

Teaching Kinetics through Differential Equations Constructed with a Berkeley MadonnaTM Flow Chart Model

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ABSTRACT

The *alias* feature of the Berkeley Madonna platform allows this author to create a chemical kinetics project manual for students, who create flow charts solving almost all kinetics problems using rate equations. The versatile and powerful platform allows students to explore any chemical kinetics problems, from simple (e.g. 1st or 2nd order kinetics) to complex (e.g. stratosphere ozone depletion, the Lotka–Volterra mechanism), bypassing complicated syntax that is required by most of powerful mathematical programs. This kinetics manual has been successfully implemented in Physical Chemistry at UW-Green Bay in the fall semester of 2017, with the students' success rate greater than 80%.

Categories and Subject Descriptors

Physical Science and Engineering, Education

General Terms

Algorithms, Documentation, Reliability, Experimentation, Theory

Keywords

Differential equations, Educational Modules, Excel®, Berkeley MadonnaTM, Undergraduate, Lower or upper division of undergraduate, chemical kinetics.

1. INTRODUCTION

Although chemical kinetics is an important subject in chemistry with many potential practical applications, the subject has a lighter coverage than other topics such as equilibrium. In the second semester of general chemistry (Gen-Chem, there is only one chapter (out of 8 chapters) dedicated to kinetics.

Furthermore, when chemical kinetics is introduced to the Gen-Chem students, they were offered formulas such as first-order and

2nd-order equations which students learn through rote memory, because most of them had not learned calculus before taking the Gen-Chem classes. The upper-division undergraduate students who take "Thermodynamics and Kinetics" classes do have more opportunity to study the kinetics in more detail and use more complex equations. Those students can use calculus to derive and understand kinetic equations. Because of the resource constraint, laboratory experiments that allow students to verify their analytical solutions in kinetics are quite limited

The upper-division students may rely on computer algebra software (such as Maple or Mathcad codes) to solve more complex and interesting kinetics problems such as the Stratospheric Ozone depletion Model. Numerical codes for solving chemical kinetics are available in numerous publications [1-7]. Benteinis [8] studied reaction mechanisms based on a stochastic simulation approach using the Chemical Kinetics Simulator (CKS) program [9]. Bigger [10] guided students to explore six fundamental kinetic processes using the ChemKinetics software.

A flow-chart based VensimTM model was presented by Metz [11, 12] in his "Computational Chemistry" manual under cCWCS (Chemistry Collaborative Workshop for Community Scholars) in 2015. Berkeley MadonnaTM [13-14] that includes a chemistry editor module has also published kinetic application examples. Applications of system-dynamics based software other than Vensim and Berkeley Madonna, such as STELLA [15], Simile [16], VisSim [17], etc have also been published, mostly in Journal of Chemical Education [18-21]. Almost all the published works cited use box and pipe diagram methods to solve kinetic problems. An *Alias-like* approach was presented by Soltzberg at 219th National American Chemical Society (ACS) meeting in 2000, and his work was cited by Metz [22] in his kinetics presentation for his Computational Chemistry for Chemical Educators (CCCE).

In this work, I select Berkeley MadonnaTM as the platform¹. The *alias*² feature of this platform allows students to create rate-

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¹ Berkeley Madonna has a free demo version that students can download and practice. Even if students choose to purchase, it is relatively low cost. The website for download is <http://www.berkeleymadonna.com/index.php?route=information/static&path=bmdownloads.tpl>.

equation-constructed flow charts to solve simple or complex kinetic problems. The rate equations that students write on the code are exactly the same as they learn from physical chemistry textbooks. Students can also by-pass much complicated syntax [23] to create the code, unlike other mathematical programs such as Maple™, Mathematica™, or Mathcad™. Once the code is created with the Berkeley Madonna™ platform, students can focus on the interpretations of the results generated from the code and engage in deep learning based on insights from the results.

The applications of the Berkeley Madonna™ code for pedagogical purposes is illustrated in the following examples.

2. MODULES AND PEDAGOGIES

The modules³ consist of five initial exercises to assist students in understanding the concepts of: (1) first and 2nd order reactions, (2) equilibrium, (3) rate-determining step, (4) steady-state approximation, (5) enzyme kinetics. The first example is a tutorial helping students learn about the Berkeley Madonna code. Examples (2) to (5) are the modules for students to gain insights through the model outputs of different experimental conditions using the code. As students become more proficient in using the dynamic software, they are challenged to develop a dynamic system analyzing stratospheric ozone depletion. Each exercise is designed to allow students to build a kinetic model based on the Berkeley Madonna software, to export the parameters from the kinetic model to an Excel spreadsheet, and to explore key kinetic concepts from the Excel spreadsheet.

2.1 First order and 2nd order reaction

The models I choose to illustrate are purposely different from the conventional way of building the models. For example, for the first-order reaction, the conventional way of building the model looks like the following graph (Figure-1)

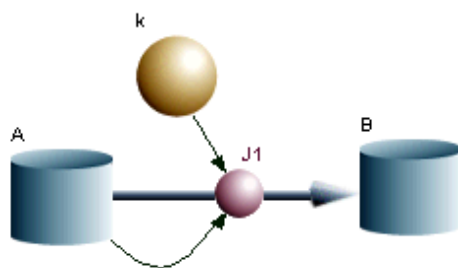


Figure-1 A conventional Berkeley Madonna model for the first-order reaction, $A \rightarrow B$ with the rate constant k .

² It must be acknowledged that dynamic software other than Berkeley Madonna also has 'alias' like feature such as *shadow variable* in Vensim and *ghost variable*.

³ All reactions discussed in this manuscript refers to elementary step reactions that actually happen in the molecular level. Differential equations to represent the rate of appearance or disappearance can therefore be written as represented in each molecular elementary step reaction.

Although the model built this way is quick and intuitive, the equation students write for $J1$ is counter-intuitive:

$$J1 = k[A] \quad \text{[Equation 1]}$$

instead of $-k[A]$. Most of the flow-chart based kinetic models as published [18-21] fall into this category.

In this module, students will learn to build the model as shown in Figure-2

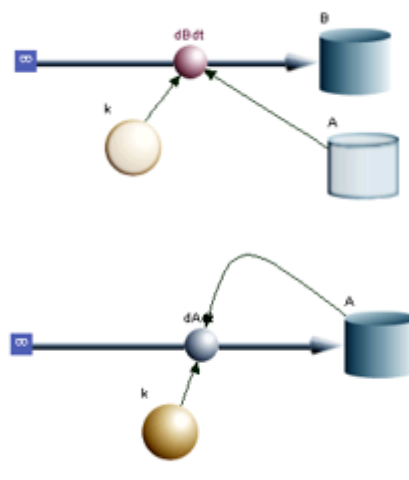


Figure-2 A tutorial Berkeley Madonna model for the first-order reaction, $A \rightarrow B$ with the rate constant k .

