

ChemKinetics

Fundamental chemical kinetics principles and analysis by computer simulation

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Abstract

The *ChemKinetics* software is a chemical kinetics simulator and tutorial package that incorporates simple first-order irreversible, first-order reversible, first-order parallel, first-order consecutive, simple second-order and general second-order irreversible processes.

Keywords

Audience: First-Year Undergraduate/General; Second-Year Undergraduate
Domain: Physical Chemistry
Pedagogy: Computer-Based Learning; Inquiry-Based/Discovery Learning
Topics: Kinetics

Technology Report

The interest in computer-based activities to illustrate chemical kinetic principles to students has been ongoing in the educational literature since the 1970's. Examples of these include: programs to treat various kinds of kinetic systems (1-5), a Monte Carlo approach to teaching kinetics (6) and a micro-computer-based reaction kinetics simulator (7). Following these earlier examples have been various specialized approaches including spreadsheet and other kinetic simulators (8-11), the use of *Mathematica* to study oscillating and chaotic reactions (12), stochastic simulation of chemical reactions (13) computational modeling that includes reaction dynamics (14) and a computer-based experiment that models a physical analogue for consecutive reaction kinetics in particular (15).

The *ChemKinetics* software incorporates six fundamental chemical kinetic processes for students to explore, namely: simple first-order irreversible, first-order reversible, first-order parallel, first-order consecutive, simple second-order and general second-order irreversible processes. The student sets the concentration and rate parameters associated with the reaction and the software calculates the concentration of each chemical species as a function of time as well as certain mathematical functions relevant to the kinetics analysis. The output data are displayed on the screen and are automatically copied to the clipboard in a tab-delimited format to enable convenient transfer to a suitable spreadsheet program such as *Microsoft Excel* for plotting, labelling and further manipulation.

The software has self-contained exercises of various degrees of complexity that are carefully designed to introduce students systematically to each of the fundamental kinetic processes. The exercises explore in quantitative detail the various systems and can serve as a basis from which students may explore the effects of changing the experimental starting conditions on the observed reaction kinetics. The observations that students should make upon completing the exercises are also contained within the software. The self-contained information in *ChemKinetics* may also assist students in compiling a set of comprehensive notes on the fundamentals of chemical kinetics. It is also anticipated that the exercises and associated information can be used as a guide to instructors in creating other original and interesting exercises and/or teaching materials.

The *ChemKinetics* software is provided as a standalone application. Versions exist that run on standard Macintosh OSX or Windows environments. The software should be run in conjunction with a standard spreadsheet program for the plotting and labeling of the output data. This approach to handling the output data provides maximum flexibility with regard to its presentation and collation.

Instructions

USER INTERFACE

The user interface comprises a **pull-down menu**; a window in which the currently **selected kinetic process** is displayed; seven **edit fields** for data input and a number of **control buttons**. The calculated data are displayed in an **output window** positioned on the right-hand side of the interface. These data are automatically copied to the **clipboard** and can be directly pasted into a spreadsheet program.

PULL-DOWN MENU

The pull-down menu enables the user to select one the following six fundamental chemical kinetic systems to study:

- **Simple first-order irreversible** process
- **First-order reversible** process
- **First-order parallel** process
- **First-order consecutive** process
- **Simple second-order** process
- **General second-order irreversible** process

A representation of the selected kinetic scheme and associated rate law is displayed below the pull-down menu.

EDIT FIELDS

Seven **edit fields** are used to input the following data:

- **Initial concentration** of species "A" and species "B"; these fields are labelled $[A]_0/M$ and $[B]_0/M$ respectively
- **Time interval in seconds** between successive calculations; this field is labelled $\Delta t/s$
- **Maximum time in seconds** up to which calculations will be performed; this field is labelled t_{max}/s
- Values of the **rate constants** relevant to the various kinetic processes; these fields are labelled k_1 , k_{-1} and k_2

Important notes:

- Edit fields will accept numbers that are entered in **scientific notation** and so entries such as: 0.015, 20, 1.50e-02, 2e+01, etc., are all acceptable as input numbers
- Edit fields **must contain appropriate data** for the selected kinetic process otherwise an **error message** will be generated. It is therefore important to check that edit fields not relevant to the selected process contain **zeros** or are left **empty**.

CONTROL BUTTONS

The five control buttons on the interface are labelled: "**Calculate**", "**Exercises**", "**Observations**", "**Instructions**" and "**Print**".

"Calculate" Button

This button starts the execution of the **kinetic simulation** using the **currently selected process** and the **current input parameters** that are contained in the edit fields.

"Exercises" Button

This button enables the user to gain access to the "**on-board**" **exercises** that can be used to explore the various kinetic processes. Each of the six kinetic processes has an associated exercise that comprises a set of steps designed to illustrate the fundamentals. Of course, the user may wish to explore **other possibilities and effects** by experimenting with the input parameters accordingly.

"Observations" Button

This button allows the user to view to the **outcomes of the recommended exercises** for the currently selected process.

"Instructions" Button

This button activates the instructions screens for **ChemKinetics**. If the "Instructions", "Exercises" or "Observations" button is pushed a set of **navigation buttons** in the lower right-hand corner of the interface enable browsing of the respective screens and return to the main program.

"Print" Button

This button produces a hard-copy printout of the **current screen**.

OUTPUT WINDOW

The numeric output from **ChemKinetics** is displayed in the output window as a series of **columns**. A **header** at the top of the output window indicates the content of each column. Contained within each exercise is **further information** about the content of columns generated for the selected kinetic process.

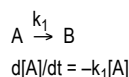
CLIPBOARD

The data in the output window are **automatically copied to the clipboard** in a **tab-delimited** format. This enables the clipboard contents to be pasted directly into a spreadsheet program such as *Microsoft Excel*, thereby providing the user with much flexibility in relation to plotting, labelling and any further manipulation of the processed data that may be required. The **header information is not included** in the exported data for ease of data manipulation within the spreadsheet program.

Exercises

1. First-Order Irreversible Reaction

The simple **first-order irreversible** process and the corresponding rate law are:



The time-dependencies of the concentration of species "A" and "B" are:

$$\begin{aligned} [A] &= [A]_0 e^{-k_1 t} \\ [B] &= [A]_0 (1 - e^{-k_1 t}) \end{aligned}$$

where k_1 is the **first-order rate constant**, $[A]_0$ is the **initial concentration** of species "A" and the initial concentration of species "B" is **zero** (i.e. $[B]_0 = 0$). To study the reaction kinetics **ChemKinetics** will require a value for $[A]_0$ and a value for k_1 . The program will calculate as functions of time: $[A]$, $[B]$, $f(a) = \ln([A])$ as well as $f(b) = \ln([A]_0 - [B])$. Upon data transfer, values of the time, t (s), will appear in Column 1 of the spreadsheet and values of $[A]$, $[B]$, $f(a)$ and $f(b)$ will appear respectively in Columns 2 to 5 of the spreadsheet.

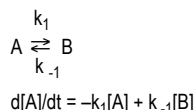
Exercise 1

- 1.1 Use **ChemKinetics** to examine first-order irreversible kinetics for a reaction where: $[A]_0 = 0.50$ M, $[B]_0 = 0$ M, $k_1 = 0.30$ s⁻¹. Set the following values: $\Delta t = 0.50$ s and $t_{\max} = 20.0$ s.
- 1.2 Transfer the data generated in the previous step to a spreadsheet.
- 1.3 Plot on the same set of axes $[A]$ and $[B]$ versus time for a first-order irreversible process where $[B]_0 = 0$. Indicate on your plot $[A]$, $[B]$ and $[A]_0$ (i.e. the initial concentration of species "A").
- 1.4 With reference to your plot produced in Step 1.3, rationalize the final concentration of species "B" in terms of the initial concentration of species "A". From your plot, estimate the half-life of the reaction and compare this with the theoretical value calculated using the rate constant (i.e. $t_{1/2} = \ln(2)/k_1$).
- 1.5 Refer to the plot produced in Step 1.3 and indicate: (i) any asymptotic behaviour of the curves and (ii) the rate of the reaction at any selected point in time. What is the rate of the reaction after an infinite time (i.e. when $t = \infty$)?

