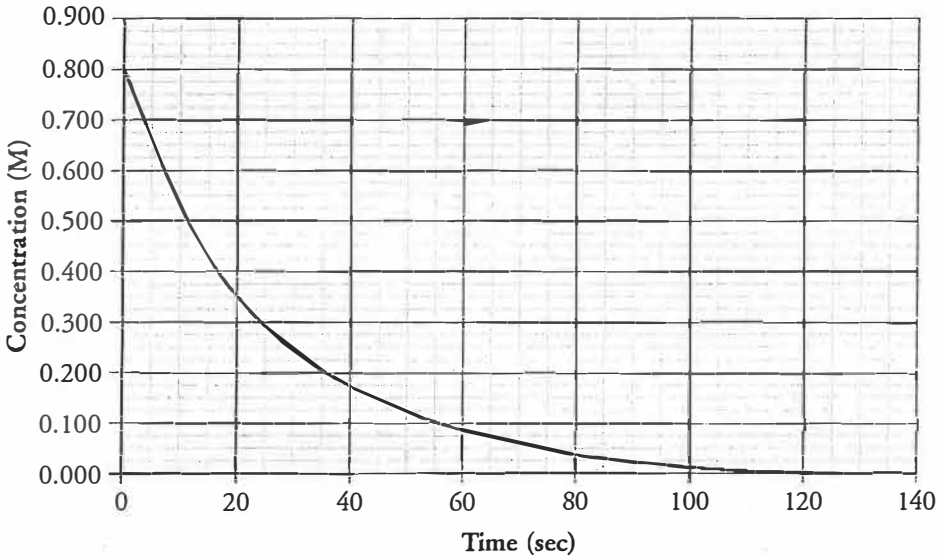
Rate of Reaction

How is the speed of a reaction measured?

Why?

Chemical reactions occur at different speeds. Some are almost instantaneous. Others require patience. For example, rust can form on iron in just a few days or over a period of months depending on the conditions. In order to study the factors that change the speed of a reaction, we must first develop an understanding of how the rate of reaction is monitored during a reaction.

Model 1 – Concentration versus Time Graph



1. The graph in Model 1 illustrates how the concentration of a species in a chemical reaction changes over time.

   a. What unit is the concentration measured in?

   M/s or mol/L*s

   b. What unit is the time measured in?

   seconds

2. Consider the data in Model 1.

   a. What was the concentration of the species when the chemical reaction was initiated?

   0.8 mol/L

   b. Did the concentration of the species increase or decrease over time?

   decrease

   c. Was the species a reactant or product in the reaction? Justify your reasoning.

   Reactant, **because it was decreasing over time.**

3. Consider the data in Model 1.

   a. What was the change in the concentration of the species in Model 1 during the first 10 seconds of the reaction? Include units in your numeric answer.

   it decreased by about -0.275M (mol/L)

   b. What was the change in the concentration of the species in Model 1 between the 60 and 70 second marks? Include units in your numeric answer.

   About -0.025 M (mol/L)

   c. Was the rate of change for this species the same during these two time periods? Justify your reasoning. If no, in which time period is the rate of change faster?

   Rate of change was much faster during the initial period

Read This!

The rate of change for a species in a chemical reaction is usually defined as the change in its concentration over a specific unit of time.

$$\text{rate} = \frac{\Delta[\ ]}{\Delta t}$$

Depending on the conditions of the reaction, this rate could have the units of molarity per second, molarity per minute, molarity per hour, etc. Note that the rate of change for a chemical species, and for the reaction, is rarely constant. As reactants are used up, the rate often slows down. Although this leads to a curved graph, the average rate between two data points can be approximated using the slope of the graph between those points.

4. Use the data in Model 1 to calculate the average rate of change for the chemical species shown for the following time periods during the reaction. Be sure to include units in your calculation.

   a. The first 10 seconds.

   -0.275mol/L*10s= -0.0275mol/L*s

   b. The time between 30 and 40 seconds.

