

*Exploring the Kinetics of
Chemical Reactions
Using Simulations
with STELLA*

Scott A. Sinex
Prince George's Community College



Submitted as part of the BLT Summer Design Institute
at University of Maryland College Park
17-28 July 2000

UNIT TITLE: *Exploring the Kinetics of Chemical Reactions Using Simulations with STELLA*

Unit goal: To introduce the concept of how fast or the speed of a chemical reaction and the factors that influence the speed or rate of a reaction. Simple reaction pathways are investigated initially then multiple pathways including reversible reactions are explored.

Grade Level (K-16): freshman college chemistry
 high school AP chemistry

General Subject Area(s): chemical kinetics

Minimum time required for the unit: 3 weeks

Concepts learned across all unit modules: deriving the rates of a reactions from concentration-time data, determining the rate law or equation for a reaction, and investigating the factors that influence the rate of a reaction. Also examining reversible chemical reactions and the concept of chemical equilibrium

Standards addressed by unit modules:

1. National Science Education Standards for content standards (9-12)
 - " content standard A science as inquiry
 - " content standard B in physical science.
2. Praxis II - chemistry: content knowledge
3. Maryland High School Core Learning Goal -
 - " goal 1 - skills and processes
 - " goal 4 - chemistry
4. National Educational Technology Standards -
 - " standard 3 - Technology productivity tools
 - " standard 5 - Technology research tools

Technology needed in unit modules: graphing calculators (or Excel), STELLA* Modeling software. The actual STELLA models required for each module are included.

* A run-only version of STELLA is available free from High Performance Systems Inc. at <http://www.hps-inc.com>

Technology-enhanced instructional strategies employed:

modeling of data using the graphing calculator or Excel
models and simulations using STELLA

Title of Each Module:

- Module 1 - The Speed of Chemical Reactions
- Module 2 - Investigating the Rate of a Chemical Reaction and the Variables that Influence Rate
- Module 3 - Simulating and Investigating Kinetics with STELLA
- Module 4 - Discovering the Nature of Reversible Chemical Reactions
- Module 5 - Exploring Chemical Equilibrium through Simulations with STELLA
- Module 6 - Kinetics of Consecutive and Competing Reactions with STELLA
- Module 7 - Putting it All Together and Then Some - an Assessment Activity

Unit Culminating Activity: This is done in Module 7 - Putting it All Together and Then Some - an Assessment Activity where a series of questions explore the concepts and models introduced in modules 1 to 6 plus examines a STELLA model simulation of competing equilibria, a situation not covered in the modules but a natural extension of the material.

Unit Author: Scott A. Sinex (Prince George's Community College)
e-mail: sinexsa@pg.cc.md.us

MODULE 1

Module Title: THE SPEED OF CHEMICAL REACTIONS

Estimated time to complete: 1 hour

Module objectives: To observe the speed of a simple reaction and to consider some influences on the speed

Concept(s) learned in this module: rate of reaction and observing factors that influence it

Standards addressed in this module (Praxis, K-12):

1. National Science Education Standards for content standards (9-12) - content standard A science as inquiry and content standard B in physical science.
2. Praxis II - chemistry: content knowledge
3. Maryland High School Core Learning Goal - goal 1 - skills and processes and goal 4 - chemistry

Technology-enhanced instructional strategies utilized in this module: none

Components	Brief description of module activities	Student Grouping*	Materials/ Technology
Engagement	observe the reaction of an Alka-Seltzer in water reaction	small group	Alka-Seltzer tablets, beakers
Exploration	consider how speed of reaction and how reactants and products change during reaction	small group	none
Explanation	following the speed from the fizzing	small group	none
Extension	hot water - cold water speed differences and the crushing of the table	small group	none
Evaluation	examining a graph of data and sketching another	individual	none

*Student grouping: Individual, paired, small group, whole class, etc.

Expected module outcomes: To observe how the speed of a reaction changes with time and some influences on this speed

Performance-based assessment of module outcomes: Examine data for the production of a reaction product and sketch how a reactant changes with time over a reaction.

MODULE 1 - THE SPEED OF CHEMICAL REACTIONS

Engagement

Place an Alka-Seltzer tablet into a container of water. Observe the system carefully until the tablet completely disappears. Describe what you observed.

Exploration

The Alka-Seltzer tablet contains the two solids sodium bicarbonate, NaHCO_3 , and citric acid, $\text{H}_3\text{Citrate}$. The chemical reaction of the Alka-Seltzer tablet in water, where the two solids are soluble, is given below:



How could you tell the reaction was slowing down?

How did the amounts of sodium bicarbonate and citric acid change with time?

Explanation

The reactants, sodium bicarbonate and citric acid, start at a high amount or concentration and decrease in amount as the reaction proceeds. The products, sodium citrate and carbon dioxide, increases in amount as the reaction occurs. The slowing down of the rate of reaction can be seen as the fizzing or production of carbon dioxide gas slows.

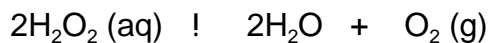
Extension

Place a whole tablet into hot water, how does it compare to results from cool or tap water?

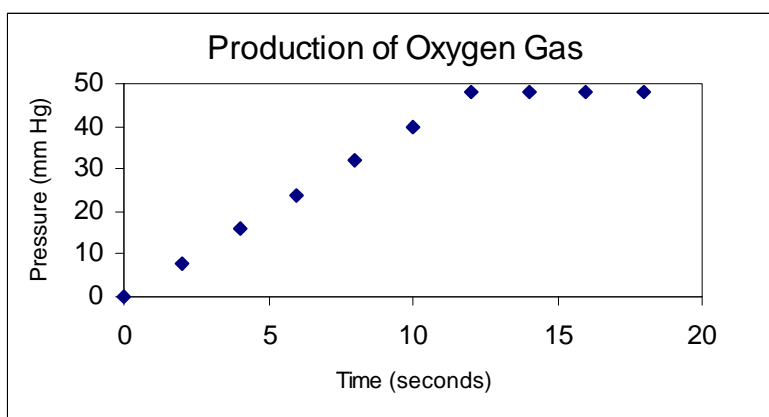
If you crushed an Alka-Seltzer tablet and placed it into water, what would happen compared to a whole tablet? (Try the experiment.)

Evaluation

Consider the graph of the pressure of oxygen gas from the decomposition of hydrogen peroxide and the addition of catalase given below:



Offer an explanation of the rate of reaction based on the graph.



Data from: http://mdk12.org/practices/support_success/hsa/biology/enzyme_activity

Sketch and label the axes a graph showing how the concentration of H_2O_2 would change.



MODULE 2

Module Title: INVESTIGATING THE RATE OF A CHEMICAL REACTION AND THE VARIABLES THAT INFLUENCE RATE

Estimated time to complete: 2-3 hours

Module objectives: Calculate the rate from concentration vs. time data and derive the rate law. Determine the influence of temperature, activation energy, and catalyst on the rate.

Concept(s) learned in this module: determining rate from concentration-time data, how to derive rate law, factors that influence the rate of reaction

Standards addressed in this module (Praxis, K-12):

1. National Science Education Standards for content standards (9-12) - content standard A science as inquiry and content standard B in physical science.
2. Praxis II - chemistry: content knowledge
3. Maryland High School Core Learning Goal - goal 1 - skills and processes and goal 4 - chemistry
4. National Educational Technology Standards - standard 3 - Technology productivity tools and standard 5 - Technology research tools

Technology-enhanced instructional strategies utilized in this module:

modeling of data using the graphing calculator or Excel
models and simulations using STELLA

Components	Brief description of module activities	Student Grouping*	Materials/ Technology
Engagement	questions on how to get horses, cars and computers to go faster	small group	none
Exploration	analysis of concentration-time data, deriving a rate law, and examining factors that influence rate	small group	graphing calculator, STELLA
Explanation	how the rate is influenced by concentration, order, temperature, activation energy, and catalyst	small group	none
Extension	another way to analyze concentration-time data and derive a rate law	small group	graphing calculator

Evaluation	graphical interpretation	Individual	graphing calculator
------------	--------------------------	------------	---------------------

*Student grouping: Individual, paired, small group, whole class, etc.

