve of interest and click OK. Alternatively, double-click the equation for the curve in the legend.

To delete a curve fit, right click on the curve or its equation in the legend. A shortcut menu is displayed. Select Properties and a "Plot properties" dialog box is displayed. Click the check box on the left of the equation for the curve to be deleted and click OK.

Scaling

Choose the menu command Plot, then choose Axes to specify the ranges to be used for the axes. There are five choices. Click Automatic to use the default scales as determined by the program. Click Unimolecular, Bimolecular, or Termolecular to use predetermined, normal ranges for these three types of data. Note that the unimolecular, bimolecular, and termolecular scales are especially useful when trying to compare reactions. Click Manual to specify the ranges manually.

Reference

To display reference information for one of the data points plotted on the graph, double-click the data point symbol on the graph. A "Select reference" dialog box is displayed. Click the squib corresponding to the desired data point symbol to select it, then click OK. The reference information is displayed in a window. Alternatively, double-click the squib corresponding to the desired data point symbol in the legend on the right to display the reference information.

Edit

To delete a data point from the graph, right click the graph or the legend on the right to bring up the shortcut menu. Select Properties and a "Plot properties" dialog box is displayed. Click the check box to the left of the squib corresponding to the desired data point symbol to deselect it, then click OK. To redisplay a data point that was deleted, simply right click the graph or the legend to bring up a shortcut menu. Select Properties to bring up the "Plot properties" dialog box. Click the desired check box and then click OK.

Copy to user plot

To generate a user plot from an Arrhenius graph, choose the menu command Plot, then choose Copy to user plot. A "Copy to user plot" dialog box will be displayed. To select all the data points and curve fits, press Shift while clicking the data points and curve fits. To select some data points, press Ctrl while selecting the data points or curve fits. Then click OK. A user plot of the information specifically chosen by the user is displayed.

Compare

Linear, nonlinear, or both fits of the data available for a particular reaction, as well as the data themselves for that reaction, can be graphically compared with the curve fits and data from other reactions of the same reaction order. Simply use the Copy to use plot option to create a new user plot using "Copy to user plot" with the desired information from the first reaction of interest. Then use the Copy to user plot option to add the information from other reactions of interest. All the information, curve fits and/or data points, are displayed on the same graph for easy comparison.

The functions available for displaying reference information and editing the information displayed on an Arrhenius graph of one channel or reaction are also available with the user plot. For example, the parameters for the curve fits and the reference information for the data points can be displayed by double-clicking on the curves or data points, respectively. Similarly, curve fits or data points can be deleted from the user plot by right clicking on the graph or legend to bring up the shortcut menu. Select Properties to bring up the Plot properties dialog box. Click on the check box to deselect the data point and click on OK.

Note, however, that different types of data cannot be compared on the same graph. The program always creates different user plots for unimolecular, bimolecular, or termolecular data.

Clear

To clear a user plot, choose the menu command Plot and select Clear.

Special Options

Options for entering user comments and data and selecting units.

Comments

To bring up a Comments Window where information can be stored on the reaction displayed in the Reactions Window, chose the menu command Edit, then chose Comments. To enter a comment, click in the entry box and begin typing. Click Save to save the comment.

To delete a comment, simply delete all the text, then click Save.

Entry of user reaction data

To bring up a Reaction Entry Window where user data for the reactant pair displayed in the Reactions Window can be entered into a separate database, choose the menu command Edit, then choose Entry. These data will be displayed and plotted the next time this reactant pair is requested. There are certain limits. There can be no more than two products per reaction. Two temperatures, the minimum and maximum of the range, and a value of A(or k) *must* be given. In addition, an identification code *must* be specified. Any three-character string can be entered for the identification code. It will appear in the Reference column of the Summary Window.

Drop-down list boxes are provided on the bottom right for specifying the units to be used for the concentration and energy activation values and for specifying the preexponential factor and the reaction order.

If a formula for a product is entered for which there are a number of isomers, a "Select isomer" dialog box is provided to display a list of isomers from which the user can choose.

If the products are unknown or are not in the database, simply type PRODUCTS into the first product entry box. No second product is allowed in this case. OTHER PRODUCTS is designed to cover those situations where one of the products is known (e.g.,

H_2O from OH + R-H), but the other products are mixed or unknown. It is not necessary to use all caps.

ADDUCT and UNKNOWN are other useful additions to normal molecules that can be specified.

These user-entered data are plotted the same way as any other data. Plotting is only over the range of the temperatures entered as is calculation of the rate constant for the Summary Window. These data are identified in the legend at the right of the graph by the identification code that the user specified.

Units selection

Choose the menu command View, then Units, to bring up the "Units" dialog box from which units can be specified for concentration, pressure, and activation. In addition, the preexponential form can be selected.

The defaults are as follows:

Units for concentration: mol/(cm**3)

Units for pressure: torr

Units for activation energy: K

Form for preexponential: A*(T/298)**n

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Whom to contact and how to reach them at NIST.

If you have comments or questions about this database or any other of the Standard Reference Databases available from the NIST Standard Reference Data Program, please let us know by contacting:

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