- 1.6 Observe the equality in the corresponding data values for $f(a)$ and $f(b)$ that appear in Columns 4 and 5 of the spreadsheet. Plot a graph of either $f(a)$ or $f(b)$ versus time. Determine the gradient of the line of best fit that passes through the data. Compare the numerical value of the gradient with that of the first-order rate constant and comment on the result.
- 1.7 In attempting to analyse the kinetics of first-order irreversible reactions, does the choice of following the "disappearance" of reactant "A" or the "appearance" of product "B" matter in theory? Explain your answer with reference to the results generated in this exercise. In practice, what factors may influence this choice?

2. First-Order Reversible Reaction

The simple **first-order reversible** process and corresponding rate law are:



where k_1 and k_{-1} are **first-order rate constants** for the **forward** and **reverse** processes respectively. The **ChemKinetics** software will require a value for $[A]_0$ (i.e. the **initial concentration** of species "A") and a value for each rate constant k_1 and k_{-1} . It will also require that the initial concentration of species "B" is **zero** (i.e. $[B]_0 = 0$) and will calculate as functions of time: $[A]$, $[B]$, $f(a) = \ln([A] - [A]_\infty)$ and $f(b) = \ln([B]_\infty - [B])$ where $[A]_\infty$ and $[B]_\infty$ are the respective concentrations of "A" and "B" when **equilibrium** has been attained. Upon data transfer, values of $[A]$, $[B]$, $f(a)$ and $f(b)$ will appear respectively in Columns 2 to 5 of the spreadsheet and time values, t (s), will appear in Column 1.

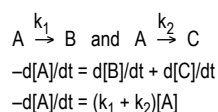
Exercise 2

- 2.1 Use **ChemKinetics** to examine first-order reversible kinetics for a reaction where: $[A]_0 = 0.50$ M, $[B]_0 = 0$ M, $k_1 = 0.30$ s⁻¹ and $k_{-1} = 0.129$ s⁻¹. Set the following values: $\Delta t = 0.25$ s and $t_{\max} = 10.0$ s.
- 2.2 Transfer the data generated in the previous step to a spreadsheet.
- 2.3 Plot on the same set of axes $[A]$ and $[B]$ versus time for a first-order reversible process where $[B]_0 = 0$. Indicate on the plot $[A]_0$ (i.e. the initial concentration of species "A") and any asymptotic behaviour of the curves, carefully estimating the values of all asymptotes and noting these on the plot.
- 2.4 Show that for a first-order reversible reaction in which $[B]_0 = 0$ then $[A]_\infty = k_{-1}[A]_0/(k_1 + k_{-1})$, $[B]_\infty = k_1[A]_0/(k_1 + k_{-1})$ and $k_1 + k_{-1} = k_1[A]_0/[B]_\infty$ where $[A]_\infty$ and $[B]_\infty$ are the respective concentrations of "A" and "B" at $t = \infty$ (i.e. at equilibrium).
- 2.5 From the plot generated in Step 2.3 estimate the value of the equilibrium constant of the reaction and compare this with the value of the ratio k_1/k_{-1} .
- 2.6 Show that, for first-order reversible kinetics, $f(a) = f(b)$ and observe the equality in the corresponding data values in Columns 4 and 5 of the spreadsheet.
- 2.7 Plot either $f(a)$ or $f(b)$ versus time and calculate the gradient of the straight line of best fit through the data. Compare the value of the gradient with the sum of the rate constants for the forward and reverse processes and comment.
- 2.8 Show how the values of the rate constants k_1 and k_{-1} can be obtained separately from the kinetic data. Confirm this by calculating values of k_1 and k_{-1} and comparing these with the values that were set when **ChemKinetics** was run.
- 2.9 Return to **ChemKinetics** and set $k_1 = 0.30$ s⁻¹, $k_{-1} = 0.012$ s⁻¹, $\Delta t = 0.50$ s and $t_{\max} = 20.0$ s. Do not change the settings $[A]_0 = 0.50$ M and $[B]_0 = 0$ M.

- 2.10 Plot on the same set of axes [A] and [B] versus time for a first-order reversible reaction obtained under the conditions where $k_{-1} \ll k_1$ and $[B]_0 = 0$. Compare this plot with that obtained for a first-order irreversible reaction (see Step 1.3 in Exercise 1). Briefly explain any similarities or differences.
- 2.11 Return to **ChemKinetics** and set $k_1 = 0.012 \text{ s}^{-1}$, $k_{-1} = 0.30 \text{ s}^{-1}$, $\Delta t = 0.50 \text{ s}$ and $t_{\text{max}} = 20.0 \text{ s}$. Do not change the settings $[A]_0 = 0.50 \text{ M}$, $[B]_0 = 0 \text{ M}$.
- 2.12 Plot on the same set of axes [A] and [B] versus time for a first-order reversible reaction obtained under the conditions where $k_{-1} \gg k_1$ and $[B]_0 = 0$. Rationalize the observed behaviour on the basis of the kinetic parameters.

3. First-Order Parallel Reactions

A **first-order parallel** (irreversible) process and its rate laws are:



where k_1 and k_2 are the **first-order rate constants** for the two processes that occur simultaneously. The **ChemKinetics** software will require you to provide a value for $[A]_0$ (i.e. the **initial concentration** of species "A") and a value for each of the rate constants k_1 and k_2 . It will require that $[B]_0$ (i.e. the **initial concentration** of species "B") is **zero** and will calculate as functions of time: [A], [B] and [C]. Upon data transfer, values of [A], [B], and [C] will appear respectively in Columns 2 to 4 of the spreadsheet and time values, t (s), will appear in Column 1.

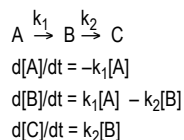
Exercise 3

- 3.1 Use **ChemKinetics** to examine first-order parallel kinetics for a process where: $[A]_0 = 0.50 \text{ M}$, $[B]_0 = 0 \text{ M}$, $k_1 = 0.30 \text{ s}^{-1}$ and $k_2 = 0.10 \text{ s}^{-1}$. Set the following values: $\Delta t = 0.25 \text{ s}$ and $t_{\text{max}} = 10.0 \text{ s}$.
- 3.2 Transfer the data generated in the previous step to a spreadsheet.
- 3.3 Plot on the same set of axes [A], [B] and [C] versus time for a first-order parallel process where the initial concentrations of "B" and "C" are zero (i.e. $[B]_0 = 0$ and $[C]_0 = 0$). Indicate on the plot $[A]_0$ (i.e. the initial concentration of species "A"), [A], [B] and [C] as well as any asymptotic behaviour of the curves, carefully estimating the values of all asymptotes and noting these on the plot.
- 3.4 Show that for a first-order parallel process in which $[B]_0 = 0$ and $[C]_0 = 0$ then $[B]_{\infty} = [A]_0 k_1 / (k_1 + k_2)$, $[C]_{\infty} = k_2 [A]_0 / (k_1 + k_2)$ where $[A]_{\infty}$ and $[B]_{\infty}$ are the respective concentrations of species "A" and "B" at $t = \infty$ (i.e. at equilibrium) and k_1 and k_2 are the respective rate constants for the reactions $A \rightarrow B$ and $A \rightarrow C$.
- 3.5 Compare the estimated values of the asymptotes obtained from the plot generated in Step 3.3 of this exercise with those calculated using the equations given in Step 3.4 above.
- 3.6 Return to **ChemKinetics** and set $k_1 = 0.10 \text{ s}^{-1}$, $k_2 = 0.30 \text{ s}^{-1}$. Do not change the settings $[A]_0 = 0.50 \text{ M}$, $[B]_0 = 0 \text{ M}$, $\Delta t = 0.25 \text{ s}$ and $t_{\text{max}} = 10.0 \text{ s}$.
- 3.7 Plot on the same set of axes [A], [B] and [C] versus time for a first-order parallel process obtained under conditions where $k_1 < k_2$, $[B]_0 = 0$ and $[C]_0 = 0$. Compare this plot with that obtained in Step 3.3 and explain any similarities or differences on the basis of the relative magnitudes of the rate constants.
- 3.8 What determines the ratio $[B]_{\infty}/[C]_{\infty}$ in a first-order parallel process? In what way is this situation similar to the case of a first-order reversible reaction?
- 3.9 Return to **ChemKinetics** and set $k_1 = 0.30 \text{ s}^{-1}$, $k_2 = 0.01 \text{ s}^{-1}$. Do not change the settings $[A]_0 = 0.50 \text{ M}$, $[B]_0 = 0 \text{ M}$, $\Delta t = 0.25 \text{ s}$ and $t_{\text{max}} = 10.0 \text{ s}$.