Expected module outcomes: be able to derive rate law from concentration-time data, understand what factor influence the rate of a reaction

Performance-based assessment of module outcomes: interpret data and graphs of concentration against time

MODULE 2 - INVESTIGATING THE RATE OF A CHEMICAL REACTION AND THE VARIABLES THAT INFLUENCE RATE

Engagement

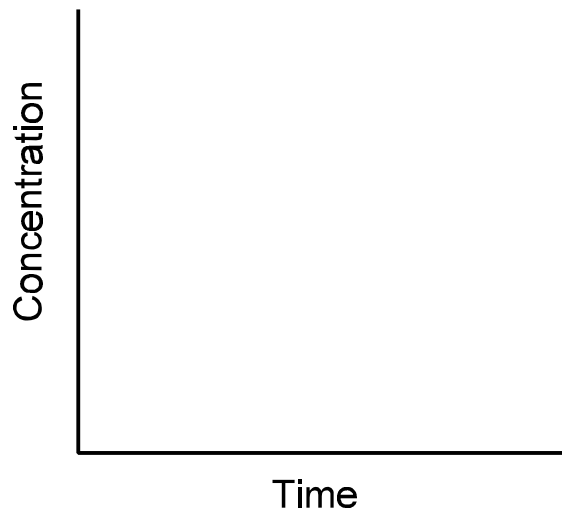
How could you get a horse you were riding to go faster?

How could you get a car you were riding in to go faster?

How could you get a computer to go faster?

How could you get a chemical reaction to go faster? List any factors you think would influence the rate or speed of a chemical reaction?

On a plot of concentration of a starting substance against time, how would you tell the difference between a substance that reacts slowly from one that reacts quickly? Illustrate on the graph.



Exploration

Now let's plot some real data for the first-order rearrangement of methyl isonitrile to methyl nitrile as given by the reaction below:



Plot the data given in the table below, which were collected at 215°C in a one liter vessel.

Time	Concentration of CH ₃ -NC	Concentration of CH ₃ -CN	Sum of A + B
0 ksec	16.5 mM		
2	11.0		
5	5.91		
8	3.14		
12	1.37		
15	0.736		

Sketch the curves for this data on your plot above. How do they agree with your initial sketch?

Now let's calculate the rate of the reaction. This is the slope of a tangent line at a point on the concentration against time curve. We will oversimplify it here by calculating the slope between each pair of data points.

Fill in the columns of the table given below. On the TI-83, use [2nd] [LIST] OPS, then select ΔList to calculate the differences as ΔList (L_n).

Time	Concentration of CH ₃ -NC	Δtime	Δconc.	Δconc/Δtime	average time*	average conc.**
0 ksec	16.5 mM					
2	11.0					
5	5.91					
8	3.14					
12	1.37					
15	0.736					

* Time + Δtime/2

** Conc + Δconc./2

The slope or change in concentration divided by the change in time is the rate at the

average time for the two points used to calculate the slope. What are the units of the rate?

How does the rate vary over time?

The rate is negative because the concentration of the reactant is decreasing over time. For a reactant disappearing we write:

$$-\frac{\Delta \text{conc.}}{\Delta \text{time}} = \text{now a positive number}$$

Plot the rate against average time for the reaction. Sketch and label the graph below.



Does the rate of the reaction depend on the concentration of $\text{CH}_3\text{-NC}$? Explain why or why not.

As the concentration of $\text{CH}_3\text{-NC}$ decreases, the rate of the disappearance of $\text{CH}_3\text{-NC}$ decreases as well.

Let's explore the relationship between rate and concentration. Plot a graph of rate against concentration. Sketch and label the graph axes below.



What type of relationship is their between rate and concentration? Perform an appropriate regression.

The slope of the linear relationship between rate and concentration is the rate constant, k , for this first-order reaction. Write an equation in terms of the variables. This is the

rate law for this reaction.

What are the units of the rate constant, k?

An alternate method of calculation is given as an extension of this module.

The order of reaction has to do with the power of the concentration term(s) in the rate law:

$$\text{Rate} = k(X)^n$$

where (X) is the concentration of X and n is the power or order. For n =1, the reaction is first order. We will explore the effect of order or the value of n shortly.

To ignite the natural gas on your stove or gas furnace, what has to happen?



The speed or the rate of a chemical reaction is influenced by a number of variables. What might some of these variables be? List some possible influences on the rate of a reaction.

Let's explore the variation of the initial rate of reaction using a STELLA model. The initial rate is the rate at the start of the reaction, when the initial concentration essentially still holds. Like a horse race, the initial rate is the rate of reaction just out of the starting gate. Call up the model "Temp_Ea_Rate" on the computer. We will examine the influence of three variables: concentration and order, activation energy (the kick to get the reaction started), and temperature. For each variable you will need to vary the variable over the total range - set it low and move it in five intervals to the high end or vice versa. Do this one variable at a time, while setting the other variables to their typical value - click on the U on the slider.

How does concentration influence initial rate?

Does order influence the relationship for concentration? If so, how?

How does temperature influence initial rate?

How does activation energy (E_a) influence initial rate?

A catalyst is a substance that lowers the activation energy of a reaction by changing the mechanism or pathway of the reaction. The catalyst is *not* consumed in the reaction. What does this do to the rate of the reaction?

Explanation

The effect of a change in concentration and order was discussed above with the introduction of the rate law. An increase in concentration increases the rate of a reaction as seen by the increased negative slope of the rate against concentration plot in this first-order example. A change in order changes the behavior of the graph, as order increases the rate increases (we will explore this further in the next module.).

When the order is zero, the rate is equal to the rate constant and the starting concentration does not influence the rate since $(A)^0 = 1$: Rate = rate constant

The variables of temperature and activation energy influence the rate constant, k , in the rate law. As seen above in the STELLA model, increasing the temperature increases the rate, while decreasing the activation energy increases the rate. The activation energy is a constant for any reaction pathway. The catalyst changes the activation energy by altering the pathway or mechanism to one with a lower activation energy and hence, faster rate.

Extension

Perform an exponential regression on the concentration against time data, place the regression equation into the function editor, **[Y=]**, and plot the curve as Y_1 . How well does it fit the data?

Now let's have the calculator determine the rate of change of this curve. Earlier you did

the slope between pairs of data points! The TI-83 will find the slope of a tangent line at many places along the curve (or regression function) and then plot it. Press **[Y=]** and place the cursor at Y_2 and then press **[(-)] [MATH]** and select nDeriv. Complete the line as: -nDeriv (Y_1 , X, X) Use **[X,T,è,n]** to get the X and **[VAR] Y-VARS** the FUNCTION to get Y_1 . Then press **[GRAPH]** to plot (it will a little time).

This will determine the numerical derivative or the slope Y_1 at numerous points along Y_1 as X varies over all the X values. The calculator determines the slope of the function, Y_1 at many pairs of points that are very close together on the original function. How does the curve fit your earlier $\Delta \text{conc}/\Delta \text{time}$ against average time data?

Now press **[Y=]** and go to Y_3 and add this line: $Y_3 = Y_2/Y_1$

Press **[GRAPH]**. What is the result?

How are rate and concentration related? Write an equation in terms of the variables plotted.

How does this method compare to your earlier calculation?

Which method do you think is the better calculation? Why?

Evaluation

For a first order reaction, how could you easily double the rate of reaction? Explain.

