

14.5: Using Graphs to Determine Rate Laws, Rate Constants and Reaction Orders

Learning Objectives

- To use graphs to analyze the kinetics of a reaction.

In [Section 14.3](#), you learned that the integrated rate law for each common type of reaction (zeroth, first, or second order in a single reactant) can be plotted as a straight line. Using these plots offers an alternative to the methods described for showing how reactant concentration changes with time and determining reaction order.

We will illustrate the use of these graphs by considering the thermal decomposition of NO_2 gas at elevated temperatures, which occurs according to the following reaction:



Experimental data for this reaction at 330°C are listed in [Table 14.4.1](#); they are provided as $[\text{NO}_2]$, $\ln[\text{NO}_2]$, and $1/[\text{NO}_2]$ versus time to correspond to the integrated rate laws for zeroth-, first-, and second-order reactions, respectively. The actual concentrations of NO_2 are plotted versus time in part (a) in [Figure 14.4.1](#). Because the plot of $[\text{NO}_2]$ versus t is not a straight line, we know the reaction is not zeroth order in NO_2 . A plot of $\ln[\text{NO}_2]$ versus t (part (b) in [Figure 14.4.1](#)) shows us that the reaction is not first order in NO_2 because a first-order reaction would give a straight line. Having eliminated zeroth-order and first-order behavior, we construct a plot of $1/[\text{NO}_2]$ versus t (part (c) in [Figure 14.4.1](#)). This plot is a straight line, indicating that the reaction is second order in NO_2 .

Table 14.4.1 Concentration of NO_2 as a Function of Time at 330°C

Time (s)	$[\text{NO}_2]$ (M)	$\ln[\text{NO}_2]$	$1/[\text{NO}_2]$ (M^{-1})
0	1.00×10^{-2}	-4.605	100
60	6.83×10^{-3}	-4.986	146
120	5.18×10^{-3}	-5.263	193
180	4.18×10^{-3}	-5.477	239
240	3.50×10^{-3}	-5.655	286
300	3.01×10^{-3}	-5.806	332
360	2.64×10^{-3}	-5.937	379

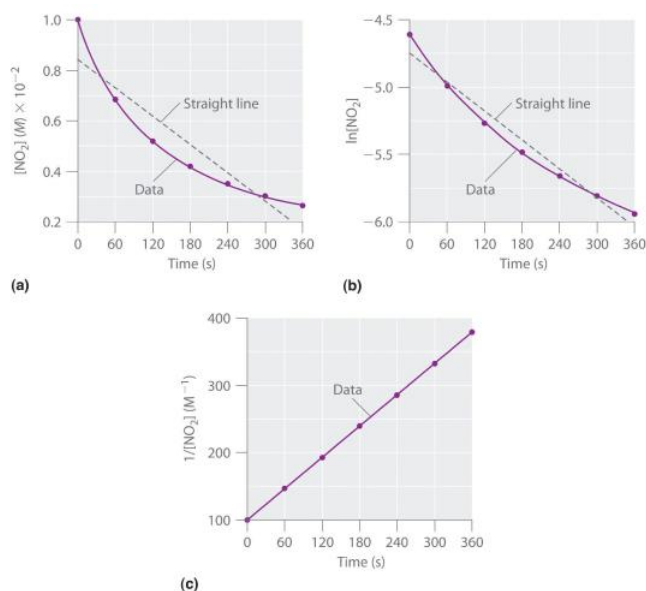


Figure 14.4.1 The Decomposition of NO₂ These plots show the decomposition of a sample of NO₂ at 330°C as (a) the concentration of NO₂ versus t , (b) the natural logarithm of [NO₂] versus t , and (c) $1/[\text{NO}_2]$ versus t .

We have just determined the reaction order using data from a single experiment by plotting the concentration of the reactant as a function of time. Because of the characteristic shapes of the lines shown in Figure 14.4.2, the graphs can be used to determine the reaction order of an unknown reaction. In contrast, the method described in Section 14.3 required multiple experiments at different NO₂ concentrations as well as accurate initial rates of reaction, which can be difficult to obtain for rapid reactions.