- 3.10 Plot on the same set of axes [A], [B] and [C] versus time for a first-order parallel process obtained under the conditions where $k_1 \gg k_2$. Again, rationalize the observed behaviour on the basis of the kinetic parameters.

4. First-Order Consecutive Reactions

A **first-order consecutive** process and corresponding rate laws are:



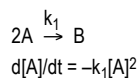
where k_1 and k_2 are the **first-order rate constants** for the two consecutive processes. The **ChemKinetics** software will require a value for $[\text{A}]_0$ (i.e. the **initial concentration** of species "A") and a value for each rate constant, k_1 and k_2 . It will require that $[\text{B}]_0$ (i.e. the **initial concentration** of species "B") is **zero** and will calculate as functions of time: [A], [B] and [C]. Upon data transfer, values of [A], [B], and [C] will appear respectively in Columns 2 to 4 of the spreadsheet and time values, t (s), will appear in Column 1.

Exercise 4

- 4.1 Use **ChemKinetics** to examine first-order consecutive kinetics for a process where: $[\text{A}]_0 = 0.50 \text{ M}$, $[\text{B}]_0 = 0 \text{ M}$, $k_1 = 0.30 \text{ s}^{-1}$ and $k_2 = 0.10 \text{ s}^{-1}$. Set the following values: $\Delta t = 0.5 \text{ s}$ and $t_{\text{max}} = 50.0 \text{ s}$.
- 4.2 Transfer the data generated in the previous step to a spreadsheet.
- 4.3 Plot on the same set of axes [A], [B] and [C] versus time for a first-order consecutive process where the initial concentration of species "B" and "C" is zero (i.e. $[\text{B}]_0 = 0$ and $[\text{C}]_0 = 0$). Indicate on the plot $[\text{A}]_0$ (i.e. the initial concentration of species "A"), [A], [B] and [C] as well as any asymptotic behaviour of the curves, carefully estimating the values of all asymptotes and noting these on the plot.
- 4.4 Return to **ChemKinetics** and set $k_1 = 0.30 \text{ s}^{-1}$, $k_2 = 100 \text{ s}^{-1}$. Do not change the settings $[\text{A}]_0 = 0.50 \text{ M}$, $[\text{B}]_0 = 0 \text{ M}$ but adjust $\Delta t = 0.25 \text{ s}$ and $t_{\text{max}} = 20.0 \text{ s}$.
- 4.5 Plot on the same set of axes [A], [B] and [C] versus time for a first-order consecutive process obtained under the conditions where $k_1 \ll k_2$, $[\text{B}]_0 = 0$ and $[\text{C}]_0 = 0$. Fully label this plot and compare it with the plot obtained in Step 1.3 of Exercise 1. Briefly explain any similarities or differences between the two plots on the basis of the relative magnitudes of the rate constants.
- 4.6 Derive an equation for [C] as a function of time for a first-order consecutive process where $k_1 \ll k_2$, $[\text{B}]_0 = 0$ and $[\text{C}]_0 = 0$. Thus rationalize the behaviour observed in Step 4.5 above.
- 4.7 Return to **ChemKinetics** and set $k_1 = 100 \text{ s}^{-1}$, $k_2 = 0.30 \text{ s}^{-1}$. Do not change the settings $[\text{A}]_0 = 0.50 \text{ M}$, $[\text{B}]_0 = 0 \text{ M}$, $\Delta t = 0.25 \text{ s}$ and $t_{\text{max}} = 20.0 \text{ s}$.
- 4.8 Plot on the same set of axes [A], [B] and [C] versus time for a first-order consecutive process obtained under the conditions where $k_1 \gg k_2$, $[\text{B}]_0 = 0$ and $[\text{C}]_0 = 0$. Fully label and compare this plot with the plot obtained in Step 1.3 of Exercise 1. Briefly explain any similarities or differences on the basis of the relative magnitudes of the rate constants.
- 4.9 Derive an equation for [C] as a function of time for a first-order consecutive process where $k_1 \gg k_2$, $[\text{B}]_0 = 0$ and $[\text{C}]_0 = 0$. Thus rationalize the behaviour observed in Step 4.8 above.

5. Simple Second-Order Irreversible Reaction

The **simple second-order irreversible** process and the corresponding rate law are:



There exists a 2:1 stoichiometry between the reactant and product. The time-dependencies of the concentration of species "A" and "B" are:

$$1/[A] = 1/[A]_0 + k_1 t$$
$$[B] = \frac{1}{2}([A]_0 - [A])$$

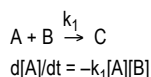
where k_1 is the **second-order rate constant**, $[A]_0$ is the **initial concentration** of species "A" and the **initial concentration** of species "B" is **zero**. To study the reaction kinetics **ChemKinetics** will require a value for $[A]_0$ and a value for k_1 . It will calculate as functions of time: $[A]$, $[B]$, $f(a) = 1/[A]$ and $f(b) = 2[B]/([A]_0([A]_0 - 2[B]))$. Upon data transfer, values of the time, t (s), will appear in Column 1 of the spreadsheet and values of $[A]$, $[B]$, $f(a)$ and $f(b)$ will appear respectively in Columns 2 to 5 of the spreadsheet.

Exercise 5

- 5.1 Use **ChemKinetics** to examine simple second-order irreversible kinetics for a reaction where: $[A]_0 = 0.50$ M, $[B]_0 = 0$ M, $k_1 = 0.30$ s⁻¹. Set the following values: $\Delta t = 2.0$ s and $t_{\max} = 200.0$ s.
- 5.2 Transfer the data generated in the previous step to a spreadsheet.
- 5.3 Plot on the same set of axes $[A]$ and $[B]$ versus time for a simple second-order irreversible process where the initial concentration of species "B" is zero. Indicate on the plot $[A]_0$ (i.e. the initial concentration of species "A"), $[A]$ and $[B]$ as well as any asymptotic behaviour of the curves, carefully estimating the values of all asymptotes and noting these on the plot. Refer to the plot and rationalize the observed final concentration of species "B" in terms of the initial concentration of species "A".
- 5.4 How is the rate at which the concentration of "A" decreases related to the rate at which the concentration of "B" increases for a simple second-order irreversible reaction?
- 5.5 Plot on the same set of axes $f(a)$ and $f(b)$ versus time. Determine the straight lines of best fit through the data using a linear regression analysis in each case. Write down the equations of the lines of best fit and confirm that, in each case, the gradient of the line is related to the second-order rate constant.
- 5.6 Show that $f(a) - f(b) = 1/[A]_0$ and hence comment on whether or not the choice of following the "disappearance" of reactant "A" or the "appearance" of product "B", in theory, is important when analysing the kinetics of simple second-order irreversible reactions.