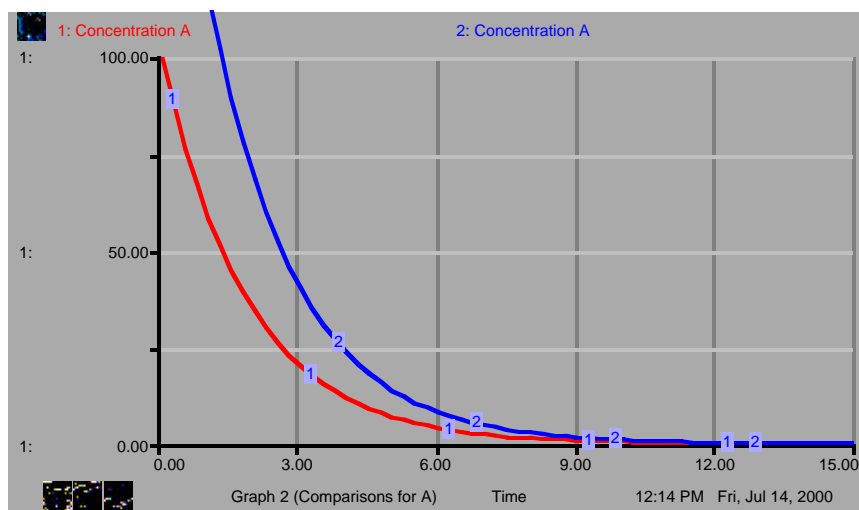
For a zeroth order reaction does the statement "the rate is independent of concentration" make sense? Explain.

Third order reactions are very rare, how would they compare in rate to second order reactions?

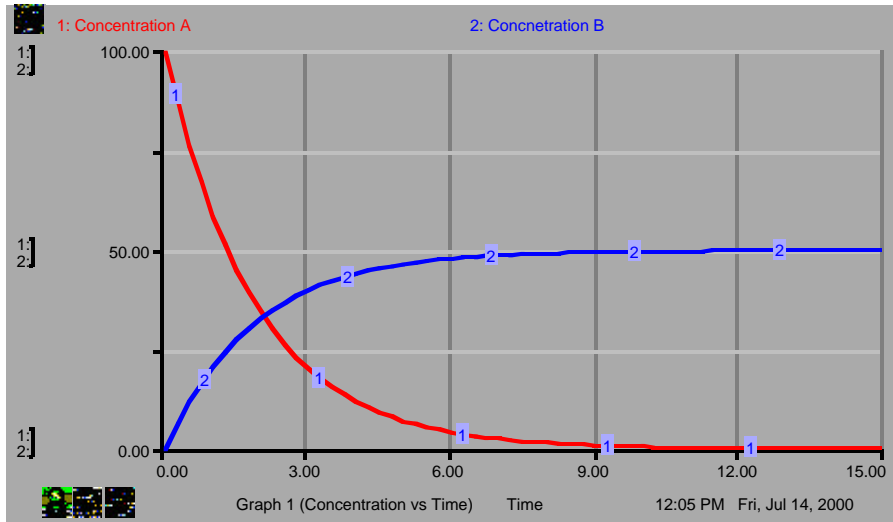
Plot the following data and determine the order of the reaction.

time	concentration	time	concentration
0 minutes	1.0 M	5	0.49
1	0.90	6	0.40
2	0.79	7	0.30
3	0.70	8	0.19
4	0.61	9	0.099

What is the difference in the graphs of concentration A for run 1 and 2 involving the same reaction?



Interpret the graph of concentration against time given below.



MODULE 3

Module Title: SIMULATING AND INVESTIGATING KINETICS WITH STELLA

Estimated time to complete: 2-3 hours

Module objectives: graphical determination of the order of a reaction

Concept(s) learned in this module: zeroth, first, and second order reactions

Standards addressed in this module (Praxis, K-12):

1. National Science Education Standards for content standards (9-12) - content standard A science as inquiry and content standard B in physical science.
2. Praxis II - chemistry: content knowledge
3. Maryland High School Core Learning Goal - goal 1 - skills and processes and goal 4 - chemistry
4. National Educational Technology Standards - standard 3 - Technology productivity tools and standard 5 - Technology research tools

Technology-enhanced instructional strategies utilized in this module:

modeling of data using the graphing calculator or Excel
models and simulations using STELLA

Components	Brief description of module activities	Student Grouping*	Materials/ Technology
Engagement	how does concentration -time graph change	small group	none
Exploration	graphical analysis of STELLA simulation results	small group	STELLA
Explanation	equations for the various orders of reactions	small group	none
Extension/ Evaluation	treating data to arrive at a rate law	Individual	graphing calculator

*Student grouping: Individual, paired, small group, whole class, etc.

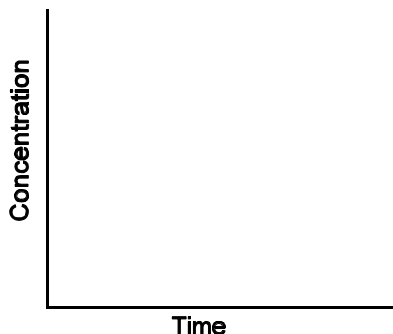
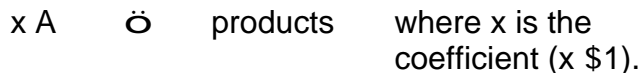
Expected module outcomes: derive relationships for various orders of reactions

Performance-based assessment of module outcomes: be able to analyze data to determine the order of a reaction

MODULE 3 - SIMULATING AND INVESTIGATING KINETICS WITH STELLA

Engagement

Let's consider how the concentration of a reactant, A, is influenced by the order of the reaction. The reaction is given by:



How is the concentration of A going to behave as the reaction proceeds? Sketch a prediction.

How would you characterize the slope of your prediction?

Exploration

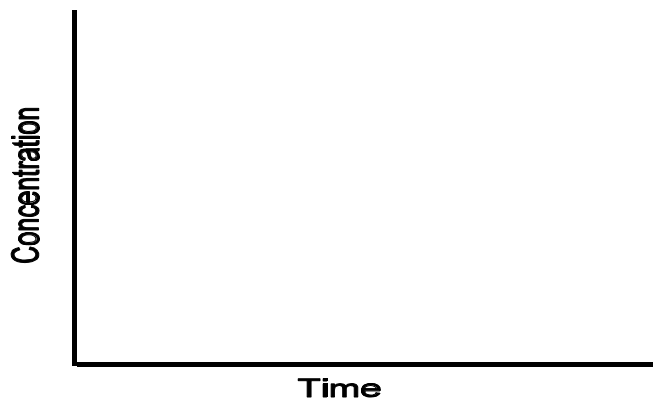
Now we want to consider what the rate law is for the disappearance of A. Here are some possibilities given in the table. Notice these relationships do not contain time as a variable. The rate or $\Delta \text{concentration} / \Delta \text{time}$ is negative due to the reactant being consumed in the reaction.

Order	Rate Law
zero	$R = k(A)^0$
first	$R = k(A)^1$
second	$R = k(A)^2$

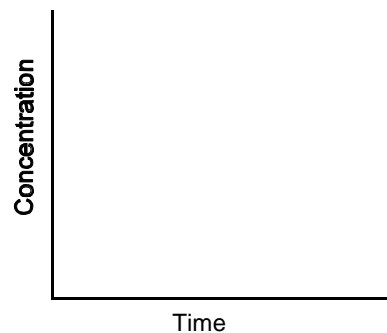
where R = rate of reaction, k = rate constant, and (A) = molar concentration of A.