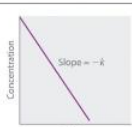
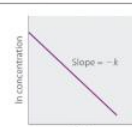

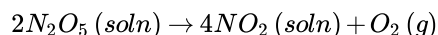
	Zeroth Order	First Order	Second Order																								
Differential rate law	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k$	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]$	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^2$																								
Concentration vs. time																											
Integrated rate law	$[A] = [A]_0 - kt$	$[A] = [A]_0 e^{-kt}$ or $\ln[A] = \ln[A]_0 - kt$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$																								
Straight-line plot to determine rate constant	 Slope = $-k$	 Slope = $-k$	 Slope = k																								
Relative rate vs. concentration	<table><tr><th>[A], M</th><th>Rate, M/s</th></tr><tr><td>1</td><td>1</td></tr><tr><td>2</td><td>1</td></tr><tr><td>3</td><td>1</td></tr></table>	[A], M	Rate, M/s	1	1	2	1	3	1	<table><tr><th>[A], M</th><th>Rate, M/s</th></tr><tr><td>1</td><td>1</td></tr><tr><td>2</td><td>2</td></tr><tr><td>3</td><td>3</td></tr></table>	[A], M	Rate, M/s	1	1	2	2	3	3	<table><tr><th>[A], M</th><th>Rate, M/s</th></tr><tr><td>1</td><td>1</td></tr><tr><td>2</td><td>4</td></tr><tr><td>3</td><td>9</td></tr></table>	[A], M	Rate, M/s	1	1	2	4	3	9
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1	1																										
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Half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$																								
Units of k , rate constant	M/s	1/s	M ⁻¹ s ⁻¹																								

Figure 14.4.2 Properties of Reactions That Obey Zeroth-, First-, and Second-Order Rate Laws

Example 14.4.1

Dinitrogen pentoxide (N₂O₅) decomposes to NO₂ and O₂ at relatively low temperatures in the following reaction:



This reaction is carried out in a CCl₄ solution at 45°C. The concentrations of N₂O₅ as a function of time are listed in the following table, together with the natural logarithms and reciprocal N₂O₅ concentrations. Plot a graph of the concentration versus t , \ln concentration versus t , and $1/\text{concentration}$ versus t and then determine the rate law and calculate the rate constant.

Time (s)	$[\text{N}_2\text{O}_5]$ (M)	$\ln[\text{N}_2\text{O}_5]$	$1/[\text{N}_2\text{O}_5]$ (M^{-1})
0	0.0365	-3.310	27.4
600	0.0274	-3.597	36.5
1200	0.0206	-3.882	48.5
1800	0.0157	-4.154	63.7
2400	0.0117	-4.448	85.5
3000	0.00860	-4.756	116
3600	0.00640	-5.051	156

Given: balanced chemical equation, reaction times, and concentrations

Asked for: graph of data, rate law, and rate constant

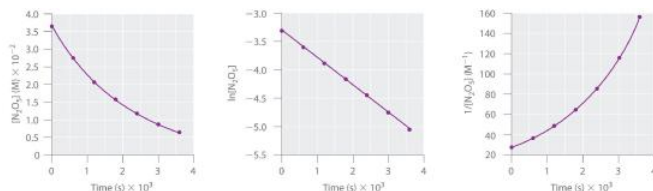
Strategy:

A Use the data in the table to separately plot concentration, the natural logarithm of the concentration, and the reciprocal of the concentration (the vertical axis) versus time (the horizontal axis). Compare the graphs with those in Figure 14.4.2 to determine the reaction order.

B Write the rate law for the reaction. Using the appropriate data from the table and the linear graph corresponding to the rate law for the reaction, calculate the slope of the plotted line to obtain the rate constant for the reaction.

Solution:

A Here are plots of $[\text{N}_2\text{O}_5]$ versus t , $\ln[\text{N}_2\text{O}_5]$ versus t , and $1/[\text{N}_2\text{O}_5]$ versus t :



The plot of $\ln[\text{N}_2\text{O}_5]$ versus t gives a straight line, whereas the plots of $[\text{N}_2\text{O}_5]$ versus t and $1/[\text{N}_2\text{O}_5]$ versus t do not. This means that the decomposition of N_2O_5 is first order in $[\text{N}_2\text{O}_5]$.

B The rate law for the reaction is therefore

$$\text{rate} = k[\text{N}_2\text{O}_5]$$

Calculating the rate constant is straightforward because we know that the slope of the plot of $\ln[A]$ versus t for a first-order reaction is $-k$. We can calculate the slope using any two points that lie on the line in the plot of $\ln[\text{N}_2\text{O}_5]$ versus t . Using the points for $t = 0$ and 3000 s,

$$\text{slope} = \frac{\ln[\text{N}_2\text{O}_5]_{3000} - \ln[\text{N}_2\text{O}_5]_0}{3000 \text{ s} - 0 \text{ s}} = \frac{[-4.756] - [-3.310]}{3000 \text{ s}} = -4.820 \times 10^{-4} \text{ s}^{-1}$$

Thus $k = 4.820 \times 10^{-4} \text{ s}^{-1}$.