   0.0075M/s

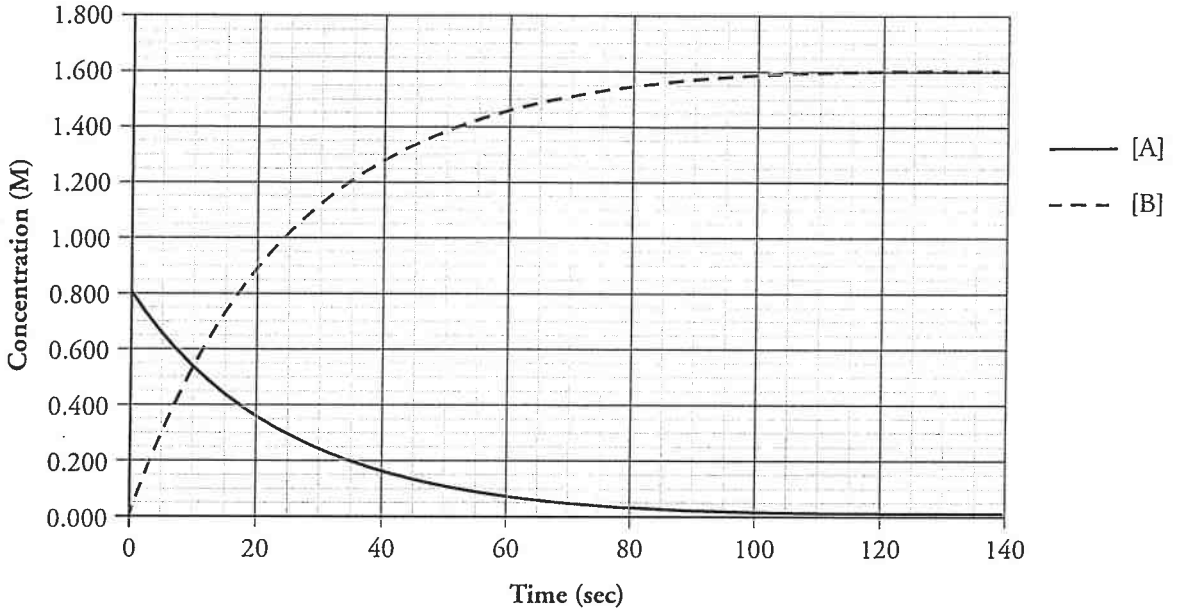
   c. The time between 60 and 70 seconds.

   -0.0025M/s

5. The rates you calculated in Question 4 should be negative values. Why does it make sense that they are negative?

   As the change in concentration is negative, a negative rate is expected

Model 2 – Two Species in the Reaction



6. The graph in Model 2 contains the same data as that in Model 1, but data about a second species in the reaction has been added to the graph.

   a. Which line in Model 2 is the same line as in Model 1, the solid or dashed line?

   A. the solid line

   b. Does the new data illustrate the change in concentration of a reactant or product of the reaction? Justify your reasoning.

   Product. It is increasing over time

7. Use the data in Model 2 to calculate the average rate of change for species B for the following time periods during the reaction. Be sure to include units and a sign (+ or –) on your calculation.

   a. The first 10 seconds.

   about 0.055M/s

   b. The time between 30 and 40 seconds.

   +.015M/s

   c. The time between 60 and 70 seconds.

   0.005M/s

8. Summarize the calculations you have performed in the previous questions in the table below.

	$\frac{\Delta[A]}{\Delta t}$	$\frac{\Delta[B]}{\Delta t}$
First 10 seconds	-0.0275	+0.055
Between 30 and 40 seconds	-0.0075M/s	+0.015M/s
Between 60 and 70 seconds	-0.0025	+.005M/s

9. Based on the information in the table in Question 8, which chemical reaction best describes the reaction that was studied for Model 2? Justify your reasoning.

I. $2A \rightarrow B$ II. $A \rightarrow 2B$ III. $A + B \rightarrow C$ IV. $A + 2B \rightarrow C$

B increased at 2x the rate that A decreases, therefore, choice II

STOP

Read This!

Depending on the mole ratios of the components of a chemical reaction, you could observe different rates of change for different species. How then can one numerical value for the rate of reaction be determined? By convention, the rate of a reaction is equal to the absolute value of the rate of change for any species that has a coefficient of one in the balanced reaction as written. Think of it as the time needed for the reaction to occur 6.022×10^{23} times.