6. General Second-Order Irreversible Reaction

The **general second-order irreversible** process and the corresponding rate law are:



where k_1 is the **second-order rate constant**. To study the reaction kinetics **ChemKinetics** will require values for $[A]_0$ and $[B]_0$ (i.e. the **initial concentrations** of species "A" and "B" respectively) and a value for k_1 . The program will calculate as functions of time: $[A]$, $[B]$, $[C]$, $f(a) = \ln([A])$ and the following function:

$$f(c) = \frac{1}{[A]_0 - [B]_0} \ln \left\{ \frac{[B]_0([A]_0 - [C])}{[A]_0([B]_0 - [C])} \right\}$$

Upon data transfer, values of the time, t (s), will appear in Column 1 of the spread-sheet and values of $[A]$, $[B]$, $[C]$, $f(a)$ and $f(c)$ will appear respectively in Columns 2 to 6 of the spreadsheet.

Exercise 6

- 6.1 Use **ChemKinetics** to examine simple second-order irreversible kinetics for a reaction where: $[A]_0 = 0.50$ M, $[B]_0 = 0.40$ M, $k_1 = 0.30$ M⁻¹ s⁻¹. Set the values: $\Delta t = 1.0$ s and $t_{\max} = 100.0$ s.
- 6.2 Transfer the data generated in the previous step to a spreadsheet.
- 6.3 Plot on the same set of axes $[A]$, $[B]$ and $[C]$ versus time for a general second-order irreversible process. Indicate on the plot $[A]_0$ and $[B]_0$ (i.e. the initial concentration of species "A" and "B" respectively), as well as $[A]$, $[B]$ and $[C]$. Also indicate any asymptotic behaviour of the curves, carefully estimating the values of all asymptotes and noting these on the plot.
- 6.4 Refer to the plot generated in Step 6.3 of this exercise and rationalize the observed final concentration of each species in terms of the initial concentrations of species "A" and "B".
- 6.5 Plot $f(c)$ versus time and determine the gradient of the line of best fit that passes through the data. Compare the numerical value of the gradient with that of the second-order rate constant and comment on the result.
- 6.6 Plot $f(a)$ for the general second-order irreversible reaction where $[A]_0 = 0.50$ M and $[B]_0 = 0.40$ M (i.e. the initial concentrations of species "A" and "B" are comparable in magnitude). Comment on the shape of this curve, explaining whether or not it would be expected to be linear.
- 6.7 Return to **ChemKinetics** and set $[A]_0 = 0.40$ M, $[B]_0 = 0.50$ M. Do not change the settings $k_1 = 0.30$ M⁻¹ s⁻¹, $\Delta t = 1.0$ s and $t_{\max} = 100.0$ s.
- 6.8 Repeat Step 6.3 in this exercise this time using the settings that were used in Step 6.7 above. Rationalize the observed final concentrations of each species in terms of the initial concentrations of species "A" and "B".
- 6.9 Starting with the integrated rate law for a second-order irreversible reaction in which the initial concentration of species "C" is zero, show that the concentration of product "C" at any time, t , in the process is given by:
- $$[C] = \frac{[A]_0[B]_0\{e^{([A]_0 - [B]_0)k_1t} - 1\}}{[A]_0e^{([A]_0 - [B]_0)k_1t} - [B]_0}$$
- 6.10 Return to **ChemKinetics** and set $[A]_0 = 0.01$ M, $[B]_0 = 0.40$ M. Do not change the settings $k_1 = 0.30$ M⁻¹ s⁻¹, $\Delta t = 1.0$ s and $t_{\max} = 100.0$ s.
- 6.11 Does the integrated rate equation for a general second-order irreversible reaction apply to the case where: (i) $[A]_0 < [B]_0$ and (ii) $[A]_0 = [B]_0$? Explain.
- 6.12 Plot $f(a)$ versus time for the general second-order reaction where $[A]_0 = 0.01$ M, $[B]_0 = 0.40$ M (i.e. $[B]_0 \gg [A]_0$) and determine the gradient of the line of best fit that passes through the data.
- 6.13 Compare the numerical value of the gradient of the plot in Step 6.12 with the product of the second-order rate constant that was set in Step 6.10 of this exercise and $[B]_0$, the initial concentration of species "B". Comment on the result.

Observations

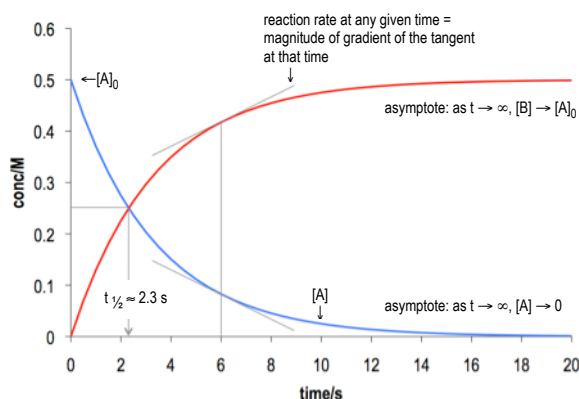
Observations – Exercise 1

A plot of [A] and [B] versus time requested in Step 1.3 of Exercise 1 is shown.

If a 1:1 mole ratio exists between species "A" and "B" then for an irreversible reaction "A" is completely converted to "B" and so $[A]_{\infty} = 0$ and $[B]_{\infty} = [A]_0$.

From the plot, the estimated half-life of the reaction is ca. 2.3 s. This compares favourably with the theoretical value: $t_{1/2} = \ln(2)/k_1 = \ln(2)/0.3 = 2.31$ s.

The asymptotic behaviour is shown in the plot and the rate of the reaction at any selected time can be found from the tangent. At $t = \infty$, $d[A]/dt = d[B]/dt = 0$.



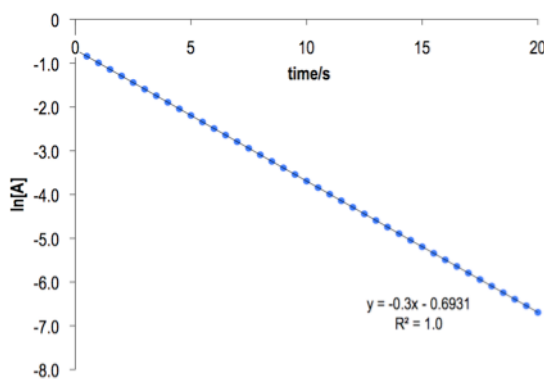
Observations – Exercise 1 cont'd

A plot of $\ln f(a)$ versus time requested in Step 1.6 of Exercise 1 is shown.

The gradient of this plot is -0.3 s^{-1} and its magnitude corresponds precisely with that of the rate constant set in the exercise. Thus the rate constant for a first-order irreversible reaction is equal to minus one times the gradient of a plot of $\ln([A])$ versus time.

Since $f(a) = f(b)$ for a first-order irreversible reaction then it doesn't matter whether one follows either the "disappearance" of species "A" or the "appearance" of species "B" when analysing the kinetics.

Experimentally, it might be easier to follow one rather than the other (e.g. if one of the species is coloured).



Observations – Exercise 2

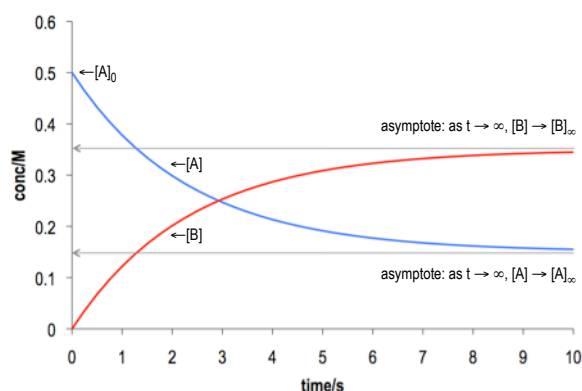
A plot of [A] and [B] versus time requested in Step 2.3 of Exercise 2 is shown.