Bring up the STELLA model "kinetics_order_of_reaction" on the computer to examine how concentration behaves with time and address the following questions:

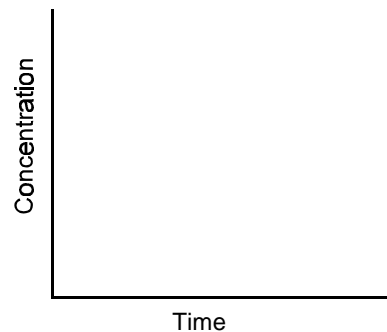
1. Run the model and then sketch and label the three curves, which show the behavior for each possible order. Which order consumes the reactant the fastest? Label the initial or starting concentration of A as A_0 .



How does changing the starting concentration influence the curves? Sketch and label two runs of the model at different starting concentrations.



How does changing the rate constant, k , influence the curves? Sketch and label two runs of the model.



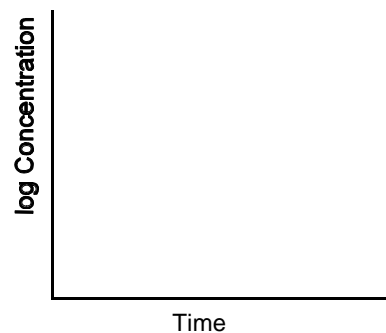
How do you determine the rate of the reaction?

2. What does taking the log of concentration for the first order reaction do to the graph? This plot is $\log(A)$ against time.

Illustrate on the graph and explain how this curve is influenced by changing:

' starting concentration?

' rate constant?



How do you determine the rate constant?

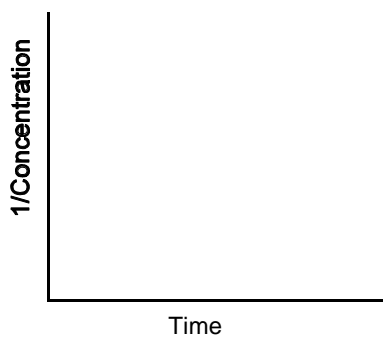
The initial (A_0) is now $\log(A_0)$ at the y-intercept. Label on the graph above.

3. What happens to a second order reaction when $1/(A)$ is plotted against time?

Illustrate on the graph and explain how this curve is influenced by changing:

' starting concentration?

' rate constant?



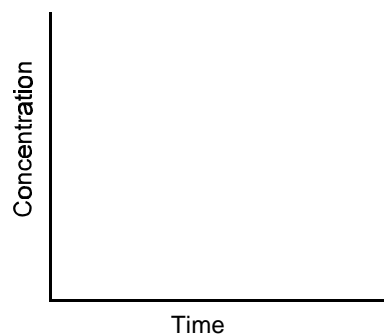
The y-intercept of the plot is the $1/(A_0)$. Label on graph above.

How do you determine the rate constant?

4. For the zero order plot, what happens to the rate when starting concentration is changed?

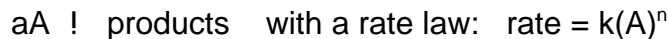
What happens to the rate when the rate constant is changed?

How do you determine the rate constant?



Explanation

Here are the characteristics of zero, first, and second order reactions for a reaction of the following:



where (A) is the concentration of A at any time, t, (A_0) is the concentration of A at time = 0 or the initial concentration and n is the order of the reaction.

Order, n	Rate Law	Relationship of concentration against time	Linear Plot $y = mx + b$	slope m	intercept b
zeroth, $n = 0$	$\text{rate} = k$	$(A) = -kt + (A_0)$	(A) against t	-k	(A_0)
first, $n = 1$	$\text{rate} = k(A)$	$\log \frac{(A)}{(A_0)} = \frac{-kt}{2.303}$	$\log (A)$ against t	$\frac{-k}{2.303}$	$\log (A_0)$
second, $n = 2$	$\text{rate} = k(A)^2$	$\frac{1}{(A)} = kt + \frac{1}{(A_0)}$	$1/(A)$ against t	k	$1/(A_0)$

You should have deduced this information from the plots and changing variables study performed using the STELLA models. By plotting concentration against time data and trying the various transformations on your graphing calculator, you can determine the order of a reaction.

Extension/Evaluation

Consider the decomposition of gaseous N_2O_5 :



Find the order of the reaction by the graphical approach outlined above using your TI-83 graphing calculator. You will want to perform linear regressions and use the r^2 value to help judge best-fit. The highest r^2 would be the best-fit linear model and thus yield the order of the reaction.

$$\text{Rate} = k(\text{N}_2\text{O}_5)^n$$

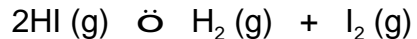
What is the value of n ?

Time, minutes	(N_2O_5)
0	0.160M
2	0.080
4	0.040
6	0.020
8	0.010
10	0.0050

Explain your choice.

Type of Plot	r^2 for linear regression
concentration vs. time	
log concentration vs. time	
1/concentration vs. time	

Now consider the uncatalyzed decomposition of hydrogen iodide:



Again using the graphical approach, what is the value of n in the rate law? Rate = $k(\text{HI})^n$

Time, hours	Concentration HI, M
0	1.00
2	0.50
4	0.33
6	0.25
8	0.20

Explain your choice.

In the presence of gold, where the gold surface acts as a catalyst, the rate becomes independent of (HI). What is the rate law in the catalyzed case?

STELLA Modeling Software is a product of High Performance Systems. The models used here are modifications of models developed by the Maryland Virtual High School CoreModels Program.

MODULE 4

Module Title: DISCOVERING THE NATURE OF REVERSIBLE CHEMICAL REACTIONS

Estimated time to complete: 2-3 hours

Module objectives: to introduce the nature of forward and backward reactions

Concept(s) learned in this module: reverse reaction, net reaction rate, equilibrium, equilibrium constant

Standards addressed in this module (Praxis, K-12):

1. National Science Education Standards for content standards (9-12) - content standard A science as inquiry and content standard B in physical science.
2. Praxis II - chemistry: content knowledge
3. Maryland High School Core Learning Goal - goal 1 - skills and processes and goal 4 - chemistry
4. National Educational Technology Standards - standard 3 - Technology productivity tools and standard 5 - Technology research tools

Technology-enhanced instructional strategies utilized in this module:
models and simulations using STELLA

Components	Brief description of module activities	Student Grouping*	Materials/ Technology
Engagement	following a simple reactions progress	small group	none
Exploration	simulation of forward and backward reaction progress, equilibrium	small group	STELLA
Explanation	defining equilibrium and equilibrium concentration	small group	STELLA
Extension	relating rate constants and equilibrium constants	small group	none
Evaluation	sketching graphs of a simple reaction	Individual	none

*Student grouping: Individual, paired, small group, whole class, etc.

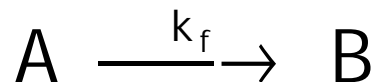
Expected module outcomes: understanding the nature of reversible reactions and the dynamic concept of equilibrium from the kinetics of forward and backward reactions

Performance-based assessment of module outcomes: understanding the graphical behavior of equilibrium systems, judging the extent of reaction

MODULE 4 - DISCOVERING THE NATURE OF REVERSIBLE CHEMICAL REACTIONS

Engagement

Consider the simple gas phase reaction that goes to completion:

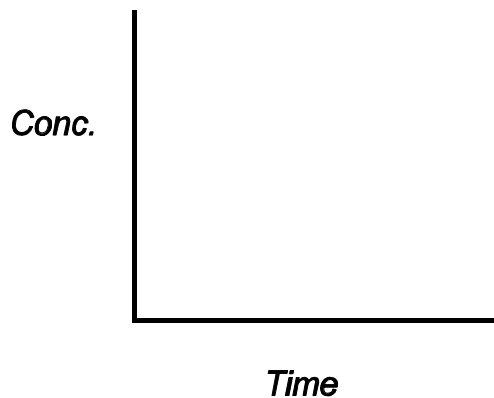


where k_f is the rate constant for this first-order reaction.

If 1.0 mole of **A** is placed into a 1.0L vessel, as **A** reacts **B** appears. Complete the table.

