



## General Chemistry Collection

# KinSimXP

**Windows-compatible computers**

## **User's Guide for Instructors**

---

Abstract	2
The KinSimXP.ini File	3
Suggestions for Grading the Experiment	5
An Alternate Method for Finding the Reaction Orders	6
Some Hints for Effective Use of KinSimXP	7
Citations	7

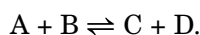
Robert D. Allendoerfer

Department of Chemistry, State University of New York at Buffalo, Buffalo, NY 14260-3000

## Abstract

KinSimXP is a 32-bit Windows adaptation of a program originally described by Merrill, Spicer, Brown, and Walling (1) and published as a software program for MS-DOS (2).

The program simulates a chemical kinetics experiment in which the student investigates the following reversible reaction:



The objective is to:

1. Find the order of reaction with respect to each of the reactants,  $n_A$ ,  $n_B$ ,  $n_C$ , and  $n_D$ .
2. Find the values of the forward and reverse rate constants,  $k_f$  and  $k_b$ , at one or more temperatures.
3. Find the values of the forward and reverse activation energies,  $E_f$  and  $E_b$ , in kJ/mol.

The isolation method, first devised by W. Ostwald, is used to find the reaction orders and rate constants. The program provides log and reciprocal plots of the concentration versus time data so that the reaction rates can be determined graphically. The concentration versus time data can also be saved to a file for more sophisticated data analysis with a spreadsheet or stand-alone statistics program.

The Arrhenius equation is used to find the activation energies. If the kinetic parameters are determined at more than one temperature, advanced students with knowledge of physical chemistry can also calculate  $\Delta G_T^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$  for the overall reaction. The parameters for the reaction are chosen from 160,000 different sets available, using a code based on the letters in the "unknown" name.

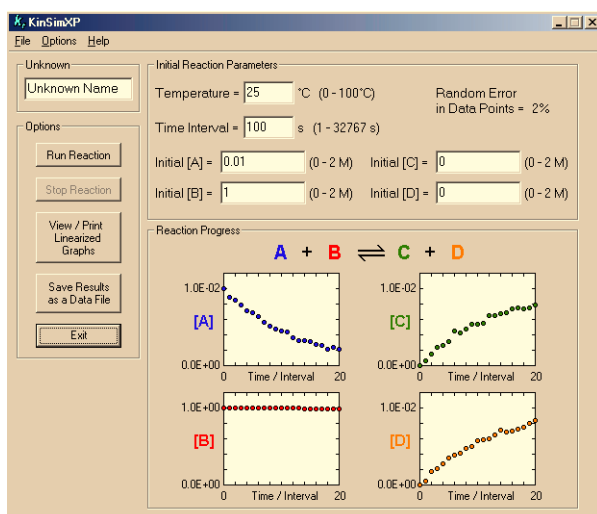


Figure 1. The simulation screen in KinSimXP.

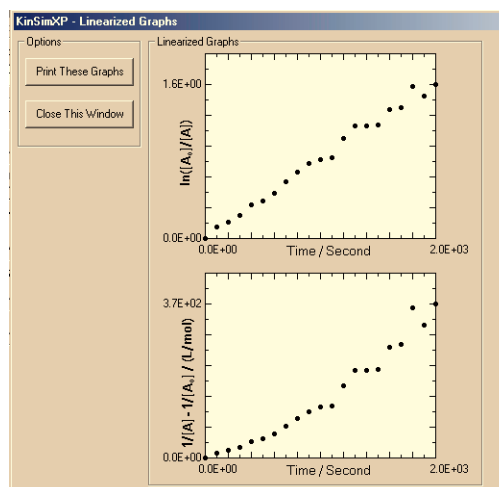


Figure 2. Sample data plots from KinSimXP.

Experience using KinSim has shown the precision of the student results is not as good as it could be, but, it is much better than using the data students get from their “real” kinetics labs. Attempts to improve the precision of their results by using Excel to plot the graphs and find the least squares slopes led to less understanding of the process and precise, but inaccurate, results. Many students had no concept of how to find the slope of a noisy graph by hand or how to define or measure the slope.

Linear least squares (as done by Excel, etc.) is the wrong way to analyze kinetics data in the presence of significant noise (3). The error estimates in the kinetic parameters generated using linear least squares are wrong. Students get upset when the rate constants and error estimates produced using linear least squares do not give the real result. Doing the graphs by hand from the printouts made by KinSimXP allows the students to get a feel for the accuracy of their results in the presence of the noise amplified by the linearization process, gives results as accurate, though not as precise, as Excel, and provides a much more meaningful laboratory data analysis experience.

