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PAPER 14

Chemulate! A Simulator of UV/VIS Kinetics Experiments for the Macintosh

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ABSTRACT
Chemulate! is a Macintosh application which simulates the use of a UV/VIS absorption spectrophotometer in performing kinetics experiments. This stand-alone application provides the user with the capability to examine the absorption spectra of all reactants and products, and to select all of the initial conditions for a kinetic run (concentrations, wavelength, temperature, etc.). A plot of absorbance vs. time is then generated, which can be printed or exported to other applications for processing. Several files, for both generic and actual chemical reactions, have been created, and it is straightforward to modify these or create more for individual use. A description of the application, its previous use in a Physical Chemistry course, and possible suggestions for its use as an introduction to kinetics in lower level courses are presented.

I. WHAT IS CHEMULATE! ?

Chemulate! is a Macintosh application which simulates the use of a UV/VIS absorption spectrophotometer in the performance of solution phase kinetics experiments. Each reaction system is represented by an individual "project file". Each project file corresponds to a unique (and in many cases imaginary) chemical system, including absorption characteristics of all reactants and products, a rate law, and a temperature dependence provided by the creator of the file (in this case, me). It is possible to create files for virtually any reaction mechanism (see Appendix 2 below for more detail). These may be based on actual chemical reactions, including empirical kinetic parameters and absorption spectra of the actual reactants and products (for example, a project file for the oxidation of ethanol by chromate is provided) or generic reactions (such as A + B --> C - two different sample projects files are provided). For a particular chemical reaction, the application models the various steps students might encounter in designing and performing a series of experiments to investigate the kinetics of the reaction using UV/VIS spectroscopy. Thus, absorption spectra may be run of all reactants and products (at concentrations selected by the user), enabling the student to determine an appropriate wavelength and concentration range to study the reaction. The user selects all of the parameters needed to perform kinetics runs: wavelength, temperature, initial

reactant concentrations, and the duration of the scan (up to 3600 seconds). The computer then performs a calculation of the absorbance at the selected wavelength as a function of time, and displays a plot of the results. These plots may be examined as generated, printed, saved, or copied and pasted into a separate application for further analysis. (We have used CricketGraph and Kaleidagraph for this.) The time to perform the calculation varies, depending upon the complexity of the rate law and the computer; calculations for the files described above typically take less than 10 seconds on a Mac SE.

II. USE OF CHEMULATE IN P. CHEM.

A. Description of Course and Computing Environment

We have used Chemulate! as part of our instruction in the first semester Junior level Physical Chemistry course for the past two years. This course, which is part of a required two-semester sequence for our majors, covers both kinetics and quantum mechanics and does not have a laboratory associated with it. (It does meet four days a week for an hour.) However, the laboratory component of the second semester of the course (primarily thermodynamics) does include kinetics experiments, and these are based on UV/VIS spectroscopy. Typically there have been about 15 - 20 students in the class, although next year we will have about 35. Almost all of our students own a Macintosh computer of some type; in addition, all students have access to Macs in the college computer laboratory. We also have a computer classroom with about 20 networked computers for student use and an instructor machine with projection pad.

B. Implementation in P. Chem.- Fall, 1991

The use of Chemulate! in each of these past two years has been somewhat different. In 1991, I was the instructor in the course. I demonstrated (in the computer classroom) the use of the application for the students (a total of 13), showing them how to select and change parameters, move the cursor, etc. and also how to copy the data to a graphics package and then display and analyze the data with the graphics application. (We used CricketGraph.) I also gave them a copy of "Abbreviated Instructions" (see Appendix 1 below) to assist them. They are all experienced Mac users, and quickly caught on to how to run the application. We had previously discussed Beer's Law and the standard methods used for determining rate laws - plotting of functions of concentration vs. time, method of initial rates, method of isolation, etc., and I reminded the students of these discussions. Each student received a disk with a copy of Chemulate! and a unique project to investigate. They were all of the A + B --> C type, but with differing rate laws and/or Arrhenius parameters. (Two of these project files are available - see III below) Their assignment was to determine which of three possible mechanisms could apply to their system (that is, determine the form of the rate law and which of the three mechanisms could provide that law), and to determine the Arrhenius constant and activation energy for the rate constant k. The students had a week to complete the assignment, and were to hand in a brief "lab report" for their experiment. Some of the students were unsure of how to proceed to accomplish the assigned tasks, and came to me for some direction. However, the majority