The new model allows students to write $d[A]/dt$ and $d[B]/dt$ consistently with what they learn in the classroom:

$$d[A]/dt = -k[A] ; d[B]/dt = k[A] \quad \text{[Equation 2]}$$

After running the model, a chart of both $[A]$ and $[B]$ as a function of time are shown as in Figure-3.

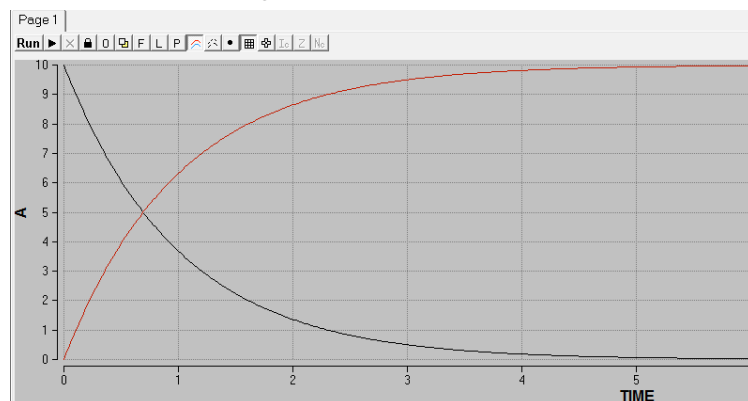


Figure-3 Concentrations of $[A]$ and $[B]$ as a function of time for the first order reaction. $[A]_0 = 10$, $[B]_0 = 0$, $k = 1$.

When $\ln([A])$ is plotted against time, a straight line is shown in Figure 4, indicative that the model built in Figure 2 is correct.

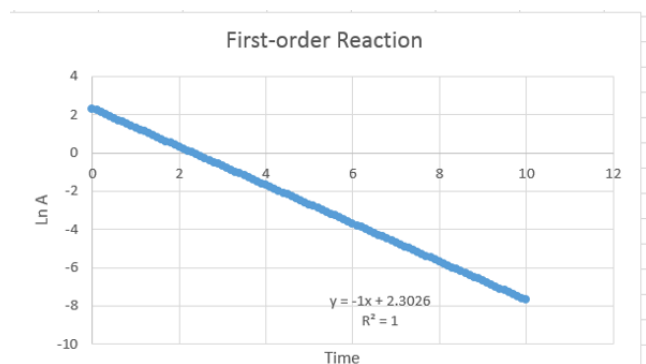


Figure-4 A plot of $\ln([A])$ as a function of time for the 1st order reaction: $A \rightarrow B$; $A [A]_0=10, [B]_0=0, k=1$. The slope is $-k$, while the intercept is $\ln([A]_0)$

In building the 1st order reaction model shown in Figure-2, students need to use the *alias* icon in Berkeley Madonna™. A tutorial for building a chemistry reaction model using the *alias* icon is presented in the supplementary material.

Similarly, the 2nd order kinetics can be built as shown in Figure 5:

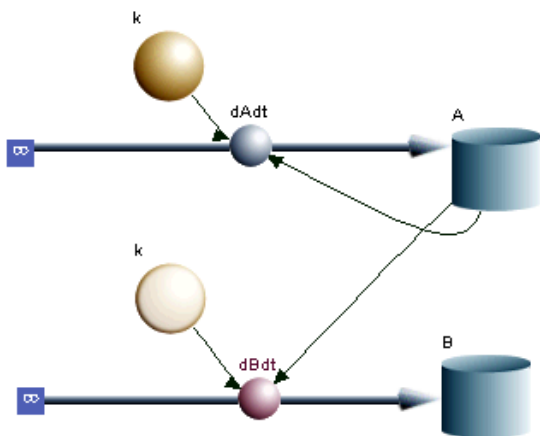


Figure-5 A tutorial Berkeley Madonna model for the 2nd order reaction, $2A \rightarrow B$ with the rate constant k . $[A]_0=10, [B]_0=0, k=1$

The differential equation expression for the 2nd order reaction is:

$$d[A]/dt = -2k[A]^2 ; d[B]/dt = k[A]^2 \quad [\text{Equation 3}]$$

The concentrations of both $[A]$ and $[B]$ as a function of time are shown in Figure-6.

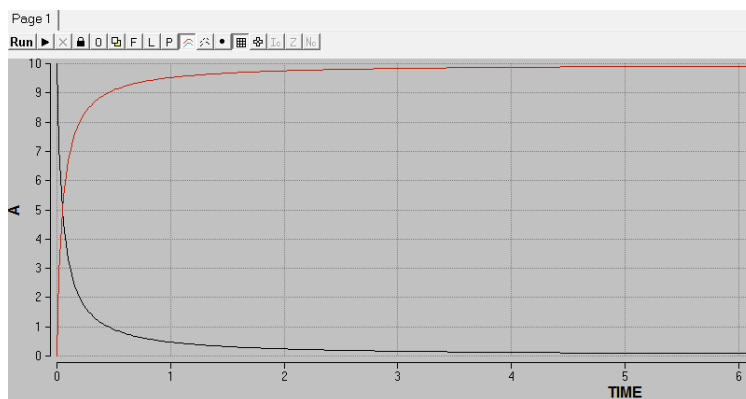


Figure-6 Concentrations of $[A]$ and $[B]$ as a function of time for the 2nd order reaction: $2A \rightarrow B$; $A [A]_0=10, [B]_0=0, k=1$.

A key signature of the 2nd-order reaction is that when $1/[A]$ is plotted against time, a linear plot is obtained. This is indeed the case:

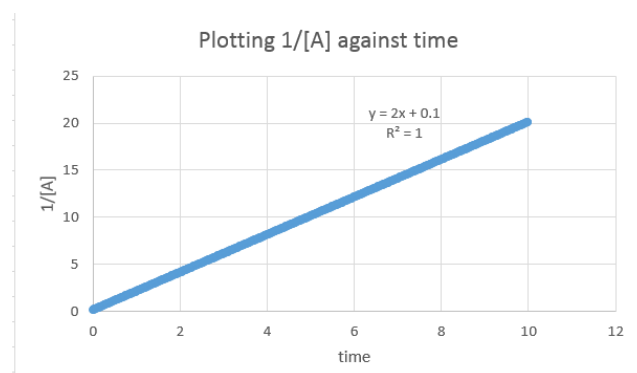
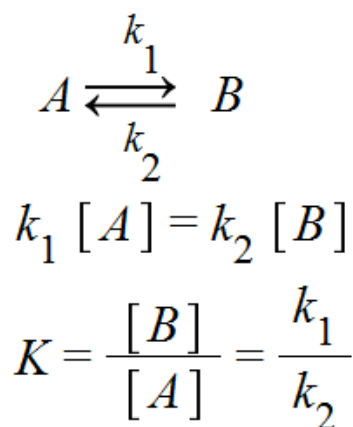


Figure-7 A plot of $1/[A]$ as a function of time for the 2nd order reaction: $2A \rightarrow B$; $A [A]_0=10, [B]_0=0, k=1$. The slope is $2k$, while the intercept is $1/[A]_0$

For upper-level students, the 1st and the 2nd order reactions can be used as an initial tutorial for learning Berkeley Madonna™ code. On the other hand, the spreadsheets generated from both models can be used as teaching materials for general chemistry students learning about the kinetics.