Mole A	Mole B	Mole A + Mole B
1.0		
0.9		
0.7		
0.5		
0.3		
0.1		
0		

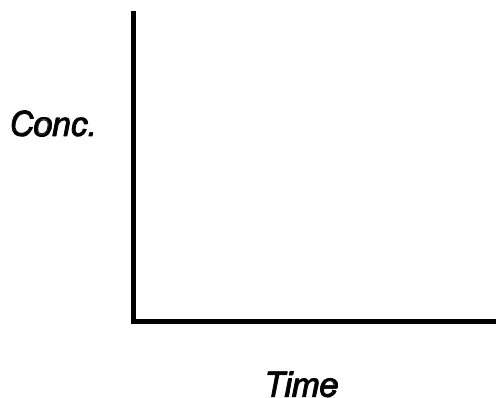
Predict by sketching a graph of concentration against time showing both **A** and **B** and remembering this is a first-order reaction.



Exploration

Now let's look at this reaction using a STELLA model "reversible reaction" where we can adjust k_f . Notice a second rate constant, k_b , set at zero.

Sketch and label the graph below for three different values of k_f .

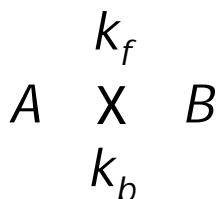


Does your earlier prediction graph agree with this plot?

How does the value of k_f influence the rate of disappearance of **A**?

How does the value of k_f influence the rate of appearance of **B**?

Now let's add a twist to this reaction. Suppose that the reaction can also go in the *reverse direction* or that **B** converts back to **A**. We can write this as shown below:

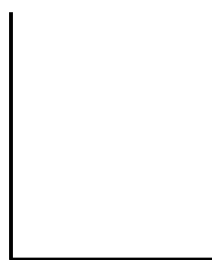


where k_f is the forward rate constant for **A** going to **B** and k_b is the backward rate constant for **B** going back to **A**.

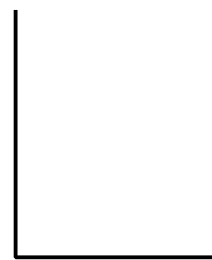
Sketch and label graphs for the following three situations.



$$k_f > k_b$$



$$k_f = k_b$$



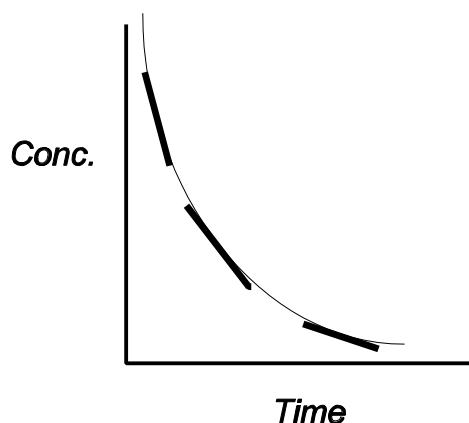
$$k_f < k_b$$

Do any of the graphs for the disappearance of **A** reach zero? Why not?

As time passes what do the concentrations of **A** and **B** do?

The concentrations of both **A** and **B** level off to a constant non-zero value. The time it takes to reach these constant levels varies with the choice of the rate constants.

Suppose we look at the rate of change of the concentration against time graph. This is like finding the slope between two points on the curve at a great number of pairs of points. See illustration of this below.



Place an X on the steepest slope segment.

The slope of a line or the rate of disappearance of **A** is given by:



$$\text{slope} = \frac{\Delta Y}{\Delta X} = \frac{Y_1 \& Y_2}{X_1 \& X_2} = \frac{\Delta \text{concentration}}{\Delta \text{time}} = \text{rate}$$

The STELLA model will plot the rate of disappearance of **A** or forward rate and the rate of appearance of **B**, backward rate.

Sketch and label the three situations:

$$k_f > k_b$$



$$k_f = k_b$$



$$k_f < k_b$$



As time passes, what happens to the forward rate and backward rate?

Notice on these plots that the NET rate (forward rate - backward rate) is also given. What does it show?

Explanation

The NET rate reaches zero, which gives the appearance that the reaction stops, but this is not true. The forward and backward rates become equal at the same time that the concentrations leveled out.

The reaction has reached equilibrium when the forward rate equals the backward rate. Notice on the graphs that this occurs at a positive value. The forward and backward reactions did **NOT** stop! They have reached a state of dynamic equilibrium.

The concentrations of **A** and **B** are constant. The STELLA model will calculate and graph the ratio of concentrations. What about the ratio of the concentrations of B over the concentration of A or (B)/(A)?

What do you notice about the (B)/(A) and k_f/k_b ?

The equilibrium constant, K_{eq} , is given by

$$K_{eq} = \frac{(B)}{(A)} = \frac{k_f}{k_b}$$

which occurs when the forward rate = backward rate.

Equilibrium occurs when the forward rate = backward rate.

Extension

Reactants are favored when K_{eq} is small or large.

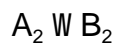
Products are favored when K_{eq} is small or large.

What is K_{eq} if the rate constants are equal?

For the simple reaction $A \rightleftharpoons B$, describe the composition for the situation of equal rate constant.

Evaluation

Sketch and label the following graphs for a system that comes to equilibrium from starting condition where the concentration of A_2 is greater than zero and B_2 is zero:



- a. Show concentrations of A_2 and B_2 against time



From your graph, what is the relative value of the equilibrium constant?

- b. show forward, backward and net rates against time



Did the reaction really stop? Explain why or why not.

MODULE 5

Module Title: EXPLORING CHEMICAL EQUILIBRIUM THROUGH SIMULATIONS WITH STELLA

Estimated time to complete: 2-3 hours

Module objectives: exploring factors that influence systems going to equilibrium

Concept(s) learned in this module: effects of changing concentration, volume, starting point (reactants only or products only, mixed), how rate constants influence the equilibrium constant

Standards addressed in this module (Praxis, K-12):

1. National Science Education Standards for content standards (9-12) - content standard A science as inquiry and content standard B in physical science.
2. Praxis II - chemistry: content knowledge
3. Maryland High School Core Learning Goal - goal 1 - skills and processes and goal 4 - chemistry
4. National Educational Technology Standards - standard 3 - Technology productivity tools and standard 5 - Technology research tools

Technology-enhanced instructional strategies utilized in this module:
models and simulations using STELLA

Components	Brief description of module activities	Student Grouping*	Materials/ Technology
Engagement	how is equilibrium constant influence by rate constants	small group	none
Exploration	STELLA simulation of equilibrium systems and they are influenced by concentration, volume, K_{eq} , k_f , and k_b	small group	STELLA
Explanation	how the rate constants influence the value of the equilibrium constant	small group	none
Extension	a disturbed equilibrium	small group	none
Evaluation	graphical interpretation of data	Individual	none

*Student grouping: Individual, paired, small group, whole class, etc.