of students were able to complete the assignment with no further instruction. Several of them later reported that they started off in the wrong direction, but were able to recognize this and then change their "experimental procedure" to obtain the desired information. All students were able to obtain the correct form of the rate law, and essentially all found acceptable values for the Arrhenius constant and activation energy. A large number of students commented on the course evaluation questionnaire at the end of the course that the Chemulate! project was particularly useful. They felt that it helped them to better understand the kinetics material (and problems) in the course.

C. Implementation in P. Chem. - Fall, 1992

Last Fall (1992), the instructor of the course (not I) demonstrated the program to the students (a total of about 20) in the computer classroom. He led the class through a group exercise in determining the rate law of a particular A + B --> C reaction. He tried to elicit suggestions from the students of experiments to be done - should the temperature be changed? concentration? to what values? and so on. The students were not very responsive and he did not find the exercise to be very useful. He will be teaching the course again in the upcoming Fall, and plans to have several class meetings in the computer classroom where the students will actively use the program (probably in pairs, as there will be about 35 in the class), and perform an exercise similar to the one I used in 1991.

D. Reasons for Developing Chemulate!

My original reasons for developing Chemulate! were twofold:

1) It seems to me that students have a much better chance of understanding the various methods used for determining rate laws, etc., and a better appreciation of how various factors influence the rate of a chemical reaction if they actually obtain kinetic data themselves, rather than manipulate numbers presented to them in textbook problems. Since we do not have a laboratory associated with the upper level course in which we teach kinetics, a computer simulation was the next best thing.

2) We are moving away from the "cookbook" approach to laboratory, and toward a more "inquiry" or "discovery" approach. That is, for the kinetics experiments in the second semester laboratory, we do not tell the students "prepare these specific solutions with these specific concentrations, set the UV/VIS to this wavelength, ..." Rather, we present them with a general description of the problem (such as, "determine the rate law for the iodination of cyclohexanone using the UV/VIS spectrophotometer"), and then let them design the experiments. My idea was that by first doing that sort of exercise with the simulation, they would have thought about what type of approach they would need to take when doing the real experiment, and thus be able to utilize the laboratory time more effectively.

E. Assessment of Chemulate! as a Teaching Tool

We have only a limited sampling of students from which to come to any conclusions regarding the usefulness of this application. The best information we have comes from the instructor of the second semester course and laboratory. Although he was aware that Chemulate! had been used in the first semester course for the past

two years, he did not know that there was any difference in how it had been employed. He had noticed that this year (Spring, 1993) the students seemed to have a much more difficult time with the kinetics experiments than they had last year (Spring, 1992). He commented that "last year, the students just got going right away and seemed to know what they were doing. This year, they got through it all right, but it seemed to take them a lot longer to figure out what to do." He believed that there was no question that the goal suggested in reason #2 above had been generally accomplished for the first group of students, but probably not the second.