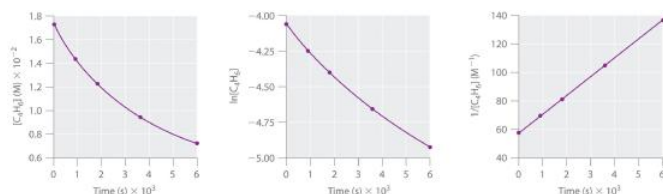
Exercise

1,3-Butadiene ($\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$; C_4H_6) is a volatile and reactive organic molecule used in the production of rubber. Above room temperature, it reacts slowly to form products. Concentrations of C_4H_6 as a function of time at 326°C are listed in the following table along with $\ln[\text{C}_4\text{H}_6]$ and the reciprocal concentrations. Graph the data as concentration versus t , \ln concentration versus t , and $1/\text{concentration}$ versus t . Then determine the reaction order in C_4H_6 , the rate law, and the rate constant for the reaction.

Time (s)	$[\text{C}_4\text{H}_6]$ (M)	$\ln[\text{C}_4\text{H}_6]$	$1/[\text{C}_4\text{H}_6]$ (M^{-1})

Time (s)	[C ₄ H ₆] (M)	ln[C ₄ H ₆]	1/[C ₄ H ₆] (M ⁻¹)
0	1.72×10^{-2}	-4.063	58.1
900	1.43×10^{-2}	-4.247	69.9
1800	1.23×10^{-2}	-4.398	81.3
3600	9.52×10^{-3}	-4.654	105
6000	7.30×10^{-3}	-4.920	137

Answer



second order in C₄H₆; rate = $k[\text{C}_4\text{H}_6]^2$; $k = 1.3 \times 10^{-2} \text{ M}^{-1}\cdot\text{s}^{-1}$

Summary

For a zeroth-order reaction, a plot of the concentration of any reactant versus time is a straight line with a slope of $-k$. For a first-order reaction, a plot of the natural logarithm of the concentration of a reactant versus time is a straight line with a slope of $-k$. For a second-order reaction, a plot of the inverse of the concentration of a reactant versus time is a straight line with a slope of k .

Key Takeaway

- Plotting the concentration of a reactant as a function of time produces a graph with a characteristic shape that can be used to identify the reaction order in that reactant.

Conceptual Problems

- Compare first-order differential and integrated rate laws with respect to the following. Is there any information that can be obtained from the integrated rate law that cannot be obtained from the differential rate law?
 - the magnitude of the rate constant
 - the information needed to determine the order
 - the shape of the graphs
- In the single-step, second-order reaction $2\text{A} \rightarrow \text{products}$, how would a graph of $[\text{A}]$ versus time compare to a plot of $1/[\text{A}]$ versus time? Which of these would be the most similar to the same set of graphs for A during the single-step, second-order reaction $\text{A} + \text{B} \rightarrow \text{products}$? Explain.
- For reactions of the same order, what is the relationship between the magnitude of the rate constant and the reaction rate? If you were comparing reactions with different orders, could the same arguments be made? Why?

Answers

- For a given reaction under particular conditions, the magnitude of the first-order rate constant does not depend on whether a differential rate law or an integrated rate law is used.
 - The differential rate law requires multiple experiments to determine reactant order; the integrated rate law needs only one experiment.
 - Using the differential rate law, a graph of concentration versus time is a curve with a slope that becomes less negative with time, whereas for the integrated rate law, a graph of $\ln[\text{reactant}]$ versus time gives a straight line with slope $= -k$. The integrated rate law allows you to calculate the concentration of a reactant at any time during the reaction; the differential rate law does not.
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3. The reaction rate increases as the rate constant increases. We cannot directly compare reaction rates and rate constants for reactions of different orders because they are not mathematically equivalent.

Numerical Problems

1. One method of using graphs to determine reaction order is to use relative rate information. Plotting the log of the relative rate versus log of relative concentration provides information about the reaction. Here is an example of data from a zeroth-order reaction:

Relative [A] (M)	Relative Rate (M/s)
1	1
2	1
3	1

Varying [A] does not alter the reaction rate. Using the relative rates in the table, generate plots of $\log(\text{rate})$ versus $\log(\text{concentration})$ for zeroth-, first- and second-order reactions. What does the slope of each line represent?

2. The table below follows the decomposition of N_2O_5 gas by examining the partial pressure of the gas as a function of time at 45°C . What is the reaction order? What is the rate constant? How long would it take for the pressure to reach 105 mmHg at 45°C ?

Time (s)	Pressure (mmHg)
0	348
400	276
1600	156
3200	69
4800	33

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