10. Based on the data in Model 2, what is the initial rate of reaction for the chemical process that was investigated?

Rate= -delta[A]/delta time =1/2* delta[B]/delta time

11. Consider the following reaction:

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

Experimental data indicate the initial rate of change for nitrogen is −0.060 M/s.

a. Calculate the initial rate of change for hydrogen.

-.18M/s

b. Calculate the initial rate of change for ammonia.

+0.12M/s

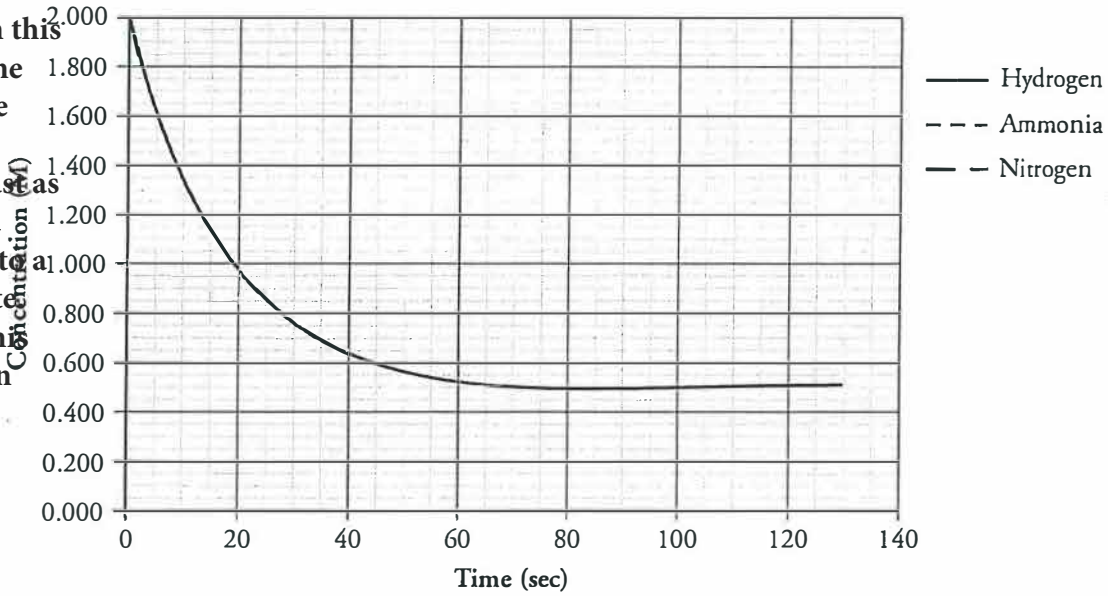
c. Calculate the initial rate of reaction.

Depends on the reactant or product chosen to follow. I would write it for N2, or 0.06M/s

12. The graph below shows the rate of change for hydrogen in the following reaction. Sketch the rate curves for nitrogen and ammonia. The initial concentration of nitrogen is 0.500 M. There is no presence of ammonia initially.

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

I cannot draw in this software. The line for H2 should be negative and decrease 3x as fast as N2. NH3 should increase from 0 to a line about 2x rate. It's hard to do this with one scale on the y-axis



Extension Questions

13. In order to gather the data required to produce the graphs in this activity, or any reaction rate graph, an experimenter must be able to quickly measure changes in concentration, either directly or indirectly, of at least one component of a chemical reaction. Match the following lab tools with the situation in which they might be used. If you are not familiar with the instruments below, use Internet or other resources to determine what the instruments measure.

A. pH meter	**C**	Used to monitor a reaction that involves a colored reactant or product.
B. Manometer	**E**	Used to monitor a reaction that involves a chiral (optically active) reactant or product.
C. Spectrophotomer	**A**	Used to monitor a reaction that involves an acidic or basic reactant or product.
D. Thermometer	**B**	Used to monitor a reaction that involves a gaseous reactant or product.
E. Optical rotation polarimeter	**D**	Used to monitor a reaction that is exothermic or endothermic, with a known enthalpy.