2.2 Equilibrium concept

The mathematical model to illustrate the equilibrium concept is shown in Equation [4]



Equation [4]

Following the tutorial presented in the first example for both the 1st or the 2nd order reactions, the finished flow chart will resemble the graph in Figure-8. The initial conditions and rate constants are: $[A]_0 = 10$, $[B]_0 = 0$, $k_1 = 2$, $k_2 = 1$. The complete code is attached in the supporting materials.

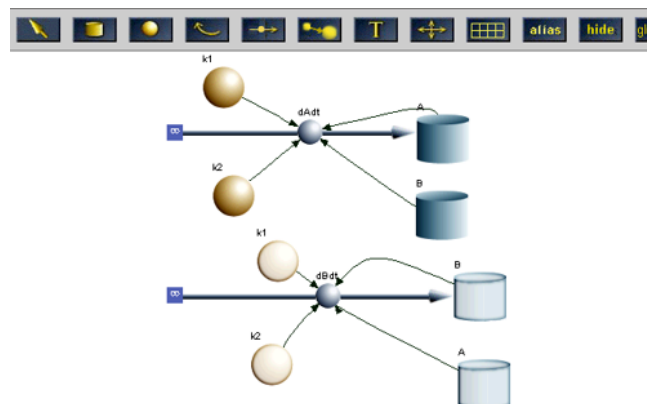


Figure-8: A flow chart to illustrate the equilibrium concept.

The differential equations for Equation [4] are:

$$\frac{d[A]}{dt} = -k_1[A] + k_2[B] \quad \frac{d[B]}{dt} = k_1[A] - k_2[B]$$

[Equation 5]

The final chart plotting both $[A]$ and $[B]$ as a function of time is shown in Figure-9

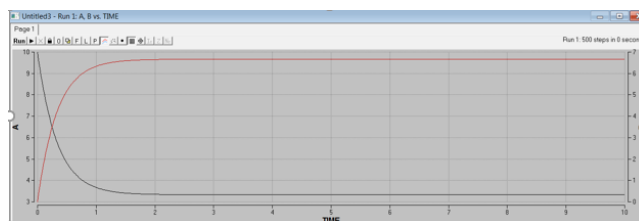


Figure-9 Concentrations of $[A]$ and $[B]$ as a function of time for the equilibrium reaction between A and B ; $[A]_0 = 10$, $[B]_0 = 0$, $k_1 = 2$, $k_2 = 1$

Madonna allows students to print out results in Excel format. When complete, the students are asked to answer the following questions:

[1] What time does the reaction reach equilibrium?

[2] What are the concentrations of $[A]$ and $[B]$ when the reaction reaches equilibrium? What is the equilibrium constant of the reaction?

The spreadsheet can also be used in general chemistry without asking students to build the flow chart model. Upper-level students can be challenged to build the model from the scratch and explain questions [1] and [2] shown above.

2.3 Rate-determining step

For a sequential reaction shown in Figure 10, the concept of the rate-determining step implies that the rate of the product formation is determined by the slowest rate constant in this sequential reaction. For example, in Figure 10, if $k_2 \ll k_1$, or k_3 , then $[D]$ should be determined by k_2 . Mathematically, it is expressed in Eq. 6.

$$[D] \sim [A]_0 (1 - e^{-k_2 t}) \quad \text{[Equation 6]}$$

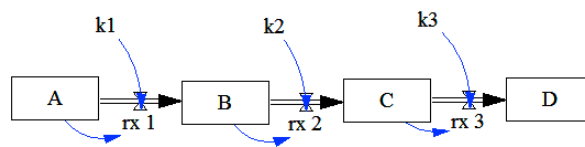


Figure-10: A flow chart to illustrate the rate-determining-step concept.

In the flow chart, the initial concentrations are $[A]_0 = 100$, $[B]_0 = [C]_0 = [D]_0 = 0$. Rate constants are: $k_1 = k_3 = 10$, $k_2 = 0.1$

The Berkeley Madonna model when finished should look like Figure 11

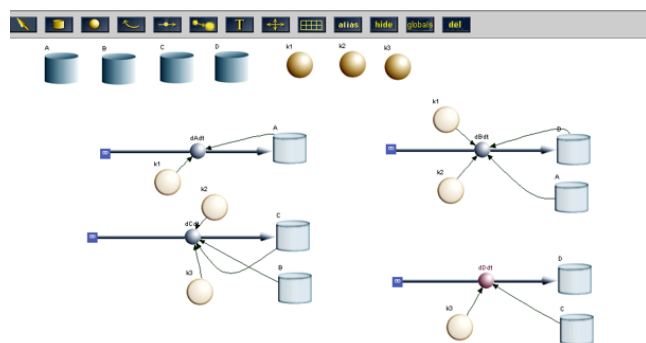


Figure-11: A complete Madonna model to illustrate the rate-determining-step concept. $A \rightarrow B \rightarrow C \rightarrow D$ in which $B \rightarrow C$ is the rate-determining step with $k_2=0.1$.

The differential equations that students need to write for the success of this model is:

$$\frac{d[A]}{dt} = -k_1[A], \quad \frac{d[B]}{dt} = k_1[A] - k_2[B], \quad \frac{d[C]}{dt} = k_2[B] - k_3[C], \quad \frac{d[D]}{dt} = k_3[C] \quad [\text{Equation 7}]$$

When [D] from the Excel spreadsheet (generated from the Madonna model) is compared against the plot obtained from Equation 5, they are almost identical as shown in Figure 12. Upper level students will be asked to generate the model from scratch. They are asked not only to generate the graph as shown in Figure 12, but also play with the numerical values of k_1 , k_2 , and k_3 to draw conclusions about under what kind of conditions do rate-determining step kinetics exist.