In advanced or honors chemistry classes or in physical chemistry, KinSimXP can be used to generate data for proper analysis by nonlinear curve fitting using a Mathcad template (3) or a commercial statistics package. Thus, KinSimXP’s lack of automated data analysis is an advantage. It generates data for later analysis, that the student can use with whatever data analysis procedure is appropriate.

---

## The KinSimXP.ini File

The KinSimXP.ini file is located in the KinSimXP folder on the General Chemistry Collection CD-ROM. The documentation included on the General Chemistry Collection CD-ROM for KinSimXP does not mention KinSimXP.ini. It is unlikely that students will discover that it is possible to customize KinSimXP and to display the answers for any unknown without the information found only here, in the User’s Guide for Instructors.

KinSimXP will work correctly without the KinSimXP.ini file or with any line missing from the file. Missing parameters are set to the default value described below. KinSimXP is not installed on the user’s hard drive by the *JCE Software Setup* program. The Setup program installs system files and shortcuts that allow you to run KinSimXP from the General Chemistry Collection CD-ROM. Because it is not possible to edit files on a CD-ROM, when KinSimXP is run from the CD, it will always open with the default parameters described below.

In order to edit the KinSimXP.ini file, first copy the entire KinSimXP folder from the General Chemistry Collection CD-ROM to your hard drive. Then open **KinSimXP.ini** in a text editor such as Notebook. The contents of the file are shown below. Make the desired changes, save the file as a plain text file, and open the copy of KinSimXP on your hard drive to see the effect.

```
SaveChanges = False
ColorA = 16711680
ColorB = 255
ColorC = 32768
ColorD = 65535
FontName = Courier New
FontSize = 12
RandomError = 2
AllowErrChange = False
ProfessorMode = False
```

---

### *SaveChanges*

The SaveChanges parameter has possible values of True or False. Its default value is False. It controls whether changes are saved in the file after the user makes a change in one of the parameters while running the KinSimXP. Thus, if SaveChanges is True, changes to the colors and fonts made using items in the Options menu will be saved between sessions, otherwise they will not. If SaveChanges is False (or the line is not present) KinSimXP will not update the KinSimXP.ini file and the next time KinSimXP is opened, it will be with the default conditions.

In a networked environment or when it is important that the users not be able to change the amount of random error added to their experiments, it would be better to erase this line than to set it to false, if that is the desired behavior, to avoid the possibility of users making changes.

---

### *ColorA, ColorB, ColorC, and ColorD*

These parameters control the colors of the reagents A, B, C, D and their labels. The values are the decimal RGB color numbers used by the KinSimXP. These numbers are not always simple to calculate in decimal notation, so it is probably best if they are changed only from the KinSimXP Options menu with SaveChanges = True.

---

### *FontName and FontSize*

The FontName and FontSize parameters control the font and its point size for printing the linearized graphs. The graphs only print correctly when fixed point fonts are used. The largest point size that can be used and still fit the graph on an 8 1/2 × 11-inch piece of paper is 12 point. When you select **Set Printer Font** in the Options menu, the dialog offers only valid fixed-point fonts in the range of 8–12 points for your computer. Manually editing the FontName and FontSize parameters in the .ini file may produce unpredictable results.

---

### *RandomError*

The RandomError parameter should be an integer in the range 0–10. The default value is 2. This parameter sets the standard deviation of the error added to each experimental point during the experiment. The amount of error added also depends on the initial reactant concentration. A parameter value of 2 means that the standard deviation of the error added to or subtracted from a reagent with a maximum possible concentration of 0.01 M is 2% or 0.0002 M. The error added or subtracted to other concentrations varies in proportion to the square root of the concentration as well as the RandomError parameter. Thus, the standard deviation of the error added to 1.0 M reagents is 0.002 M and the standard deviation of the error added to 0.0001 M reagents is 0.00002 M.

---

### *AllowErrChange*

The AllowErrChange parameter has possible values of True or False. Its default value is False. It controls whether the user is allowed to change the RandomError parameter while running KinSimXP. If AllowErrChange = True, a text box is presented on KinSimXP's main screen allowing the user to change the random error standard deviation in the allowable range of 0–10%. If AllowErrChange = False, the main screen displays the value of the random error, but it cannot be changed by the user.