14. Consider the following reaction:

$$N_2O_4(g) \rightarrow 2NO_2(g)$$

The rate of the reaction above can be studied at constant temperature using a pressure probe. However, the data are complicated due to the presence of two gases.

a. If the reaction vessel initially contained only dinitrogen tetroxide, would you expect an overall increase or decrease in pressure as the reaction proceeds? Justify your reasoning.

There should be an increase. NO2 increases at 2x the rate that N2O4 decreases, leading to a net increase.

b. Suppose the above reaction showed an increase of 0.500 kPa in 10 seconds. What would be the change in pressure for dinitrogen tetroxide in the same time period?

0.5=2x-1x; x=0.5kPa. N2O4 decreased by 0.5kPa, while NO2 increased by 1.0kPa Net change +0.5kPa.

Method of Initial Rates

How can you use rate data to determine the order of a reaction?

Why?

In most cases, the rate law for a chemical reaction cannot be derived theoretically. If the reaction is a multi-step reaction, the rate law does not correspond to the balanced chemical equation. Finding the rate law would be simple if we could observe the reactions at the molecular level, but that is not possible. We must use indirect evidence. There are many experimental techniques that can be used to determine the rate law for a reaction. Determining the initial rate of a reaction and seeing how that initial rate changes when the concentrations of reactants are changed is one way of using experimental data to determine the rate law.

Model 1 – The Effect of Exponents

$y = kx^n$

where $k = 5$

x	If $n = 0$, then $y = ?$	If $n = 1$, then $y = ?$	If $n = 2$, then $y = ?$
1	5	5	5
2	5	10	20
3	5	15	45
4	5	20	80

1. Consider the mathematical equation in Model 1.
   a. What letter represents a constant in the equation?

   k

   b. What is the value of the constant?

   5

   c. What letter represents the exponent in the equation?

   n

   d. Does x in the equation represent the independent variable, dependent variable or a constant?

   independent . It is the variable you are controling
2. Fill in the table in Model 1 using the mathematical equation provided. Divide the work among group members.

3. Refer to Model 1. Use complete sentences to describe the change in y as x increases when $n = 0$. Justify the pattern you see using your knowledge of mathematics.

Since anything raised to the exponent '0' is 1, x^0 is 1 for all values of x. So , rate is a constant, k.

4. Refer to the column in the Model 1 table where $n = 1$.

   a. When x doubles, what happens to y?

   it doubles this can be seen going from x=1 to x=2, or 2 to 4

   b. When x triples, what happens to y?

   y triples

5. Use a complete sentence to describe the change in y as x increases when $n = 1$. Justify the pattern you see using your knowledge of mathematics.

There is a linear relationship between concentration and the rate

6. Refer to the column in the Model 1 table where $n = 2$.

   a. When x triples, what happens to y?

   it is raised by a factor of 3^2, or 9.

   b. When x quadruples, what happens to y?

   it is raised by a factor of 4^2, 16, from 5 to 80

7. Use a complete sentence to describe the change in y as x increases when $n = 2$. Justify the pattern you see using your knowledge of mathematics.

It is an exponential plot, to the power of 2.

8. Consider the data below and determine the value of the exponent q. Justify your answer with an explanation or a mathematical equation.

$r = st^q$

t	r
5	15
10	30
15	45

As "t" doubles, the value of "r" also doubles. This is a linear relationship and the value of "q" is 1

9. Solve for the constant s in Question 8 above.

s=3

10. Consider the data below and determine the value of the exponent q. Justify your answer with an explanation or a mathematical equation.

$r = st^q$

t	r
10	3
20	3
30	3

q must have a value of 0, since t^q is always the same and has a value of 1. Once again, s =3

11. Consider the data below and determine the value of the exponent q. Justify your answer with an explanation or a mathematical equation.