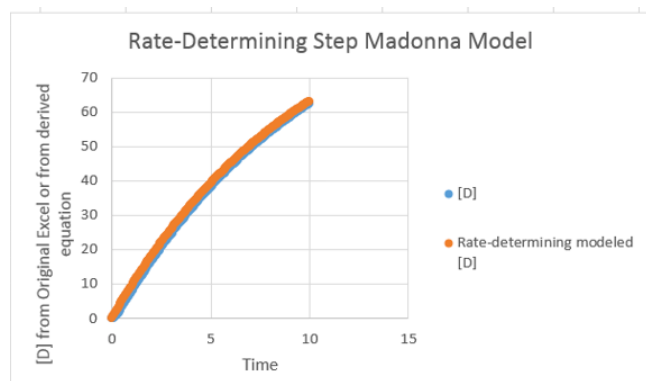


Figure-12: Excel output graph to illustrate the concentration changes of product [D] based on the Madonna output and [D] based on Equation 6.

2.4 The steady-state approximation

A flow chart to illustrate steady-state kinetics is illustrated in Figure-13, with the constraint that $k_2 \gg k_1$ so that $d[B]/dt = 0$.

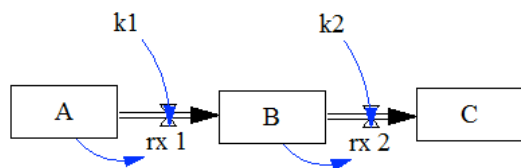


Figure-13: A flow chart to illustrate the steady-state equilibrium concept.

This implies that after an induction period in which the concentration of the intermediate, B, rises from zero, and during the major part of the reaction, the rate changes of the intermediate is negligibly small. The essential part of this exercise is that the intermediate concentration [B] should remain constant with time. A Berkley Madonna model is presented in Figure 14.

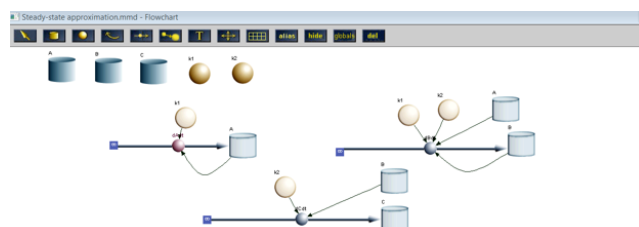


Figure-14: A complete Madonna model to illustrate the steady-state kinetics concept. $A \rightarrow B \rightarrow C$ in which the rate constant k_2 for $B \rightarrow C$ is much greater than the rate constant k_1 for $A \rightarrow B$. $[A]_0=100$, $[B]_0=0$, $[C]_0=0$, $k_1=0.1$, $k_2=10$.

The differential equations that student will write are: $\frac{d[A]}{dt} = -k_1[A]$, $\frac{d[B]}{dt} = k_1[A] - k_2[B]$, $\frac{d[C]}{dt} = k_2[C]$. [Equation 8]

Figure-15 illustrates that $d[B]/dt = 0$ in which [B] is shown as the orange plot.

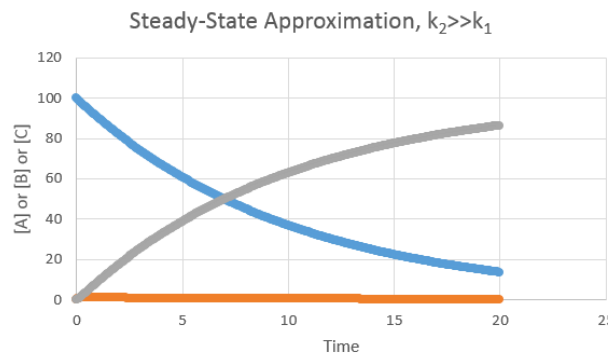
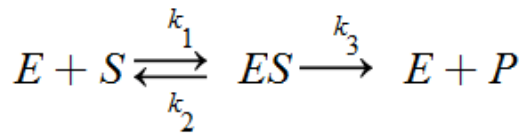


Figure-15: Excel output graph to illustrate the steady-state kinetics concept in which $d[B]/dt = 0$ (shown orange). The reactant, [A] (blue) decreases while the product [C] (grey) increases with time.

Upper-level students are asked to reproduce this steady-state approximation from scratch. The Excel spreadsheet can be used for general chemistry students

2.5 The enzyme kinetics approximation and the Lineweaver-Burk Equation

A schematic description of enzyme kinetics is illustrated as follows:



[Equation 9]

In this mechanism, E is the enzyme, S is the substrate, ES is the complex, and P is the product. In the limit where the initial substrate concentration is substantially greater than that of the enzyme ($[S]_o \gg [E]_o$), the rate of product formation [24] is given by

$$R_o = \frac{d[P]}{dt} = \frac{k_3 [S]_o [E]_o}{[S]_o + K_m}$$

[Equation 10]

The composite constant, K_m , in Eq.6 is referred to as the Michaelis constant of the enzyme kinetics. K_m is given by [24]

$$K_m = \frac{k_2 + k_3}{k_1}$$

[Equation 11]

Eq.10 is referred to as the Michaelis-Menten rate law. A reciprocal plot of the reaction rate can also be constructed by inverting Eq.10 which results in the Lineweaver-Burk equation,

$$\frac{1}{R_o} = \frac{1}{R_{max}} + \frac{K_m}{R_{max}} \frac{1}{[S]_o}$$

[Equation 12]

where $R_{MAX} = k_3 [E]_o$.

In this equation form, the plot of $1/R_o$ against $1/[S]_o$, will yield a straight line with a slope of K_m/R_{max} and an intercept of $1/R_{max}$, with $R_{max} = k_3 [E]_o$, and K_m given by Equation 11.

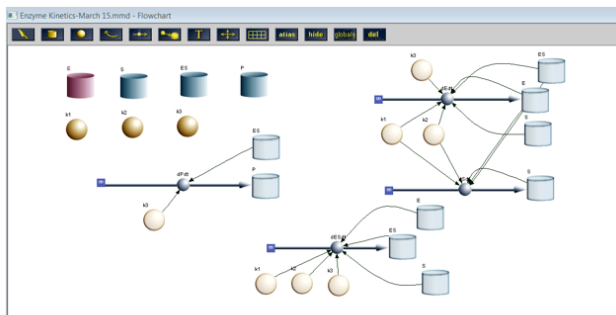


Figure-16: A Berkeley Madonna model to illustrate the enzyme kinetics mechanism. $K_1=2$, $k_2=20$, $k_3=2$, $[E]_o=2.3$, $[ES]_o=0$, $[P]_o=0$, $[S]_o$ varies from 2 to 20.

In this model, the differential equations expressing this kinetics are:

$$d[E]/dt = -k_1 [E][S] + k_2 [ES] + k_3 [ES]$$

$$d[S]/dt = -k_1 [E][S] + k_2 [ES]$$

$$d[P]/dt = k_3 [ES]$$

$$d[ES]/dt = k_1 [E][S] - k_2 [ES] - k_3 [ES]$$

[Equation 13]

The chart generated from the Excel spreadsheet is shown in Figure-17.