The following estimates of the asymptotes can be made from the plot:

$$[A]_{\infty} \approx 0.15 \text{ M}$$

$$[B]_{\infty} \approx 0.35 \text{ M}$$

The above values were obtained upon estimating the respective positions of the asymptotes and then extrapolating the asymptotes to the points at which these intersect the vertical axis.



Observations – Exercise 2 cont'd

For a first-order reversible reaction in which the initial concentration of species "B" is zero:

$$[A] = \frac{k_{-1}[A]_0}{(k_1 + k_{-1})} \left[1 + \frac{k_1}{k_{-1}} e^{-(k_1 + k_{-1})t} \right] \quad \text{Hence as } t \rightarrow \infty, [A] \rightarrow [A]_{\infty} = k_{-1}[A]_0 / (k_1 + k_{-1}).$$

Similarly,

$$[B] = \frac{k_1[A]_0}{(k_1 + k_{-1})} \left[1 - e^{-(k_1 + k_{-1})t} \right] \quad \text{Hence as } t \rightarrow \infty, [B] \rightarrow [B]_{\infty} = k_1[A]_0 / (k_1 + k_{-1}).$$

$$k_1[A]_0/[B]_{\infty} = k_1[A]_0 / (k_1 + k_{-1}) / k_{-1}[A]_0 = k_1 + k_{-1}$$

The equilibrium constant, $K = [B]_{\infty}/[A]_{\infty} = k_1/k_{-1}$. A value of K can be estimated from the plot generated in Step 2.3 of this exercise in which case $K = [B]_{\infty}/[A]_{\infty} \approx 0.35/0.15 = 2.333$. The latter result compares favourably with the theoretical value of K obtained from the ratio of the rate constants that were set in the exercise, $K = k_1/k_{-1} = 0.30/0.129 = 2.325$.

Observations – Exercise 2 cont'd

Since $[A]_0 = [A] + [B] = [A]_{\infty} + [B]_{\infty}$

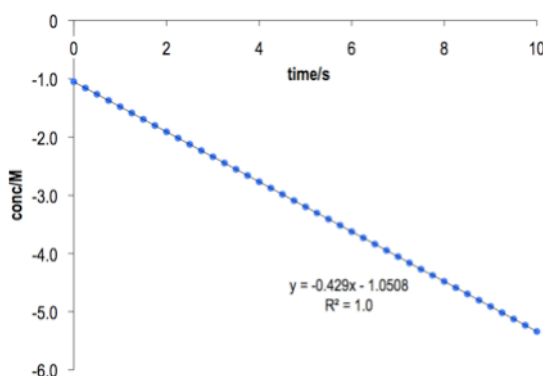
$$\Rightarrow [A] - [A]_{\infty} = [B]_{\infty} - [B]$$

$$\Rightarrow f(a) = f(b).$$

A plot of $f(a)$ versus time requested in Step 2.7 of Exercise 2 is shown. The gradient of this plot obtained from a linear regression analysis is -0.429 s^{-1} .

$$\begin{aligned} \text{Now: } k_1 + k_{-1} &= 0.300 + 0.129 = 0.429 \\ &= -1 \times \text{gradient of } f(a) \text{ versus time plot} \end{aligned}$$

Thus for a first-order reversible process, the magnitude of the gradient of the $f(a)$ versus time plot is equal to the sum of the rate constants for the forward and reverse processes.



Observations – Exercise 2 cont'd

Chemical kinetics is an experimental discipline that enables rate constants, equilibrium constants, etc., to be obtained from laboratory measurements. It is important to understand how kinetics measurements can be used to calculate parameters of interest. Recall:

$$\begin{aligned} k_1 + k_{-1} &= k_1[A]_0/[B]_{\infty} \\ &= -1 \times \text{gradient of } f(a) \text{ versus time plot} \end{aligned}$$

The previous equalities can be used to determine k_1 and k_{-1} separately. In particular:

$$k_1 = -1 \times \text{gradient of } f(a) \text{ versus time plot} \times [B]_{\infty}/[A]_0$$

The gradient is determined directly from the experimentally derived plot. The value of $[B]_{\infty}$ is obtained by monitoring the concentration of "B" (or indeed "A") for a sufficiently long time during the experiment and the value of $[A]_0$ is set as an experimentally (known) variable. Thus:

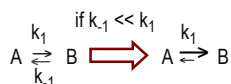
$$\begin{aligned} k_1 &= -1 \times (-0.429) \times 0.35/0.5 = 0.300 \text{ s}^{-1} \\ k_{-1} &= 0.429 - 0.300 = 0.129 \text{ s}^{-1} \end{aligned}$$

These calculated values of the rate constants compare favourably with those originally set for the purposes of the exercise.

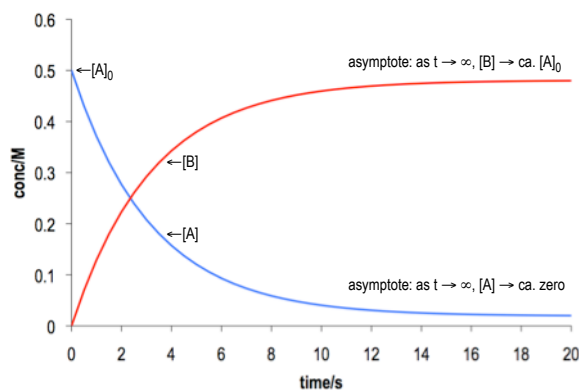
Observations – Exercise 2 cont'd

A plot of [A] and [B] versus time requested in Step 2.10 of Exercise 2 is shown.

In this case $k_{-1} \ll k_1$ and so the reaction can be represented as follows:



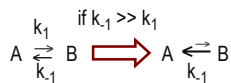
Thus the kinetics approximate to a *first-order irreversible* reaction that has a rate constant of k_1 . The plot is very similar to that obtained in Step 1.3 of Exercise 1.



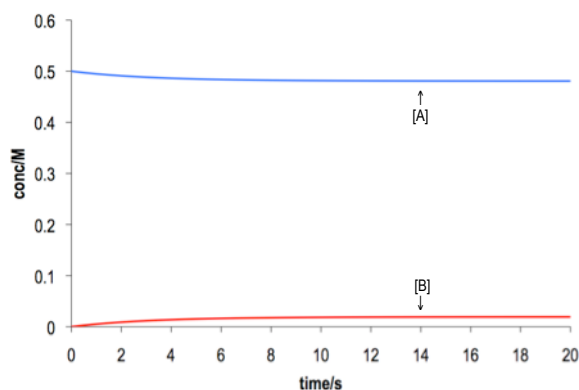
Observations – Exercise 2 cont'd

A plot of [A] and [B] versus time requested in Step 2.12 of Exercise 2 is shown.

In this case $k_{-1} \gg k_1$ and so the reaction can be represented as follows:



The equilibrium constant, $K = k_1/k_{-1} \ll 1$ and the reverse reaction predominates. The reaction does not progress far towards the formation of product, "B" and this can be clearly seen in the plots of concentration versus time.