Expected module outcomes: how the rate constants influence the value of the equilibrium constant and starting concentration and volume influence the equilibrium concentrations

Performance-based assessment of module outcomes: interpretation of graphical results based on various ratios of the rate constants

MODULE 5 - EXPLORING CHEMICAL EQUILIBRIUM THROUGH SIMULATIONS WITH STELLA

Engagement

All chemical reactions do not go to completion. Many reactions after a period of time reach equilibrium, a state of dynamic balance between the forward and reverse reactions. Let's examine a simple gas phase reaction:



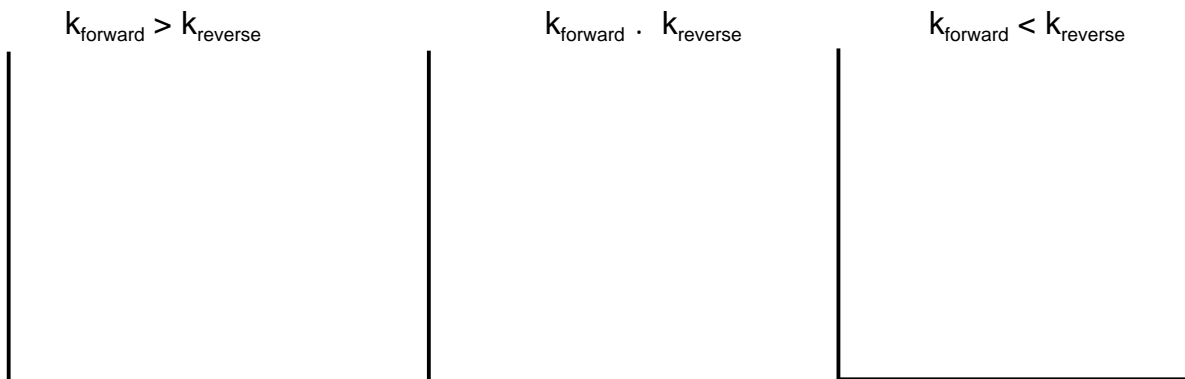
The equilibrium constant, K_{eq} , for the reaction would be given by the ratio of the rate constants, k :

$$K_{\text{eq}} = \frac{(B)}{(A)} = \frac{k_{\text{forward}}}{k_{\text{reverse}}}$$

As the rate constants vary, how is the equilibrium constant influenced?

Exploration

Call up the STELLA model "Basic_equil_from_rate_constants" and run the simulation. Sketch and label A and B on the graphs below for the following three condition:



From the graphs, how do you know when the system is at equilibrium? Label on a graph.

If you change the starting concentration of A, how does the graph change?

For changing concentrations, does the value of the equilibrium constant change?

Describe how can you change the value of the equilibrium constant?

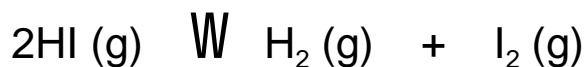
Once a system comes to equilibrium, how does the equilibrium constant behave over time?

What is the difference between the following two situations where $K_{eq} = 2$?

$$\begin{aligned} k_f &= 2 \\ k_b &= 1 \end{aligned}$$

$$\begin{aligned} k_f &= 0.2 \\ k_b &= 0.1 \end{aligned}$$

Now close the above model and click on "Don't Save" and then open the model "Equil_system_HI" which uses the reaction:



This model lets you vary the concentration of the reactant and/or the two products. The volume of the container can also be changed. The results can be viewed as a concentration versus time graph. Run the default model where *only* 1.0 mole of HI is placed into a 1-L vessel. Sketch and label (HI, H₂, and I₂) the graph below.

Does changing the volume of the vessel change the equilibrium constant?

Run the model with 1.0 mole of all three substances in a 1-L vessel. Sketch and label the graph below.

Does the reaction come to equilibrium?
Explain.



Run the model with 0.01 mole HI and 1.0 mole of both products in a 1-L vessel. Sketch and label the graph below.

Does the reaction come to equilibrium from the reverse direction, starting with lots of products?
How do you know?

Are there lots of products and little reactant?
Explain why or why not.



Now close the model and click on “Don’t Save.”

Explanation

Since the equilibrium constant, K , is given by the following ratio of rate constants, k :

$$K_{\text{eq}} = \frac{k_f}{k_b}$$

We can construct the following table that summarizes the results you investigated above with the STELLA models.

Reaction is	Rate constants	Equilibrium constant
product-favored	$k_f > k_b$	$K_{eq} > 1$
reactant-favored	$k_f < k_b$	$K_{eq} < 1$
~equal mix of both	$k_f \sim k_b$	$K_{eq} \sim 1$

Equilibrium can be achieved from either direction, starting with all reactants or all products. Equilibrium concentrations are influenced by the starting concentrations but the equilibrium constant is NOT changed. For the HI reaction above the volume does not influence the equilibrium because there are an equal number of molecules on both sides of the reaction.

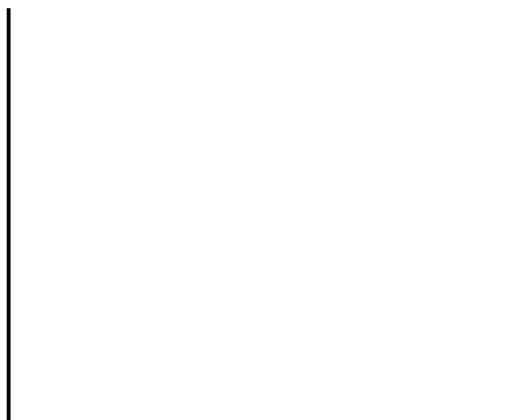
Extension

Suppose a system like one of the above was at equilibrium and then **disturbed** by the addition of one of the components. *Show an example with a disturbance labeled on the graph.*

Predict and show on the graph how the system would respond and return to a new equilibrium.

Does the value of the equilibrium constant change?

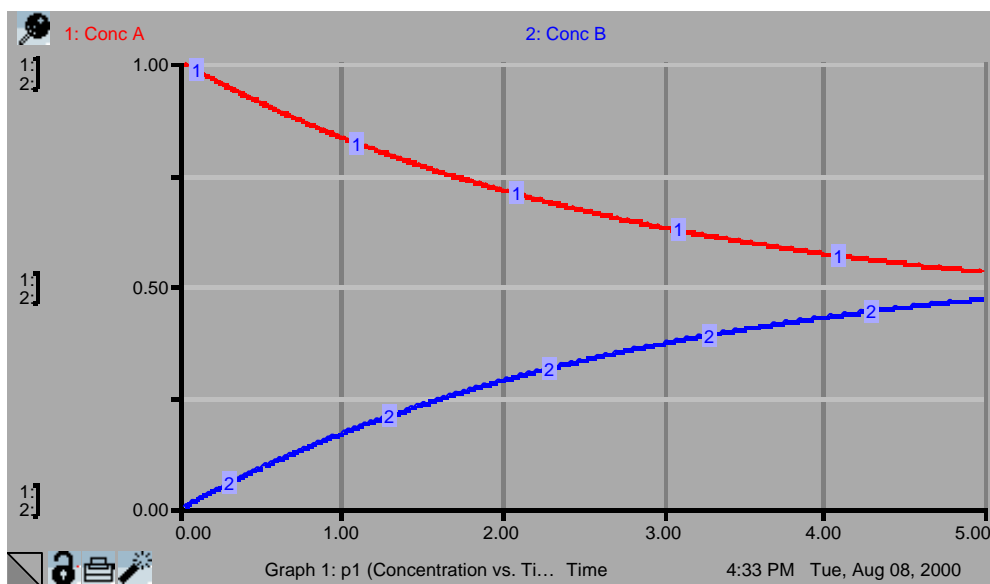
Explain why or why not.



Evaluation

Is the following system in equilibrium? Explain why or why not.

A ! B



Can you estimate an approximate value of the equilibrium constant at this point?

If this system is not at equilibrium, what would you have to do to allow it to get to equilibrium?

MODULE 6

Module Title: KINETICS OF CONSECUTIVE AND COMPETING REACTIONS USING STELLA

Estimated time to complete: 2-3 hours

Module objectives: introduction to competing and consecutive reactions

Concept(s) learned in this module: competing and consecutive reactions and how the rate constants control the overcome of the products

Standards addressed in this module (Praxis, K-12):

1. National Science Education Standards for content standards (9-12) - content standard A science as inquiry and content standard B in physical science.
2. Praxis II - chemistry: content knowledge
3. Maryland High School Core Learning Goal - goal 1 - skills and processes and goal 4 - chemistry
4. National Educational Technology Standards - standard 3 - Technology productivity tools and standard 5 - Technology research tools

Technology-enhanced instructional strategies utilized in this module:
models and simulations using STELLA

Components	Brief description of module activities	Student Grouping*	Materials/ Technology
Engagement	review of a single step reaction	small group	none
Exploration	competing and consecutive reaction models in STELLA	small group	STELLA
Explanation	comparison of competing and consecutive reactions	small group	none
Extension/ Evaluation	addition of an equilibrium step to the first step of a consecutive reaction - a simulation with STELLA	small group	STELLA

*Student grouping: Individual, paired, small group, whole class, etc.