F. Possible Implementation of Chemulate! for Introductory Kinetics

The reasons expressed above for originally developing Chemulate! for the Junior level course apply equally well to the student's first exposure to chemical kinetics. In our current program, the general chemistry student's exposure to kinetics is limited to what is presented in the textbook and during lecture - we do not have any experiments investigating rates of chemical reactions. A typical exercise in General Chemistry texts is to deduce the order of a chemical reaction with respect to each of the reactants using presented data of initial rates of reaction for various initial reactant concentrations. Although our students are generally capable of solving these types of problems correctly once they understand the algorithm involved, it is not clear that they understand what the data actually mean. For example, what is "the initial rate of reaction"? Using Chemulate!, the students could generate curves of absorbance vs. time, paste them into a graphics application, convert them to concentration vs. time using Beer's Law, and finally measure an initial rate by fitting a straight line to the early data points. The instructor could tell the students what wavelength to use, and the extinction coefficient for that wavelength, or guide the students into making those determinations. The students could then discover the rate law by generating their own data, rather than simply analyzing the tables presented in the textbook. This approach is likely to provide greater insight to the students than learning how to solve a particular type of problem given a particular set of data using a particular algorithm.

III. RUNNING CHEMULATE!

I have refrained from providing any further detailed description of the application because I think the best way to get an idea of what the application can do and how it might be used in instruction is to try it out. I have made available the application itself, Chemulate! 1.75, and three project files: Ox of EtOH.chemb, ABC1.chemb, and ABC5.chemb. The application should run on a Mac SE or higher, and is system 7 compatible (but not required). In Appendix 1 of this paper, I have included some brief instructions for experienced Mac users. Please read these before running Chemulate!. Although for the most part the application is transparent in its operation, there are a few particularly useful aspects of the program you may not discover on your own. Although the application is quite usable, it is still under the final stages of development and refinement. Any comments or suggestions for improvements would be greatly

appreciated.

QUESTIONS FOR READERS

1) There are varying opinions of the general usefulness and/or effectiveness of computer simulations in the teaching of chemistry. How does Chemulate! (and its use as described above) support and/or refute your opinion about the use of simulations in teaching?

2) Do you think that Chemulate! might be an effective teaching tool at your institution? If so, at what level and in what context might it be used? If not, what are the difficulties you see with its implementation.

APPENDIX 1 - ABBREVIATED INSTRUCTIONS FOR CHEMULATE! (FOR EXPERIENCED MACINTOSH USERS)

TO BEGIN:

Double-click on CHEMULATE! 1.75, or double click on the Project File you wish to open (for example, ABC1.CHEMB). A window appears describing the project. Once you have read the information you may close the window. It is readily accessible at any time from the <Experiment> menu.

EXAMINE ABSORPTION SPECTRA OF REACTANTS AND PRODUCTS:

This may be done by selecting the component you wish to examine from the <Spectra> menu. Once you have produced a spectrum of a component, you may take a new spectrum with a different concentration (if you wish) by double-clicking in the "Concentration" region at the top of the spectrum. Note that the maximum absorbance of the CHEMULATE! absorption spectrophotometer is 2.40.

Once the absorption spectrum of a reagent has been observed, a check mark will appear next to its name in the <Spectra> menu. If the component showed no absorbance in the spectral region, a minus sign (-) appears next to it.

These absorption spectra can not be saved, but they can be printed. Select <Print> from the <File> menu.

CURSOR:

The cursor always begins coincident with the y axis. Its position is noted in the lower left corner of the window along with the corresponding absorbance value. The cursor may be moved in several ways:

1) Click on the left and right arrows at the upper left of the spectrum.

2) Use the left and right pointing arrows on the bottom row of the keyboard.

3) Grab the cursor by pointing at it with the pointer and then holding down the mouse button. The cursor may then be dragged as long as the mouse button is down.

4) Double click in the "w" and "a" region at the bottom left. This will bring up a dialog box in which you may input the desired wavelength (or absorbance).

5) Select <Find..> from the <Edit> menu. A dialog box appears which can be used as in 4) above.

EXPERIMENT:

To run a kinetics experiment, select <Run Experiment> from the <Experiment> menu. You can then input all desired parameters. You can cycle through the parameters using <command-up arrow> and <command-down arrow> or you can double-click to select a specific parameter to change. DO NOT HIT <RETURN> UNTIL ALL PARAMETERS ARE SET. To run the experiment, hit <Return> or click on <OK>.