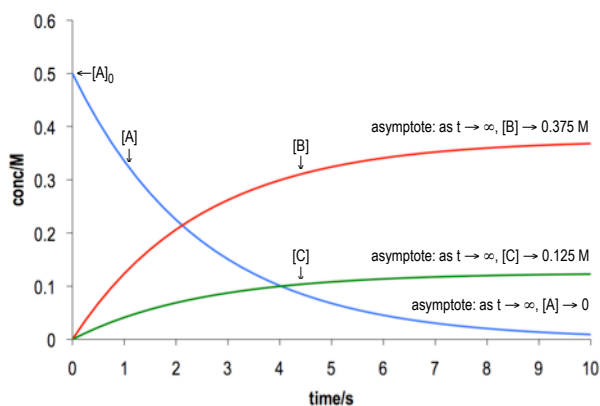
Observations – Exercise 3

A plot of [A], [B] and [C] versus time as requested in Step 3.3 of Exercise 3 is shown.

The following estimates can be made from the plot:

$$\begin{aligned} [A]_{\infty} &\approx 0 \text{ M} \\ [B]_{\infty} &\approx 0.375 \text{ M} \\ [C]_{\infty} &\approx 0.125 \text{ M} \end{aligned}$$

The above values were obtained upon estimating the respective positions of the asymptotes and then extrapolating the asymptotes to the points at which these intersect the vertical axis.



Observations – Exercise 3 cont'd

For a first-order parallel process where the initial concentrations of species "B" and "C" are both zero:

$$[A] = [A]_0 e^{-(k_1 + k_2)t}$$

$$[B] = \frac{k_1[A]_0}{(k_1 + k_2)} [1 - e^{-(k_1 + k_2)t}] \quad \text{Hence when } t = \infty, [B]_{\infty} = k_1[A]_0/(k_1 + k_2).$$

$$[C] = \frac{k_2[A]_0}{(k_1 + k_2)} [1 - e^{-(k_1 + k_2)t}] \quad \text{Hence when } t = \infty, [C]_{\infty} = k_2[A]_0/(k_1 + k_2).$$

Using the above equations and the values of the experimental parameters set in Step 3.1 of this exercise the following results are obtained:

$$[B]_{\infty} = (0.3 \times 0.5)/(0.3 + 0.1) = 0.375 \text{ M}$$

$$[C]_{\infty} = (0.1 \times 0.5)/(0.3 + 0.1) = 0.125 \text{ M}$$

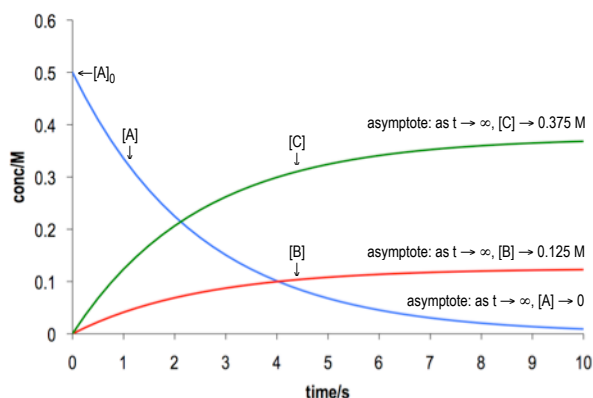
These results compare favourably with the respective estimates of the asymptotes that were made in Step 3.3.

Observations – Exercise 3 cont'd

A plot of [A], [B] and [C] versus time as requested in Step 3.7 of Exercise 3 is shown.

These curves are analogous to those obtained in Step 3.3 except in this case species "B" and "C" are interchanged.

This can be rationalized by recognising that in the case of a first-order parallel process the observed order in which the kinetic profiles appear on the plot simply depends on the arbitrary designation of the two species "B" and "C".



Observations – Exercise 3 cont'd

The ratio $[B]_{\infty}/[C]_{\infty}$ is determined by the ratio of the rate constants k_1 and k_2 . Recall from Step 3.4 of Exercise 3 the following:

$$[B]_{\infty} = k_1[A]_0/(k_1 + k_2) \text{ and } [C]_{\infty} = k_2[A]_0/(k_1 + k_2)$$

Thus for a first-order *parallel* process:

$$[B]_{\infty}/[C]_{\infty} = k_1/k_2$$

This result indicates that the ratio of the rate constants directly determines the final concentration ratio. This can be compared to the case of a *first-order reversible* reaction (see Steps 2.3 to 2.5 of Exercise 2) where:

$$[A]_{\infty} = k_{-1}[A]_0/(k_1 + k_{-1}) \text{ and } [B]_{\infty} = k_1[A]_0/(k_1 + k_{-1})$$

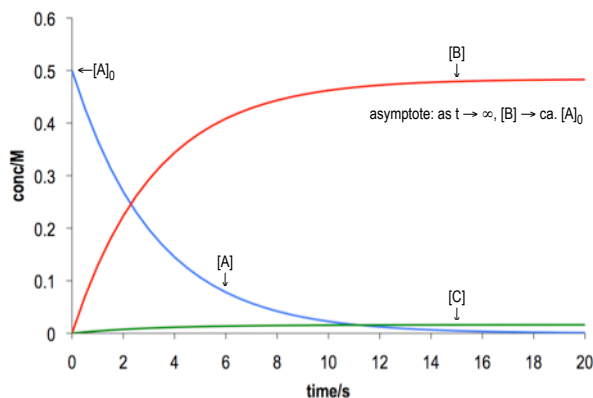
In the case of a *first-order reversible* reaction $[B]_{\infty}/[A]_{\infty} = k_1/k_{-1}$ and again the ratio of the rate constants determines the final ratio of the concentrations.

Observations – Exercise 3 cont'd

A plot of [A], [B] and [C] versus time that was requested in Step 3.10 of Exercise 3 is shown.

This is a case of a first-order parallel process where $k_1 \gg k_2$. The competition between the reactions that produce "B" and "C" is such that there is little "C" produced because "B" is formed much more quickly.

These conditions approximate those of a *first-order irreversible* reaction. Hence this plot is similar to that obtained in Step 1.3 of Exercise 1.



Observations – Exercise 4

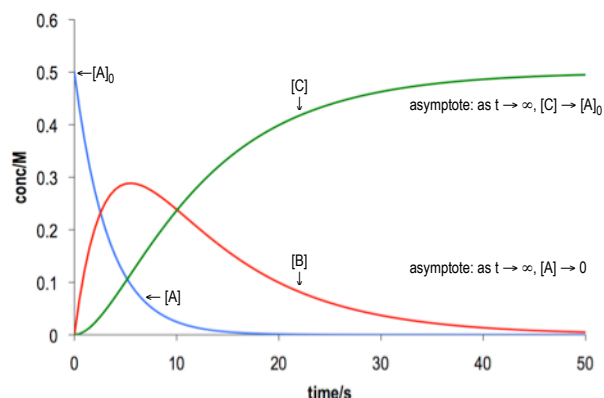
A plot of [A], [B] and [C] versus time as requested in Step 4.3 of Exercise 4 is shown.

The asymptotes are indicated on the plot and are expected, given the theoretical equations describing [A], [B] and [C] as functions of time for a first-order consecutive process:

$$[A] = [A]_0 e^{-k_1 t}$$

$$[B] = \frac{k_1 [A]_0 (e^{-k_1 t} - e^{-k_2 t})}{(k_2 - k_1)}$$

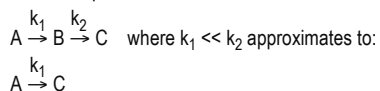
$$[C] = [A]_0 \left[1 - \frac{k_2 e^{-k_1 t}}{k_2 - k_1} + \frac{k_1 e^{-k_2 t}}{k_2 - k_1} \right]$$



Observations – Exercise 4 cont'd

A plot of [A], [B] and [C] versus time as requested in Step 4.5 of Exercise 4 is shown.