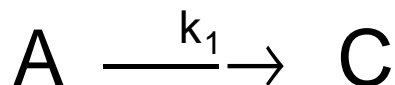
Expected module outcomes: an understanding of competing and consecutive reactions

Performance-based assessment of module outcomes: how an additional step (addition of an equilibrium step to the first step of a consecutive reaction) influences the overall reaction

MODULE 6- KINETICS OF CONSECUTIVE AND COMPETING REACTIONS USING STELLA

Engagement

Consider the simple first-order reaction below with a rate constant k_1 .



How do the rates compare for the disappearance of A to the appearance of C?

What would a graph of concentration against time look like (consider both A and C)? Sketch and label a graph.

Exploration

Now call up the STELLA™ model, "What_is_going_on" and run it for a number of different rate constants. Does it confirm your graph above assuming the simple reaction?

However, notice that the experimental results do not match the simple single step reaction that we assumed was the case. The production of C is not as fast and falls below the single step model. Something else must be going on in our reaction. Let's explore some possibilities.

Consider the following two-step reaction:



Each step is controlled by the first order rate constant, k , for the particular step. This type of multi-step reaction is called **consecutive reactions**. This type of reaction is very important for many reactions especially in organic chemistry. The substance B could be an intermediary in a mechanism. Using STELLA™, we want to explore this two-step reaction to see how the rates of each step control the final product, C.

Think about how the rate constants, k_1 and k_2 , are going to control the reaction for the following situations.

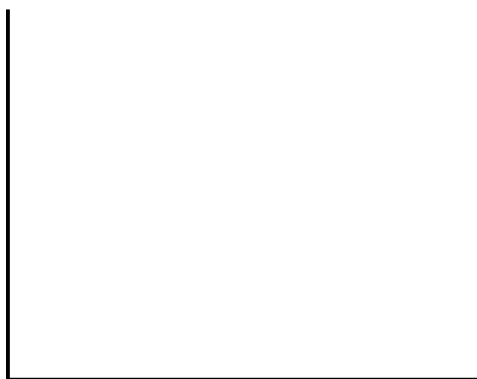
Both are very small?

Both are very large?

One is large and the other is small?

Now call up the STELLA™ model, “Two_Step_Reaction” and run it. You can adjust the rate constants, k_1 and k_2 , with the two different sliders. Set-up the following five runs and sketch and label the four curves on the graphs for them. As you run these five cases, think about what controls the overall rate of reaction.

$k_1 > k_2$



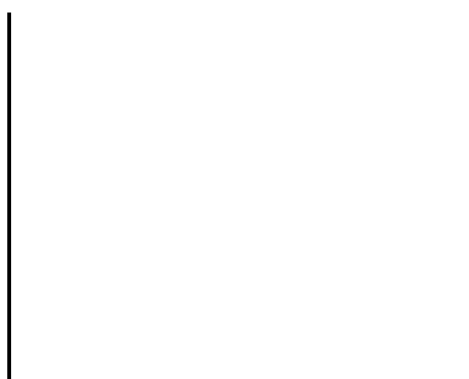
$k_1 = 0$; k_2 any value

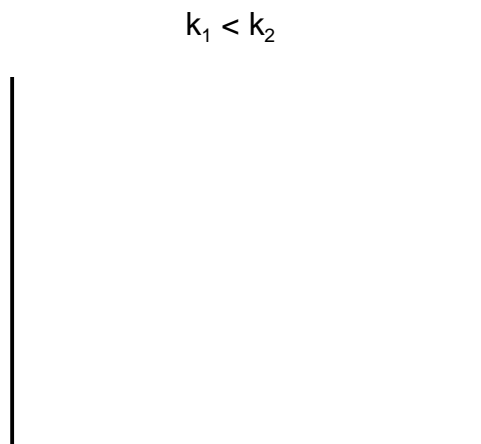


k_1 any value; $k_2 = 0$



$k_1 = k_2$



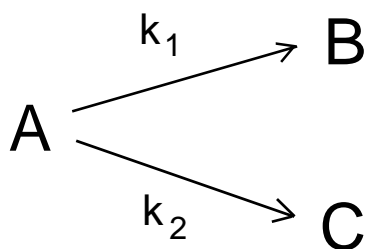


How is the overall rate of reaction influenced by the two rate constants, k_1 and k_2 ?

Summarize are the two rate constants control the rate of production of the product, C

On all the graphs for any run was a fourth line: "A + B + C" What does this line demonstrate? Explain.

Now consider the following two first order reactions that both consume reactant A:



These two reactions are called **competing reactions**. Each reaction is controlled by the first order rate constant, k .

How is this set of reactions different from the two consecutive reactions discussed above?

Now call up the STELLA™ model, “Two_Competing_Reactions” and run it. You can adjust the rate constants, k_1 and k_2 , with the two different sliders. Set-up the same five runs and sketch and label the four curves on the graphs for them. As you run these five cases, think about what controls the final product. Competing reactions are also very important such as unwanted side reactions during a synthesis of one compound or isomeric products (two or more different isomers such as cis and trans or positional placement on a molecule) are produced.

$$k_1 > k_2$$



$$k_1 = 0; k_2 \text{ any value}$$

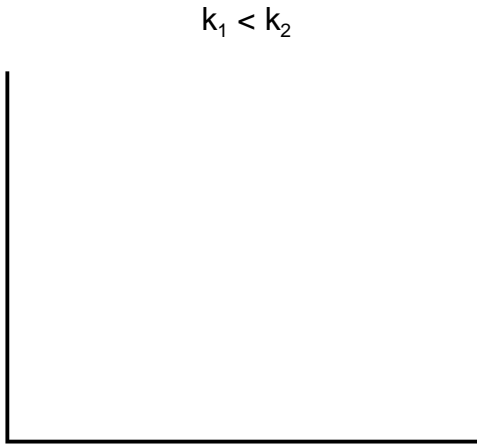


$$k_1 \text{ any value}; k_2 = 0$$



$$k_1 = k_2$$





What controls the final product?

Are B and C produced in proportional amounts? Why or why not?

Does the law of conservation of matter hold for competing reactions?

How do the competing reactions differ from the consecutive reactions in the production of the final product material?

Explanation

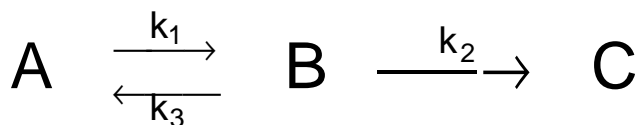
The table below compares consecutive and competing reactions.

Property	CONSECUTIVE REACTIONS	COMPETING REACTIONS
final product	single product with no intermediate if enough time is allowed	mixed product that depends on the difference in the rate constants
rate controlling step	<i>slowest</i> step controls overall rate	major product is associated with step with larger rate constant or <i>faster</i> rate
effect of temperature change	composition of product is unchanged overall production rate is changed	composition of products change proportion since rate constant change at different rates
initial reactant	totally consumed	totally consumed

In any reaction or series of reactions, the law of conservation of matter **MUST** always be obeyed!

Extension/Evaluation

What would happen in consecutive reactions, such as $A \rightleftharpoons B \rightarrow C$, if an equilibrium was established between A and B as shown by the case below:



Would this influence the production of C? Explain why or why not.