## ProfessorMode

The ProfessorMode parameter has possible values of False or a valid hexadecimal number. The default value is False. If a valid hexadecimal number is present, it is used as an encoded password that is required to open KinSimXP. When KinSimXP is run, an additional button, Answers, appears on the main screen. Click the **Answers** button to display the kinetic parameters  $k_f$ ,  $k_b$ ,  $E_f$ ,  $E_b$ , etc., associated with the current Unknown as in Figure 3. This feature is intended for use by instructors for checking and grading student work. To use this feature, the ProfessorMode line in the KinSimXP.ini file must be manually edited to read **ProfessorMode = 4B**. This corresponds to a case sensitive password of **P**. Any valid hexadecimal number will cause the password dialog to appear when KinSimXP is started. The first time the program is run after making this change, the password can be changed to something more secure (with SaveChanges = True). After that, SaveChanges can be set to False preventing further changes in the password.



Please note that “True” is not a valid hexadecimal number. If the line is entered **ProfessorMode = True**, the password dialog and **Answer** button will not appear.

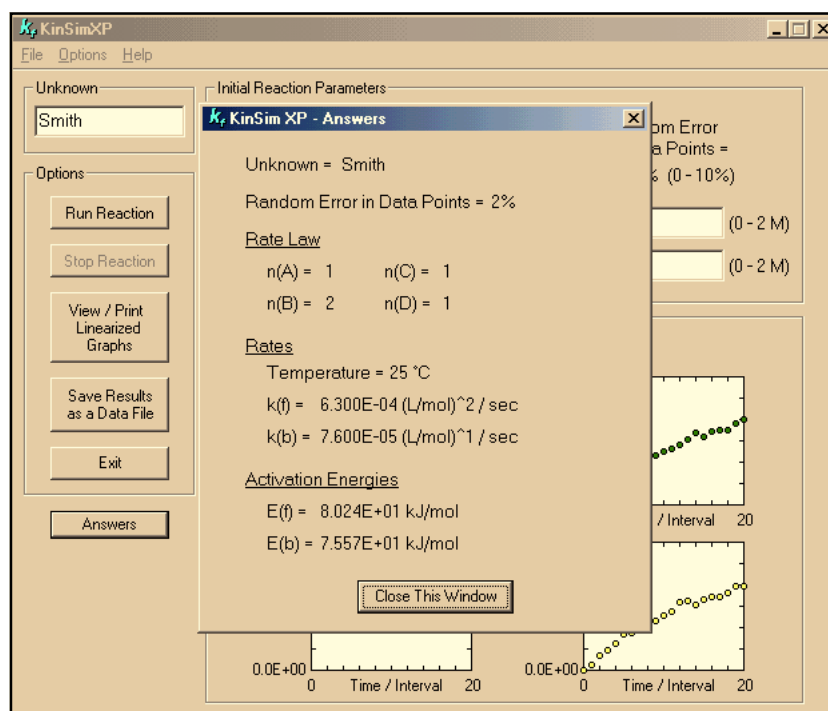


Figure 3. KinSimXP in the Professor Mode.

## Suggestions for Grading the Experiment

This experiment should not be graded using a numerical scale based on the precision of the results obtained. Because of the random nature of the selection of rate constants, it is harder to obtain results of a particular precision for some unknowns than for others. What should be graded is the data analysis procedure. Following is a grading scale recommended by the author.

### Reaction Orders (20%)

There are four reaction orders that can be determined (worth 5% each). They can be determined either by the method described in the Sample Experiment and Data Analysis in the User's Guide or by the alternate procedure discussed

below. Using the method in the User's Guide, the judgment of which line, 1st or 2nd order, is straight should be made by eye and if the correct choice cannot be easily made this way, another run under different conditions should have been done. Experience has shown that even when the F-test is appropriately applied using nonlinear least squares fitting, what is obvious to the computer, i.e., with a >95% confidence level, is also obvious to the untrained observer. The  $R^2$  value obtained from unweighted linear least squares analysis is statistically inappropriate for making this type of decision and no partial credit should be given for using it when it fails.