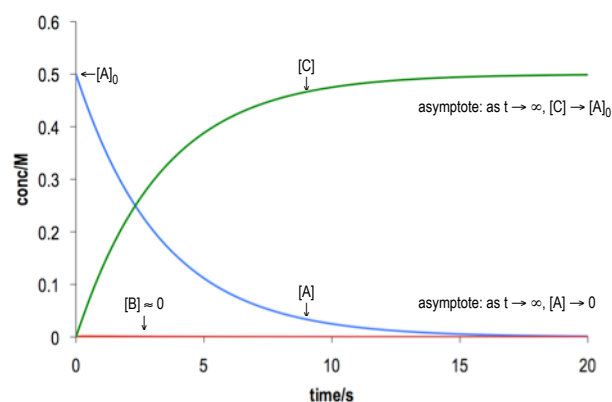
The plot is very similar to than obtained in Step 1.3 of Exercise 1. In particular:



Thus one would expect to observe a kinetic profile similar to a *first-order irreversible* reaction. Recall:

$$[C] = [A]_0 \left[1 - \frac{k_2 e^{-k_1 t}}{k_2 - k_1} + \frac{k_1 e^{-k_2 t}}{k_2 - k_1} \right]$$

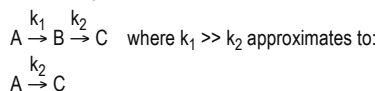
$$\Rightarrow [C] \approx [A]_0 (1 - e^{-k_1 t}) \text{ for } k_2 \gg k_1$$



Observations – Exercise 4 cont'd

A plot of [A], [B] and [C] versus time as requested in Step 4.8 of Exercise 4 is shown.

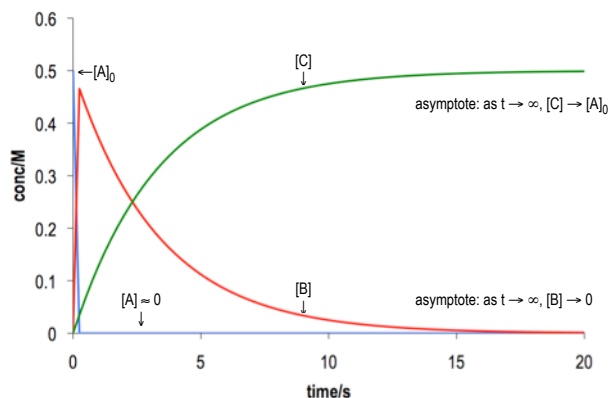
The plot is very similar to than obtained in Step 1.3 of Exercise 1. In particular:



Thus one would expect to observe a kinetic profile similar to a *first-order irreversible* reaction. Recall:

$$[C] = [A]_0 \left[1 - \frac{k_2 e^{-k_1 t}}{k_2 - k_1} + \frac{k_1 e^{-k_2 t}}{k_2 - k_1} \right]$$

$$\Rightarrow [C] \approx [A]_0 (1 - e^{-k_2 t}) \text{ for } k_1 \gg k_2$$



Observations – Exercise 5

A plot of [A] and [B] versus time requested in Step 5.3 of Exercise 5 is shown.

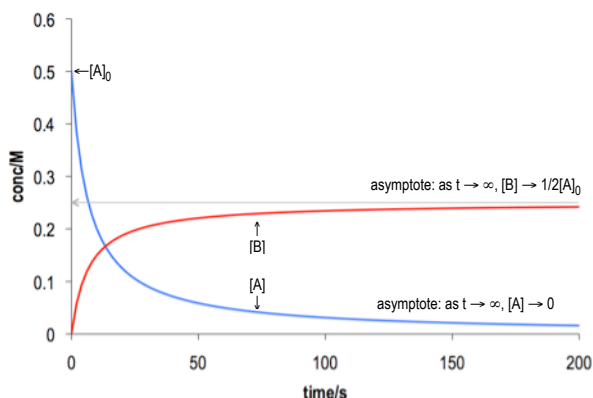
The asymptotes are clearly indicated on the plot.

Since $2A \rightarrow B$ then:

$$[B]_{\infty} = \frac{1}{2}[A]_0 = 0.25 \text{ M in this case}$$

$$d[B]/dt = -\frac{1}{2}d[A]/dt$$

The latter implies that throughout the reaction the concentration of species "B" increases at half the rate at which the concentration of species "A" decreases.



Observations – Exercise 5 cont'd

A plot of f(a) and f(b) versus time requested in Step 5.5 of Exercise 5 is shown.

Recall:

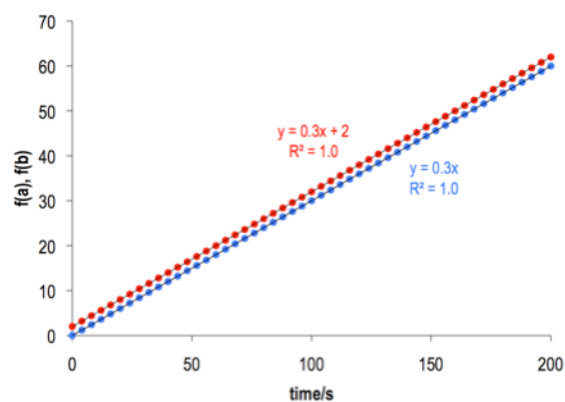
$$f(a) = 1/[A]$$

$$f(b) = 2[B]/([A]_0([A]_0 - 2[B]))$$

From the gradients obtained in the regression analyses it is clear that:

$$df(a)/dt = df(b)/dt = 0.30 \text{ M}^{-1} \text{ s}^{-1} \text{ (in this case) } = k_1$$

Thus for a simple second-order irreversible process, the gradient of the f(a) or f(b) versus time plot is equal to the second-order rate constant for the process.



Observations – Exercise 5 cont'd

Recall that for the simple second-order irreversible process being studied $f(b)$ is defined as follows:

$$f(b) = \frac{2[B]}{[A]_0([A]_0 - 2[B])} = \frac{X}{[A]_0} + \frac{Y}{[A]_0 - 2[B]}$$

$$\Rightarrow X([A]_0 - 2[B]) + Y[A]_0 = 2[B]$$

Equating coefficients of $[A]_0$ and $[B]$: $X + Y = 0$; $-2X = 2$ and so $X = -1$, $Y = +1$

$$\Rightarrow f(b) = -1/[A]_0 + 1/([A]_0 - 2[B]) = -1/[A]_0 + f(a) \text{ since } [A] = [A]_0 - 2[B] \text{ and } f(a) = 1/[A]$$

$$\Rightarrow f(a) - f(b) = 1/[A]_0$$

Since $f(a)$ and $f(b)$ differ by a constant then one can use either of these functions to analyse the kinetics of a second-order irreversible reaction. The use of $f(a)$ will involve monitoring the "disappearance" of reactant "A" with time whereas the use of $f(b)$ involves monitoring the "appearance" of product, "B". Experimentally, it may be easier to follow one rather than the other (see also Step 1.7 in Exercise 1).

Observations – Exercise 6

A plot of $[A]$, $[B]$ and $[C]$ versus time as requested in Step 6.3 of Exercise 6 is shown.

The asymptotes are indicated on the plot.

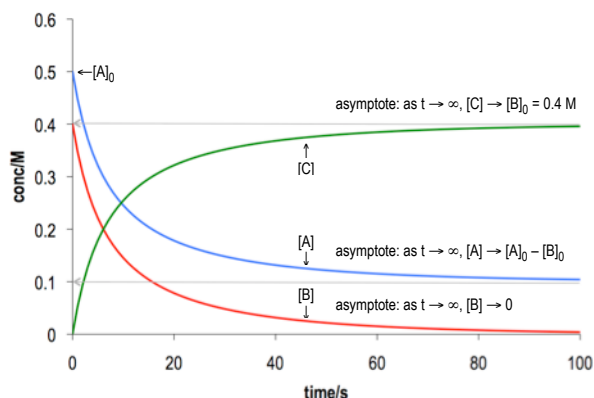
Since $1 \text{ mol A} + 1 \text{ mol B} \rightarrow 1 \text{ mol C}$, and B is the limiting reagent, then for the current case:

$$[A]_{\infty} = [A]_0 - [B]_0 = 0.1 \text{ M}$$

$$[B]_{\infty} = 0$$

$$[C]_{\infty} = [B]_0 = 0.4 \text{ M in this case}$$

The stoichiometry that exists amongst species "A", "B" and "C" implies that the concentration of species "C" increases at the same rate at which the concentration of species "A" and "B" decreases.