The spectrum of absorbance vs. time will appear with the cursor at t = 0. Cursor operation is the same as for absorption spectra. The parameters under which each experiment was run may be obtained by <option-click> in the Drag Bar at the top of the window.

After the first experiment has been run, you can run another experiment by double-clicking in the "Wavelength" region at the top of the spectrum. This will bring up the dialog box in which parameters may be set. Several experiments may be run without losing the data from any of them. There will be a single window for each experiment. You can access these previous experiments, and the spectra of the reactant and product solutions, from the <Spectra> menu. Note that it is also possible to resize the windows so that several are visible at once.

SAVING DATA:

Experimental data may be saved in a data file by selecting <Save Experiment As> from the <File> menu. This file may then be opened by a separate graphics program for analysis. (The only applications which have been tried so far are CricketGraph and Kaleidagraph, and they both worked. With CricketGraph, the Experiment File is visible as a TEXT file. With Kaleidagraph, you should indicate a Tab as a delimiter.) You may also Print the experimental data by selecting <Print> from the <File> menu. In addition, you can copy the data directly into a graphics file. This is particularly useful if you are using Multifinder. This may be done by selecting <Copy> from the <Edit> menu. Then open the Graphics application and <Paste> into the upper left cell.

APPENDIX 2 - A FEW MORE DETAILS ABOUT CHEMULATE! FOR PEOPLE WHO ARE REALLY INTERESTED

A. The Project File

If anyone is interested in how to create and/or modify project files, I will be happy to discuss it with you in detail on an individual basis. Here, I will simply describe what is in the files, to give you an idea of what is involved in generating them. They were all created with Microsoft Word, saved as text files, and then converted to Chemulate! files using the ResEdit utility. The absorption spectra data for each component is present as a concentration and a list of wavelength, absorption pairs. These were copied in from JCAMP files provided by our absorption spectrophotometer. (It would also be possible to type in the data by hand, if you really wanted to.) The file also contains the description of the project which appears upon initiation, and the stoichiometric coefficients, rate law for the overall reaction, and Arrhenius parameters for each rate constant

which appears in the law. (See below for more explanation of the rate law.). In generating the 13 files necessary for the students in class, I simply made 13 copies of an original Word file, changed the rate law and/or Arrhenius parameters for each one, and then converted each to a Chemulate! file using ResEdit. After I had the original file made, it took less than a minute to do each of the others. Although all of the files then had the same set of absorption spectra, they were otherwise unique.

B. The Rate Law

As mentioned in the main body of the text, virtually any reaction mechanism can be accommodated by Chemulate! in a project file. The only requirement is that the rate law be expressible as an arithmetic function of rate constants and concentrations (or powers of concentrations). For example, the rate law for the oxidation of ethanol project appears in the original Word file as the single line

r = k0 * [HCrO4-]^2 * [H+] * [EtOH]

followed by lines containing he Arrhenius constant and activation energy for k0. A project file (which I have not sent along) for the reduction of hexacyano iron(III) by ascorbic acid has a rate law line which reads

r = (2 * k0 * k1 * [C6H8O6] * [Fe(III)CN6]) / (k2 * [H+] + k1 * [Fe(III)CN6])

In this case, Arrhenius parameters for each of the three rate constants must be provided. (I must admit that I don't know what the correct values are for those three rate constants, but if they were known they could be included. I just inserted ones which I thought were reasonable based on the experimental results some students had obtained because I wanted to test the capabilities of Chemulate!. It takes a little longer to do the calculations than for the simpler rate laws, but it does work.)

C. Noise in the Spectra and Kinetic Runs

In order to more accurately model the absorption spectra obtained on real instruments, we have added noise to the spectra generated by Chemulate!. For each absorption spectrum present in a project file, there is an associated noise factor. This factor, which again is under the control of the creator of the file, is used to add noise (based on a Gaussian distribution function) to the calculated spectra. For the files I have provided, the noise factor is less than 0.001, and so its presence is only noticeable when the absorbance is quite low.