Now call up the STELLA™ model, "Two_Step_Reaction_with_equil" and run it. You can adjust the rate constants, k_1 , k_2 , and k_3 , with the three different sliders. The new first-order rate constant k_3 is for the establishment of the equilibrium between A and B. Run the model with $k_3 = 0$ to see the original case of no backward reaction. Then explore the effect of increasing k_3 . Adjust the other rate constants to see that your answer is universal.

Sketch and label a graph showing how the extent of equilibrium ($K_{eq} \gg 1$, $K_{eq} > 1$, $K_{eq} = 1$, $K_{eq} < 1$, $K_{eq} \ll 1$) influences the production of C.

$$K_{eq} = \frac{k_1}{k_3}$$



For an industrial preparation reaction, what would the overall effect be on your production schedule?

For an industrial preparation involving competing reactions an unwanted product can be produced. How can you change the proportion of the products? (Hint: how can you influence rate constants?)

MODULE 7

Module Title: PUTTING IT ALL TOGETHER AND THEN SOME: AN ASSESSMENT ACTIVITY

Estimated time to complete: 2-3 hours

Module objectives: Assesses the concepts and models introduced in modules 1 to 6 plus examines a STELLA model simulation of competing equilibria, a situation not covered in the modules but a natural extension of the material.

Concept(s) learned in this module: examining a system of competing equilibria

Standards addressed in this module (Praxis, K-12):

1. National Science Education Standards for content standards (9-12) - content standard A science as inquiry and content standard B in physical science.
2. Praxis II - chemistry: content knowledge
3. Maryland High School Core Learning Goal - goal 1 - skills and processes and goal 4 - chemistry
4. National Educational Technology Standards - standard 3 - Technology productivity tools and standard 5 - Technology research tools

Technology-enhanced instructional strategies utilized in this module:

modeling of data using the graphing calculator or Excel
models and simulations using STELLA

Components	Brief description of module activities	Student Grouping*	Materials/ Technology
Evaluation	Assesses concepts from modules 1 to 6 plus the ability to extend knowledge to new situation	individual	graphing calculator, STELLA

*Student grouping: Individual, paired, small group, whole class, etc.

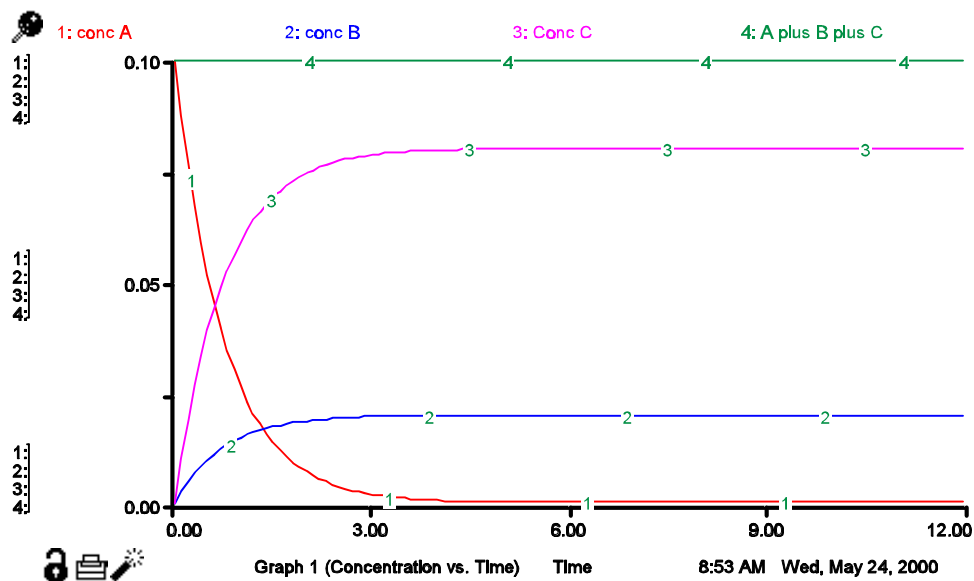
Expected module outcomes: assessment of student knowledge from previous modules

Performance-based assessment of module outcomes: Assessment of knowledge of chemical kinetics

MODULE 7 - PUTTING IT ALL TOGETHER AND THEN SOME: AN ASSESSMENT ACTIVITY

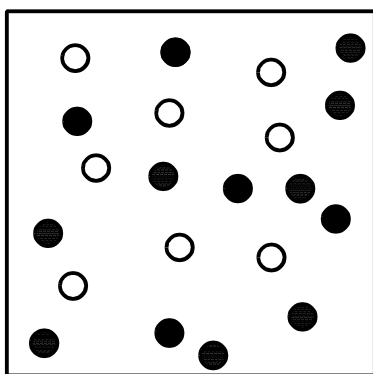
Feel free to run any of the models or use a graphing calculator to help address the questions.

- From the graph given below starting with compound A, is the reaction consecutive or competing? Explain.



What is the composition of the final products?

- Consider the box below which shows the composition at about midway through the reaction.



○ A

● B

● C

At this point can you decide if the reaction of A is consecutive or competing? Justify your answer.

3. In competing reactions, changing the temperature changes the proportion of the two products. Why?

4. In a reaction of the type below, does compound A get totally consumed? Explain why or why not.

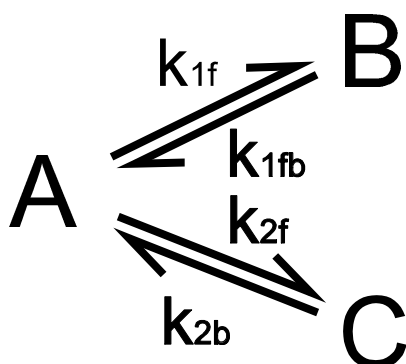


Does an equilibrium between A and B ever get established? Explain.

5. From the concentration versus time data given below for a reaction not completely finished, is the reaction consecutive or competing? Explain.

Time	(A)	(B)	(C)
0	1.00	0.00	0.00
0.50	0.72	0.25	0.03
1.00	0.59	0.31	0.10
1.50	0.51	0.31	0.18
2.00	0.45	0.29	0.26
2.50	0.41	0.27	0.33
3.00	0.37	0.24	0.39
3.50	0.33	0.22	0.45
4.00	0.30	0.20	0.50
4.50	0.27	0.18	0.55
5.00	0.25	0.16	0.59
5.50	0.22	0.15	0.63
6.00	0.20	0.13	0.66
6.50	0.18	0.12	0.70
7.00	0.17	0.11	0.72
7.50	0.15	0.10	0.75
8.00	0.14	0.09	0.77
8.50	0.12	0.08	0.80
9.00	0.11	0.07	0.81
9.50	0.10	0.07	0.83
10.00	0.09	0.06	0.85

6. Go to the computer and examine the STELLA model on “Competing_Equilibria” that illustrates the situation below:



How does this model for competing equilibria differ from any of the other competing or consecutive reactions examined earlier?

Do the competing equilibria actually achieve a state of equilibrium? If so, explain how you determined this.

ADDITIONAL WEB-BASED RESOURCES

Two natural extension activities to go with this unit produced as part of the BLT project (<http://education.umd.edu/blt>)

- Radioactive Decay by Doria Hillsman
- Enzyme Kinetics by George Morse

Maryland Virtual High School CoreModeling Program
<http://mvhs1.mbhs.edu/>

Chemical kinetics simulator
<http://>

TI-Graphing Calculator
<http://education.ti.com>

Data Handling and Analysis on the TI-82/83/83Plus Graphing Calculator: A Resource for Science and Mathematics Student by J.L. McClure, S.A. Sinex, and B.A. Gage, PGCC Press (2000), 18 pp. (Download as pdf file at http://academics.pg.cc.md.us/psc/TI83_booklet.pdf)