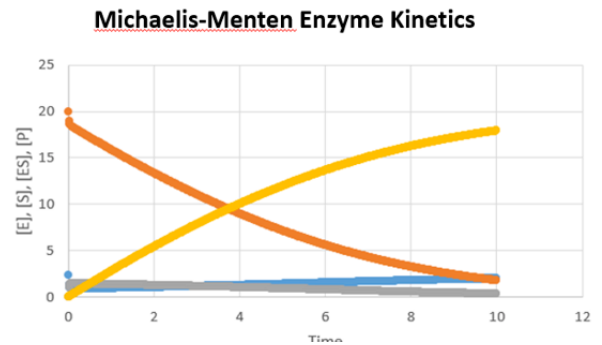


Figure-17: Excel output graph to illustrate the enzyme kinetics concept in which $d[ES]/dt = 0$ (shown grey). Other outputs include $[S]$ (substrate, orange), product $[P]$ (yellow), enzyme $[E]$ (blue)

For our Madonna model we have $R_{max} = 4.6$, $K_M = 11$. The plot of $1/R$ versus $1/[S]_o$ shown in Figure-18 is called the Lineweaver-Burk plot. A regression equation of this plot gives a slope of 1.011 , and the intercept = 0.0032 . These results deviate from the theoretical value in which the slope (K_M/R_{max}) is 2.3913 and the intercept ($1/R_{max}$) is 0.2174 . The percent of deviation are 81% for the slope and 195% for the intercept. This deviation becomes smaller if we use a smaller initial enzyme concentration. For example, when the initial enzyme concentration is 10-fold smaller, or $[E]_o = 0.23$ instead of $[E]_o = 2.3$, then $R_{max} = 0.46$, $K_M = 11$, slope = $K_M/R_{max} = 23.913$, intercept = $1/R_{max} = 2.174$. The new Lineweaver-Burk plot yields a slope of 26.85 , an intercept = 2.0342 . These values only deviate from the theoretical values by 11.5% for the slope, and 6.6% for the intercept. In the laboratory set up, usually the enzyme concentration is in the nM range while the substrate concentrations are in the mM range, so the Lineweaver-Burk equation is a useful approximation for finding the K_m values.

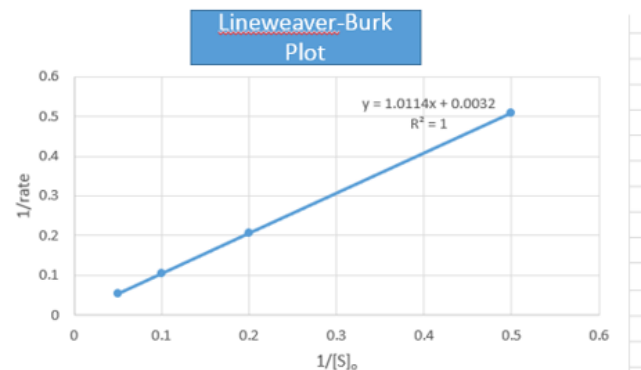


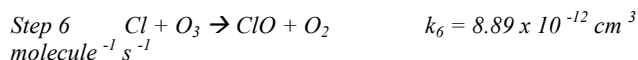
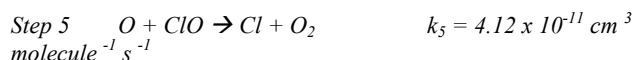
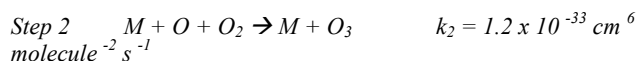
Figure-18: The Lineweaver-Burk plot of the enzyme kinetics.

2.6 Stratospheric ozone depletion kinetics model

Stratospheric (10-50 km above the sea level) ozone protects living beings from the harmful UV radiation from the sun. It was reported [25] that there was a 2.9% decline of stratosphere ozone from 1973 to 1997. The decline was due to the excess chlorofluorohydrocarbons (used as a refrigerant) released to the stratosphere. In 1995, a Nobel Prize was awarded to Professors Paul Crutzen, Mario Molina, and F. Sherwood Rowland for this important discovery.

Understanding the chemistry that controls the formation of the ozone layer, and the effects of man-made chemicals on the ozone layer, are areas in which physical chemists can impact society. Both experimental data from the laboratory and field data collected from the atmosphere are available [26]. In this unit, students learn to use Berkeley Madonna code to express both the flow-charts and differential equations for the depletion of stratosphere ozone due to chlorofluorohydrocarbons.

The elementary steps of the chemical reactions are shown as follows:



[Equation 14]

Steps 1-4 are the elementary steps of the Chapman mechanism. Step-2 is the essential step of the ozone formation. Because it involves a 3-body collision of O , O_2 , and an inert solid, M , the rate constant k_2 is many orders of magnitude smaller than the rate constants of other steps. The much smaller rate constant of ozone formation in the Chapman mechanism makes it susceptible to depletion in the presence of chlorine oxygen compounds as shown in steps 5-6.

The initial concentrations of O , O_2 , O_3 , M , ClO , and Cl taken from the same NASA resources [26] are:

$$[O]_o = 1 \times 10^7 \text{ molecules/cm}^3$$

$$[O_2]_o = 2 \times 10^{17} \text{ molecules/cm}^3$$

$$[O_3]_o = 7 \times 10^{12} \text{ molecules/cm}^3$$

$$[M]_o = 9 \times 10^{17} \text{ molecules/cm}^3$$

$$[ClO]_o = 1 \times 10^8 \text{ molecules/cm}^3$$

$$[Cl]_o = 5 \times 10^4 \text{ molecules/cm}^3$$

With [Equation 14] and the initial concentrations of each species, students are asked to construct two Berkeley Madonna flow charts: One for the Chapman mechanism (Steps 1-4 in Equation 14); the other including steps 5-6 in addition to the Chapman mechanism.

The flow chart for the Chapman mechanism should look like the chart shown in Figure 19.