Observations – Exercise 6 cont'd

A plot of $f(c)$ versus time requested in Step 6.5 of Exercise 6 is shown.

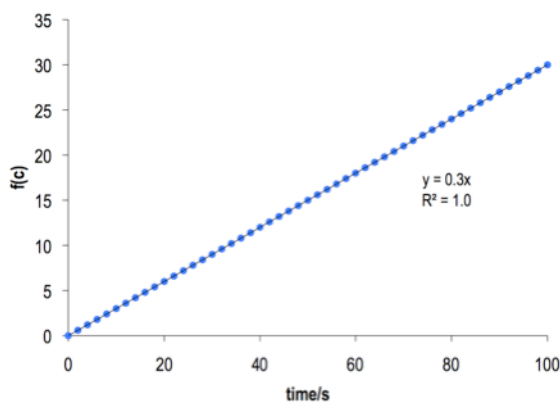
Recall:

$$f(c) = \frac{1}{[A]_0 - [B]_0} \ln \left\{ \frac{[B]_0([A]_0 - [C])}{[A]_0([B]_0 - [C])} \right\}$$

From the gradient obtained in the regression analysis it is clear that:

$$df(c)/dt = 0.30 \text{ M}^{-1} \text{ s}^{-1} \text{ (in this case)} = k_1$$

Thus for a general second-order irreversible process, the gradient of the $f(c)$ versus time plot is equal to the second-order rate constant for the process.

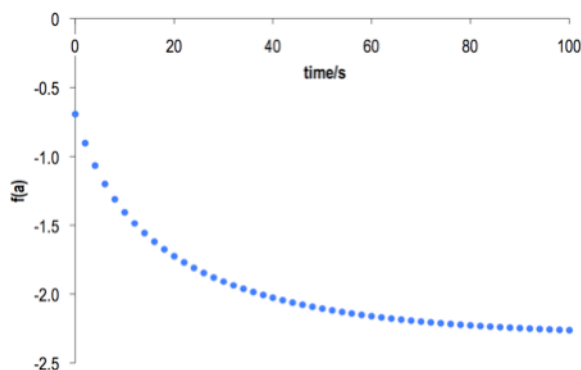


Observations – Exercise 6 cont'd

A plot of $f(a)$ versus time requested in Step 6.6 of Exercise 6 is shown.

Clearly, this plot is not linear. A plot of $f(a)$ versus time for a general second-order irreversible reaction will only be linear if the concentrations of one of the reactants is significantly greater than the concentration of the other one. In this way the concentration of the reactant present at higher concentration remains effectively constant throughout the reaction and pseudo first-order conditions are said to occur.

Since $[A]_0 \approx [B]_0$ in this case the above condition is not met and the plot is not linear.



Observations – Exercise 6 cont'd

The integrated rate law for a general second-order irreversible reaction (initial concentration of species "C" is zero) is as follows:

$$k_1 t ([A]_0 - [B]_0) = \ln \left\{ \frac{[B]_0([A]_0 - [C])}{[A]_0([B]_0 - [C])} \right\}$$

$$\Rightarrow [A]_0([B]_0 - [C])e^{([A]_0 - [B]_0)k_1 t} = [B]_0([A]_0 - [C])$$

$$\Rightarrow [A]_0[B]_0e^{([A]_0 - [B]_0)k_1 t} - [A]_0[C]e^{([A]_0 - [B]_0)k_1 t} = [A]_0[B]_0 - [B]_0[C]$$

$$\Rightarrow [A]_0[C]e^{([A]_0 - [B]_0)k_1 t} - [B]_0[C] = [A]_0[B]_0e^{([A]_0 - [B]_0)k_1 t} - [A]_0[B]_0$$

$$\Rightarrow [C]\{[A]_0e^{([A]_0 - [B]_0)k_1 t} - [B]_0\} = [A]_0[B]_0\{e^{([A]_0 - [B]_0)k_1 t} - 1\}$$

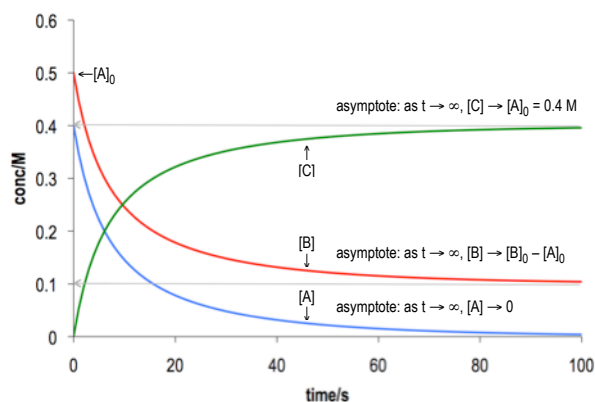
$$\Rightarrow [C] = \frac{[A]_0[B]_0\{e^{([A]_0 - [B]_0)k_1 t} - 1\}}{[A]_0e^{([A]_0 - [B]_0)k_1 t} - [B]_0} \quad \dots \text{as required in Step 6.9 of Exercise 6.}$$

Observations – Exercise 6 cont'd

A plot of $[A]$, $[B]$ and $[C]$ versus time as requested in Step 6.9 of Exercise 6 is shown.

If $[A]_0 < [B]_0$ one obtains an analogous behaviour to the case where $[A]_0 > [B]_0$ (see Step 6.3 of Exercise 6) except that species "A" and "B" are interchanged. Thus from the kinetic point of view it does not matter which of the two species is assigned as "A" and which is "B".

If $[A]_0 = [B]_0$ then the solution to the integrated rate law for the general second-order irreversible reaction is indeterminate. Integrating the simple second-order rate law for an irreversible process is a way to solve systems such as these.



Observations – Exercise 6 cont'd

A plot of $f(a)$ versus time as requested in Step 6.12 of Exercise 6 is shown.

In this case $[B]_0 \gg [A]_0$ and pseudo first-order conditions are met. The pseudo first-order rate constant, k' , is:

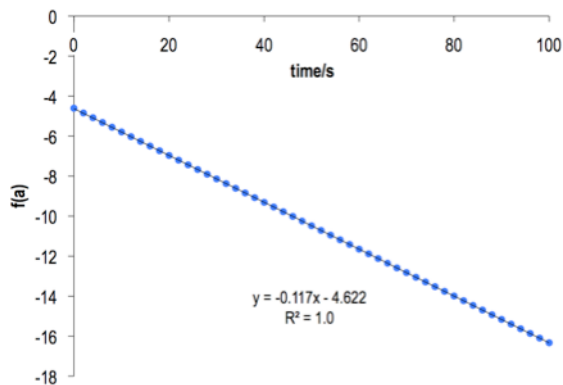
$$k' = -1 \times \text{gradient of } f(a) \text{ versus time plot} \approx k_1[B]_0$$

Thus:

$$-0.117 \approx -k_1 \times 0.4$$

$$\Rightarrow k_1 = 0.117/0.4 = 0.293 \text{ M}^{-1} \text{ s}^{-1}$$

The latter result compares favourably with the value of the second-order rate constant set in Step 6.10 of Exercise 6.



Acknowledgements

SWB is grateful to Dr. Robert A. Craig and Mr. Andrew S. Bigger for their assistance during the development of this project.

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