$r = st^q$

t	r
2	12
4	48
6	108

q has the value of 2, since doubling "t" from 2 to 4 increases r by a factor of 4, which is 2^2. This is further shown when t increases by a factor of 3, from 2 to 6. The value of r increases by a factor of 9 (3^2)

12. Solve for the constant s in Question 11 above.

The value of s is 3 for all data sets. For example, $3*2^2=12$. $3*4^2=48$

Model 2 – Decolorization of a Dye

rate = k[dye]^n

where $k = 3.40 \times 10^3$

[dye]	If n = 0, then rate = ?	If n = 1, then rate = ?	If n = 2, then rate = ?
0.10 M	3.40×10^3	3.4×10^2	34
0.20 M	3.40×10^3	6.8×10^2	136
0.30 M	3.40×10^3	1.02×10^3	306

13. Identify the reactant in the process being studied in Model 2.

dye

14. Refer to Model 2.

a. Circle the rate law for the decolorization of a dye in Model 2.

I high-lighted it

b. What variable represents the constant in the rate law?

k

c. What variable represents the order of the reaction?

n

15. Fill in the table in Model 2. Divide the work among group members. *Note:* The unit for rate should be "molarity per second" in all cases.

16. How does the initial rate of reaction change as the concentration of the reactant increases when the order of the reaction is zero?

it doesn't

17. How does the initial rate of reaction change as the concentration of the reactant increases when the order of the reaction is one?

it shows a linear relationship, doubles when the concentration doubles

18. How does the initial rate of the reaction change as the concentration of the reactant increases when the order of the reaction is two?

it goes up as a square function

19. Consider the data below.

rate = $k[O_3]^n$

$[O_3]$	Initial Rate
0.44 atm	0.01848 atm/min
0.88 atm	0.03696 atm/min

a. Determine the order of the reaction with respect to ozone. Justify your answer with an explanation or a mathematical equation.

It is first order in O_3. That is, as the P_{O3} doubles, the rate doubles

b. Use one set of data from the table to calculate the value and unit of *k*. *Hint:* What unit must *k* have in order for the rate to have the unit atm/min?

the units of k must be min^{-1} such that rate is atm/min. The value of k =0.042min^{-1}

20. Consider the data below.

rate = $k[KI]^n$

[KI]	Initial Rate
0.10 M	8.4×10^{-6} M/s
0.30 M	7.6×10^{-5} M/s

a. Determine the order of the reaction with respect to potassium iodide. Justify your answer with an explanation or a mathematical equation.

As the concentration of KI triples, the rate goes up by a factor of 9. Thus, the reaction order (n) is 2.

b. Use one set of data from the table to calculate the value and unit of the rate constant *k*. *Hint:* The units of *k* in this question will not be the same units as the *k* in Question 19.

The value of k is 0.0008 L/mol*s. The reason for these units is that $[KI]^2$ will be mol^2/L^2 multiplying that by L/mol*s, the result is in mol/L*s, which are the proper units for rate in this case

21. Consider the data below.

rate = $k[H_2O_2]^n$

$[H_2O_2]$	Initial Rate
0.20 M	382 M/s
0.56 M	382 M/s

a. Determine the order of the reaction with respect to hydrogen peroxide. Justify your answer with an explanation or a mathematical equation.

this is a 0-order reaction. The rate does not change as the concentration of H_2O_2 changes rate=k, since [H2O2]^0 is always 1. k=382 mol/L*s

b. Use one set of data from the table to calculate the value and unit of the rate constant *k*.

see above

Read This!

The rate of a reaction is obtained by determining the concentration of a reactant or product in the reaction over time. This could occur through spectrophotometry for colored solutions, pressure changes for gaseous components, temperature changes for highly endothermic or exothermic reactions or pH for acids or bases—just to name a few. When concentration data are graphed versus time the slope of the curve is the rate of the reaction at that moment. Because the rate may change as the concentrations of reactants change the initial rate is the most dependable data point to use when determining the order of a reaction.

Model 3 – Reaction with Two Reactants

	$[N_2]$	$[H_2]$	Initial Rate
Trial 1	4.3×10^{-3} M	2.2×10^{-4} M	9.60×10^{-6} M/s
Trial 2	4.3×10^{-3} M	4.4×10^{-4} M	9.60×10^{-6} M/s
Trial 3	8.6×10^{-3} M	4.4×10^{-4} M	1.92×10^{-5} M/s

22. What are the reactants of the process being studied in Model 3?

N_2 and H_2

23. Consider the data in Model 3.

a. Compare the concentration of nitrogen in trials 1 and 2.

it is constant

b. Compare the concentration of nitrogen in trials 1 and 3.

it doubles

Read This!