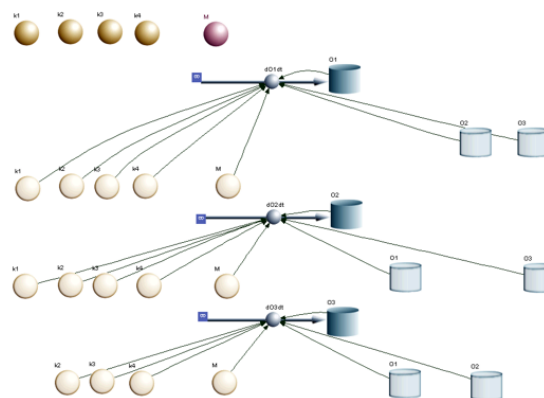


Figure-19: A Berkeley Madonna model to illustrate the Chapman mechanism. The O1, O2, and O3 shown in the chart stand for $[O]$, $[O_2]$, and $[O_3]$

The differential equations for the Chapman mechanism (Step-1 to Step-4) are:

$$d[O]/dt = 2 k_1 [O_2] - k_2 [M][O][O_2] + k_3 [O_3] - k_4 [O][O_3]$$

$$d[O_2]/dt = -k_1 [O_2] - k_2 [M][O][O_2] + k_3 [O_3] + 2 k_4 [O][O_3]$$

[Equation 15]

Figure-19: A Berkeley Madonna model to illustrate the Chapman mechanism. The O1, O2, and O3 shown in the chart stand for $[O]$, $[O_2]$, and $[O_3]$

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$$d[O_2]/dt = -k_1 [O_2] - k_2 [M][O][O_2] + k_3 [O_3] + 2 k_4 [O][O_3]$$

[Equation 15]

The complete mechanism is represented in the Berkeley Madonna flow chart attached as supplementary material to this manuscript.

The Excel output of $[O_3]$ in the absence and in the presence of ClO_x interference is shown in Figure 20.

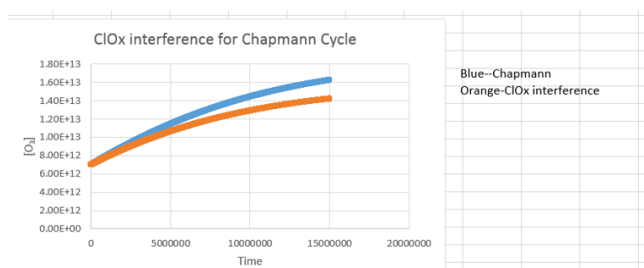


Figure-20: Ozone concentrations as a function of time in the absence and presence of ClO_x interference.

3. PROJECTS AND EXERCISES

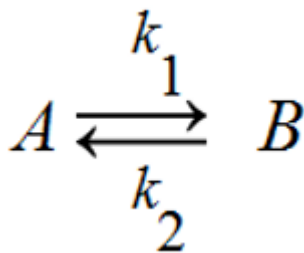
A tutorial to use differential-equation constructed flow charts with the Berkeley Madonna is presented as supplementary material to this manuscript. Although the following projects and exercises are for upper-level students, some of the Excel output can be used for general chemistry students.

3.1 First-order kinetics: $A \rightarrow B$ with rate constant $k_1=1$, and $[A]_o=10$

- (1) Write differential equations for $d[A]/dt$, and $d[B]/dt$.
- (2) Following the tutorial, construct Berkeley Madonna flow charts representing $d[A]/dt$, and $d[B]/dt$.
- (3) After running the program, proceed to save the results ($[A]$ and $[B]$ as a function of time) in Excel[®] format.
- (4) Plot $[A]$ and $[B]$ as a function of time, and discuss the results.
- (5) Create another column for $\ln([A])$, and plot $\ln([A])$ as a function of time. Discuss the results.
- (6) Create another column for $[A]_o(1-e^{-k_1 t})$. Plot both $[B]$ and $[A]_o(1-e^{-k_1 t})$ as a function of time and discuss the results.

3.2 Equilibrium concept

The equilibrium concept is represented as:



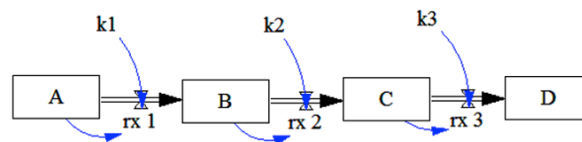
with $k_1=2$, and $k_2=1$. The initial concentrations for $[A]$ and $[B]$ are: $[A]_o=10$, and $[B]_o=0$.

- [1] What is an equilibrium? What is the expected equilibrium constant even before running the program?
- [2] Write differential equations for $d[A]/dt$ and $d[B]/dt$ for this equilibrium.
- [3] Construct Berkeley Madonna flow charts based on the differential equations for $d[A]/dt$ and $d[B]/dt$.
- [4] Run the code and save the Excel outputs. Study the Excel output and answer the following questions:

- (i) Approximately when do $[A]$ and $[B]$ reach equilibrium?
- (ii) What are the equilibrium concentrations for $[A]$ and $[B]$?
- (iii) What is the equilibrium constant?
- (iv) Show that the equilibrium constant $K = k_1/k_2$

3.3 Rate-determining step kinetics

In this exercise, students are asked to construct differential equation-based Madonna flow charts for the following diagram:

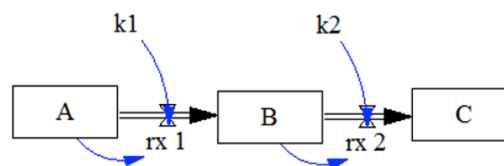


The inputs for the rate constants and initial concentrations of species are: $[A]_o=100$, $[B]_o=[C]_o=[D]_o=0$, $k_1=k_3=10$, $k_2=0.1$.

- [1] Express in words what 'the rate-determining-step' means in chemical kinetics.
- [2] Write differential equations for $d[A]/dt$, $d[B]/dt$, $d[C]/dt$, and $d[D]/dt$.
- [3] Construct Berkeley Madonna flow charts based on this set of differential equations with proper inputs for k_1 , k_2 , k_3 , $[A]_o$, $[B]_o$, $[C]_o$ and $[D]_o$.
- [4] Run the code and study the Excel outputs by creating another column with the equation form, $[A]_o(1-e^{-k_2 t})$. Plot both $[D]$ and $[A]_o(1-e^{-k_2 t})$ together as a function of time, and discuss the results.

3.4 The Steady-state approximation

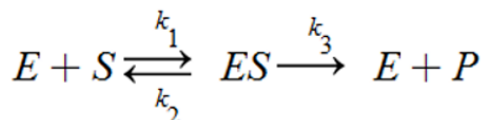
In this exercise, students are asked to construct a differential equation based Berkeley Madonna chart diagram such that $d[B]/dt=0$ in the following flow chart.



- (1) Write differential equations for $d[A]/dt$, $d[B]/dt$, and $d[C]/dt$.
- (2) Construct differential equation-based Berkeley Madonna chart diagrams with initial $k_1=0.5$, $k_2=20$, $[A]_o=10$, $[B]_o=0$, $[C]_o=0$.
- (3) Run the code, and save the results in Excel format. Plot $[A]$, $[B]$, and $[C]$ with time. Also record $d[B]/dt$ at time = 10 s.
- (4) Change the ratio of k_1/k_2 and observe how $d[B]/dt$ changes with the ratio.
- (5) Change $[A]_o$ and observe how $d[B]/dt$ changes with $[A]_o$.