---

### *Reaction Rate Constants (40%)*

When nonlinear least squares fitting is used, the best-fit rate constant and its standard error as provided by the analysis program should be reported. When the User's Guide method is used, as in the Sample Experiment and Data Analysis section, a best-fit straight line should be drawn on the printed graph with a ruler as well as the maximum and minimum slope lines. The best-fit line should give decreasing weight to the points as the time increases. All lines should go exactly through the origin since there is no error in the initial point. A minor penalty should be deducted if this procedure is not followed. The best-fit rate constant should be reported along with the average maximum error. In general, students whose maximum and minimum rate constants span the correct answer should receive full credit. Experience indicates that typical students can achieve maximum error ranges in the 5%–15% range and that the best-fit rate constants are generally within 5% of the expected value. Results outside of these ranges merit further investigation to determine if a valid data analysis method was used. If an error is found in the procedure, appropriate credit should be deducted, but it must be remembered that it is harder to obtain precise results for some unknowns than for others.

---

### *Activation Energies (40%)*

Activation energies should be determined from Arrhenius plots of the logarithm of the rate constant over a range of temperatures versus the reciprocal of the absolute temperature. 5–6 points taken 5 °C intervals seems to work best. In principal, the largest temperature range possible should be used, but occasionally this causes the reaction rate to be outside the capabilities of the program at one temperature extreme or the other. Linear least-squares using a spreadsheet like Excel is the preferred data analysis technique here. The error in the slope should be reported using the graphical maximum-minimum slope method illustrated in the Sample Experiment and Data Analysis section of the User's Guide or by taking the standard deviation of the slope from the results provided by the analysis program. If a proper procedure has been followed, the student result should span the correct value. The percentage error range for the activation energy should be similar to that for the rate constant. Again, experience shows that student values are typically within 5% of the expected value and values lying outside that range should be inspected for errors in the analysis procedure.

---

### **An Alternate Method for Finding the Reaction Orders**

The author's students discovered a quick and accurate way of choosing between first and second order reactions when these are the only two choices which does not involve plotting the linearized graphs as described in the User's Guide. The method is based on the fact that the half-life of first order reactions is independent of the initial reactant concentration while that of a second order reaction depends on this concentration. To use this method to find  $n_B$ , for example, you might initially choose  $[A] = 1.0 \text{ M}$  and  $[B] = 0.010 \text{ M}$ . Then, adjust the time

interval so that at the end of a run (20 points), the concentration of B has decreased to about 50% of its initial value. The total time taken ( $20 \times$  the time interval) is the half-life for this reaction. Next, make a big change in only the initial B concentration, for example let  $[B] = 0.0010$  M, a ten fold decrease, and run the reaction again. The new reaction will be noisier but will again go to about 50% completion if the reaction is first order, because the half-life of the reaction is the same. If the reaction is second order, it will have been slowed down tenfold by this decrease in the initial B concentration and this difference will be readily visible on the screen. Thus, in as few as two runs you can tell if  $n_B = 1$  or 2.

---

## Some Hints for Effective Use of KinSimXP

### *Choosing an Unknown Name*

Students should choose their last name as the Unknown name. This gives variety in unknowns and prevents most problems of mixing up printouts at public printers. Allowing any word or name to be used can lead to bizarre or offensive choices.

---

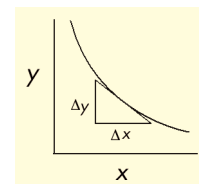
### *Choosing the Initial Concentrations*

It is useful to ask students not to choose exactly 1.0 M as the larger concentration; that which is not supposed to vary during an experiment. This concentration generally works well, but using it makes the slope of the graph numerically equal to the rate constant regardless of the reaction order. Thus, the distinction between  $k_f$  and  $k'_f$  is lost and the students are unable to make the units of the rate constant come out right.

---

### *Finding the Slope of a Graph*

Students often use very small triangles, covering as few as two data points when determining the slope of a graph manually. This may come from their experience with calculus textbooks in which the slope is often pictured this way for curves. For a straight line, it is much more accurate to use the entire  $x$ -axis for  $\Delta x$  and as much of the  $y$ -axis as is required for  $\Delta y$ .



---

## Citations

1. Merrill, J. C.; Spicer, L. D.; Brown, R.; Walling, C. *J. Chem. Educ.* **1975**, *52*, 528.
2. Allendoerfer, R. D. *Chemical Laboratory Simulations*; ComPress, a Division of Queue Inc., 1989. Program KinSim was adapted from a program described in *J. Chem. Educ.* **1975**, *52*, 528 with permission from J. C. Merrill, L. D. Spicer, R. Brown, and C. Walling, Department of Chemistry, University of Utah, Salt Lake City, UT. (No longer available.)
3. Zielinski, T. J.; Allendoerfer, R. D. *J. Chem. Educ.* **1997**, *74*, 1001–1007.