When there are multiple reactants in a process, each reactant must be studied independently while the other reactant is held at constant concentration. This allows the experimenter to determine the effect of changing the concentration of a specific reactant on the initial rate.

24. Consider the data in Model 3.

    a. Which trials should be considered when determining the order of reaction with respect to nitrogen gas?

    2 and 3 (hydrogen is held constant and nitrogen doubles).

    b. Which trials should be considered when determining the order of reaction with respect to hydrogen gas?

    1 and 2 (nitrogen is constant and hydrogen doubles).

25. Explain why no useful conclusion about the exponents of the rate law could be drawn by comparing the data in trials 1 and 3 of Model 3.

    because the concentrations of both reactants are changing. You don't know if one or both are affecting the rate.

26. Determine the order of reaction with respect to nitrogen.

    2nd order

27. Determine the order of reaction with respect to hydrogen.

    0 order (rate does not change when $[H_2]$ doubles).

28. Write the full rate law for the process in Model 3.

    rate=$k[N_2][H_2]^0 = k[N_2]$ By the way, k has a value of 2.2×10^{-3} mol/L*s

29. Use data from Model 3 to determine the value and unit of the rate constant, k, in the rate law.

see above

30. Use the data below to determine the rate law for the process shown. Include the value and units on the rate constant k in your answer.

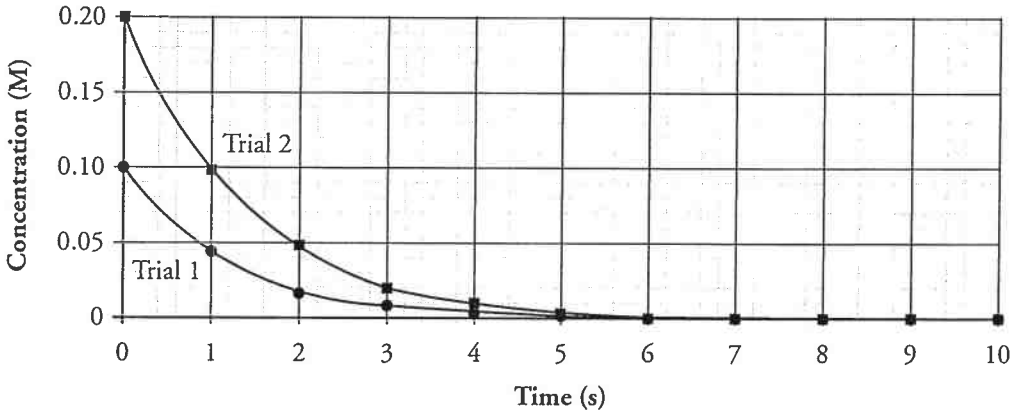
$2NO(g) + O_2(g) \rightarrow NO_2(g)$

Experiment	Initial [NO] (mole L^{-1})	Initial [O_2] (mole L^{-1})	Initial Rate of Formation of NO_2 (mole $L^{-1}s^{-1}$)
1	0.10	0.10	2.5×10^{-4}
2	0.20	0.10	5.0×10^{-4}
3	0.20	0.40	8.0×10^{-3}

first order in NO (lines 1 and 2) , second order in O_2 (lines 2 and 3, concentration quadruples rate goes up by factor of 16).
rate=$k[NO][O_2]^2$
the reaction is 3rd order overall. Thus, k =0.25 L^2 mol^{-2} sec^{-2}

Extension Questions

32. Consider the graph below.



a. What were the initial concentrations of the reactant being studied in the two trials for this rate law experiment?

0.1 and 0.2 mol L^{-1}

b. Estimate the initial rate for each trial using data from the graph.

You would draw a tangent line and estimate it's slope. I won't do that here.

c. Estimate the rate for each trial between 4 and 5 seconds into the reaction.

d. Why is the initial rate preferred to rates determined later in the process for determining the order of reaction with respect to a particular reactant?

because the rate is decreasing (and may be competing with the "back" reaction) as the reaction proceeds.