3.5 Enzyme kinetics

In this exercise, students are asked to construct a differential equation-based Berkeley Madonna chart diagram based on the enzyme kinetics flow chart diagram shown below:



- (1) Write differential equations for $d[E]/dt$, $d[S]/dt$, $d[ES]/dt$, and $d[P]/dt$.
- (2) Construct differential equation based Berkeley Madonna chart diagrams with initial inputs of $[E]_o = 2.3$, $k_1 = 2$, $k_2 = 20$, $k_3 = 2$, $[S]_o = 2$.
- (3) Run the code and plot $[E]$, $[S]$, $[P]$, and $[ES]$ with time.
- (4) Record $d[P]/dt$ and $d[ES]/dt$ at 0.1 s.
- (5) Repeat the procedures of (3) and (4), but with $[S]_o = 5$, 10, 20 then record the new $d[P]/dt$ and $d[ES]/dt$ at 0.1 s for each new $[S]_o$.
- (6) Construct a Lineweaver-Burk plot, obtaining the slope and the intercept of the plot, and compare the values with the theoretical values (slope = K_m/R_{max} , intercept = $1/R_{max}$, $R_{max} = k_3 [E]_o$, $K_m = ((k_2 + k_3)/k_1)$). Calculate the percent of error between your experimental value (from the chart) and theoretical values (from the rate constants and the initial enzyme concentration).
- (7) Repeat procedures (3), (4) (5) and (6) but with the new initial enzyme concentration of $[E]_o = 0.23$.
- (8) Report your finding in words that discuss the conditions in which the Lineweaver-Burk plot applies to finding K_m in enzyme kinetics problems.

3.6 Stratospheric Ozone

In this more advanced unit, students are challenged to apply their skills to solve the stratospheric ozone depletion problems. The kinetics of stratospheric ozone consists of two parts: The Chapman mechanism (step 1-step 4) for the ozone formation, and the chloro-carbon ozone depletion (step 5-step 6). They are summarized as follows:

Step 1	$O_2 + h\nu \rightarrow 2O$	$k_1 = 3 \times 10^{-12} s^{-1}$
Step 2	$M + O + O_2 \rightarrow M + O_3$	$k_2 = 1.2 \times 10^{-33} cm^6 molecule^{-2} s^{-1}$
Step 3	$O_3 + h\nu \rightarrow O + O_2$	$k_3 = 5.5 \times 10^{-4} s^{-1}$
Step 4	$O + O_3 \rightarrow 2O_2$	$k_4 = 6.9 \times 10^{-16} cm^3 molecule^{-1} s^{-1}$
Step 5	$O + ClO \rightarrow Cl + O_2$	$k_5 = 4.12 \times 10^{-11} cm^3 molecule^{-1} s^{-1}$
Step 6	$Cl + O_3 \rightarrow ClO + O_2$	$k_6 = 8.89 \times 10^{-12} cm^3 molecule^{-1} s^{-1}$

- (1) Write differential equations for $d[O]/dt$, $d[O_2]/dt$, $d[O_3]/dt$, for Step-1 to Step-4; the other for $d[O]/dt$, $d[O_2]/dt$, $d[O_3]/dt$, $d[ClO]/dt$ and $d[Cl]/dt$. for Step-1 to Step-6.
- (2) Construct differential equation-based Berkeley Madonna chart diagrams using the rate constants given and initial conditions for: $[O]_o = 1 \times 10^7$, $[O_2]_o = 2 \times 10^{17}$, $[O_3]_o = 7 \times 10^{12}$, $[M] = 9 \times 10^{17}$, $[ClO]_o = 1 \times 10^8$, and $[Cl]_o = 5 \times 10^4 molecules/cm^3$.
- (3) Run the code twice, once for Step-1 to Step-4; the other for Step-1 to Step- 6. The parameters used for running these two codes are: Numerical method Rosenbrock (stiff), stop-time = 1.5×10^7 , $\Delta T_{min} = 500$, $\Delta T_{max} = 1000$, $\Delta T_{out} = 0$, tolerance = 0.01.

- (4) Plot $[O_3]$ versus t, once for Step 1-Step 4; the other for Step-1 to Step-6
- (5) Discuss the results of your plots.

4. SELECTIVE ANSWERS TO THE PROJECTS AND EXERCISES

4.1 First-order kinetics: $A \rightarrow B$ with rate constant $k_1=1$, and $[A]_o=10$

$$d[A]/dt = -k_1 [A], \quad d[B]/dt = k_1 [A] ; [A] = [A]_o e^{-k_1 t}, [B] = [A]_o (1 - e^{-k_1 t})$$

A plot of $\ln[A]$ against t will give a straight line with a slope of $-k_1$. The Excel output for [B] should be the same as $[A]_o (1 - e^{-k_1 t})$.

4.2 Equilibrium concept

An equilibrium is reached when the rates of forward and backward reactions are equal. When $k_1 = 2$, and $k_2 = 1$, the forward rate is $k_1 [A]$, and the backward rate is $k_2 [B]$, $k_1 [A] = k_2 [B]$. The equilibrium constant, K , $K = [B]/[A] = k_1/k_2$.

4.3 Rate-determining step kinetics

When a given step is the rate-determining step, the rate constant for this specific step is many orders of magnitude smaller than the rate constants of the other steps. In this case, the rate of product formation is determined by the rate constant for this rate-determining step. Thus, if rate constant of the rate-determining step is k_2 , then $[P] \sim [A]_o (1 - e^{-k_2 t})$.

4.4 The Steady-state approximation

In a mechanism of $A \rightarrow B \rightarrow C$, B is the intermediate. The steady-state approximation relies on the premise that $d[B]/dt = 0$. To make this approximation valid, as soon as B is formed, it is immediately converted into C, or k_2 (rate constant for $B \rightarrow C$) is many orders of magnitude larger than k_1 (rate constant for $A \rightarrow B$). Under this circumstance, $d[B]/dt \sim 0$.

4.5 Enzyme kinetics

When differential equations are properly written and the Berkeley Madonna chart diagrams are properly constructed, a double reciprocal plot of $1/(d[P]/dt)$ versus $1/[S]_o$ will give a straight line with a slope = K_m/R_{max} , and intercept = $1/R_{max}$ in which $R_{max} = k_3 [E]_o$, $K_m = (k_2 + k_3)/k_1$. The agreement between the experimental value (from the double-reciprocal plot) and the theoretical plot (from Equation 12) will improve as the initial enzyme concentration is reduced.

4.6 Stratosphere ozone

The most important part of this exercise is to properly write the differential equations for $d[O]/dt$, $d[O_2]/dt$, and $d[O_3]/dt$ for the Chapman mechanism (Step-1 to Step 4) given in the exercises; $d[O]/dt$, $d[O_2]/dt$, $d[O_3]/dt$, $d[ClO]/dt$, and $d[Cl]/dt$ for the complete mechanism (Step-1 to Step-6).

The differential equations for the Chapman mechanism (Step-1 to Step-4) are:

$$d[O]/dt = 2 k_1 [O_2] - k_2 [M][O][O_2] + k_3 [O_3] - k_4 [O][O_3]$$

$$d[O_2]/dt = -k_1 [O_2] - k_2 [M][O][O_2] + k_3 [O_3] + 2 k_4 [O][O_3]$$

$$d[O_3]/dt = k_2 [M][O][O_2] - k_3 [O_3] - k_4 [O][O_3]$$

When Steps 5-6 are involved, we would modify $d[O]/dt$, $d[O_2]/dt$, and $d[O_3]/dt$ to include both Cl and ClO species.

$$d[O]/dt = 2 k_1 [O_2] - k_2 [M][O][O_2] + k_3 [O_3] - k_4 [O][O_3] - k_5 [O][ClO]$$

$$d[O_2]/dt = -k_1 [O_2] - k_2 [M][O][O_2] + k_3 [O_3] + 2 k_4 [O][O_3] + k_5 [O][ClO] + k_6 [Cl][O_3]$$

$$d[O_3]/dt = k_2 [M][O][O_2] - k_3 [O_3] - k_4 [O][O_3] - k_6 [Cl][O_3]$$

$$d[ClO]/dt = -k_5 [O][ClO] + k_6 [Cl][O_3]$$

$$d[Cl]/dt = k_5 [O][ClO] - k_6 [Cl][O_3]$$

When Berkeley Madonna chart diagrams are properly constructed and the output is saved into an Excel format, a plot of $[O_3]$ versus time with and without Cl/ClO interference will look like Figure 20.

5. TESTING AND EVALUATION

5.1 General chemistry testing and evaluations

During the spring semester of 2017, two weeks before the first exam for a general chemistry class, I provided an Excel output of first-order kinetics, $A \rightarrow B$ with rate constant k_f . I asked students to plot $\ln[A]$ versus t , using the regression equation to find the slope, and the rate constant k_f . Fifteen students out of 130 students made a mistake of taking the slope (which is a negative number) as k_f . After explanations to the class, when a similar question appeared in the first exam, only 6 out of 130 students made the same mistake.

5.2 Upper-level chemistry testing and evaluations

During the fall semester of 2016, I implemented VensimTM projects almost exactly the same as what was presented during the 2015 cCWCS (Chemistry Collaboration and Workshop for Community Scholars) to my students of Thermodynamics and Kinetics class of 12 students. In that study, 10 out of 12 students were able to completely follow the tutorial, create the diagrams and answer the questions correctly; 2 out of 10 did not answer questions related to the equilibrium concept correctly even though they had created the model correctly. Even with this success, students were unable to obtain a realistic Michaelis constant, K_M through the Lineweaver-Burk plot. The class soon realized that VensimTM was unable to model stratosphere ozone depletion problems.

The Berkeley Madonna code was implemented in the fall semester of 2017. The grading rubric is (1) Stratosphere ozone, 25/60; (2) Enzyme kinetics and Lineweaver-Weaver plot, 15/60; (3) First order kinetics, 5/60; (4) Equilibrium Concept, 5/60; (5) Rate-Determining Step, 5/60; and (6) Steady-State Approximation, 5/60. The average grade for this project was

82%. Grade distribution for this project for 26 students is shown in Figure-21.

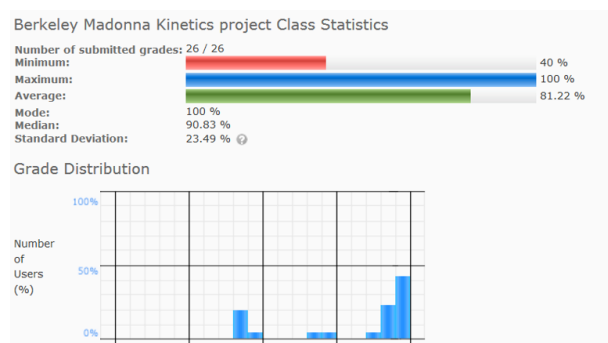


Figure 21 Grade distribution for the Berkeley Madonna Project Introduced at UW-Green Bay in Fall, 2017.

About 5 out of 26 students did not succeed in the Stratospheric Ozone problem. The common mistake was that in creating $[O_3]$ versus time in the presence of Cl and ClO species, they did not create flow charts that include $d[Cl]/dt$, and $d[ClO]/dt$. This mistake can be easily remedied by writing instructions in the manual if this project manual is introduced in 2018, or adopted by other physical chemistry instructors. Also, approximately 6 students lost points in the 1st-order kinetics plot to show a match between the product $[B]$ versus time and $[A]_0 (1 - \exp(-k_f t))$. If this manual is introduced again in 2018, I would add an additional assignment asking students to derive $[B(t)] = [A]_0 (1 - \exp(-k_f t))$. This way, students will appreciate why this plot is included in the assignment.

At the end of the semester, the final exam (take-home exam) included a project of using the Berkeley Madonna code to create the Lotka-Volterra mechanism [27]. A successful code will create a chart similar to that shown in Figure 22. Everyone succeeded for this problem in the final exam.

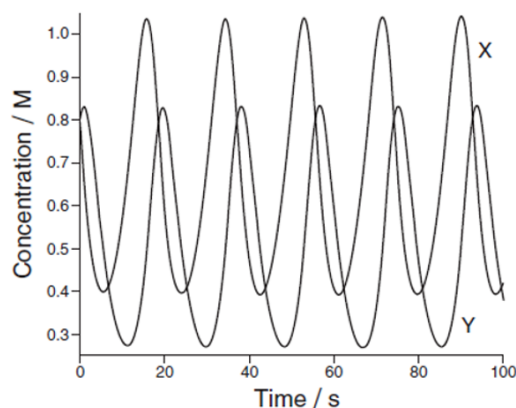


Figure-22 The oscillation pattern of the $[X]$, and $[Y]$, for the Lotka-Volterra mechanism.

6. CONCLUSION

Berkeley Madonna code was successfully adopted as a powerful and versatile platform that offers substantial pedagogical advantages for students to quickly create code and engage in interpretations. The learning outcomes for upper-level students at UW-Green Bay are encouraging. Instructors can also use the platform to create Excel spreadsheets for Gen-Chem students learning key concepts of chemical kinetics.

7. ACKNOWLEDGEMENT

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