



Using Graphs to Determine Integrated Rate Laws

Skills to Develop

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

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 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.

Table 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

The actual concentrations of NO_2 are plotted versus time in part (a) in Figure 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 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 1). This plot is a straight line, indicating that the reaction is second order in NO_2 .

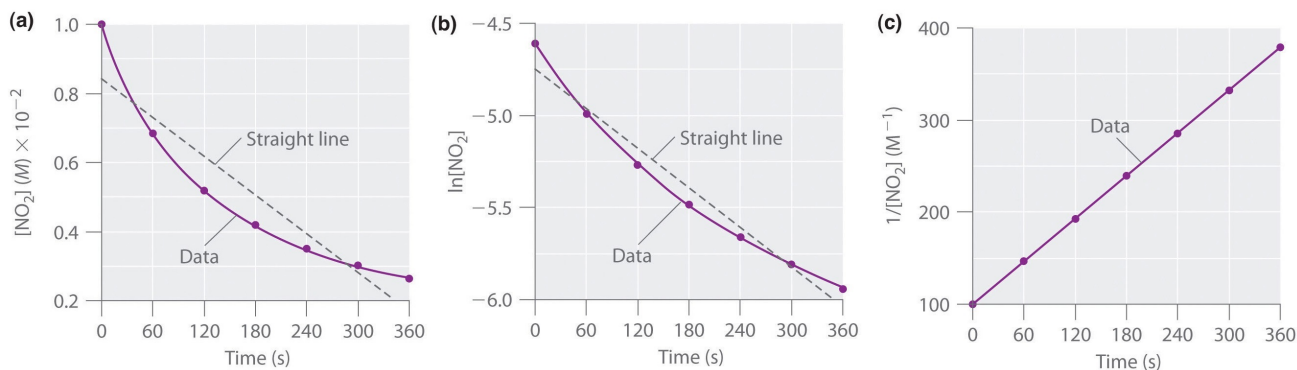


Figure 1: The Decomposition of NO_2 . These plots show the decomposition of a sample of NO_2 at 330°C as (a) the concentration of NO_2 versus t , (b) the natural logarithm of $[\text{NO}_2]$ versus t , and (c) $1/[\text{NO}_2]$ versus t .

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 2, the graphs can be used to determine the reaction order of an unknown reaction. In contrast, the method of initial rates required multiple experiments at different NO_2 concentrations as well as accurate initial rates of reaction, which can be difficult to obtain for rapid reactions.



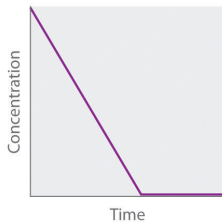
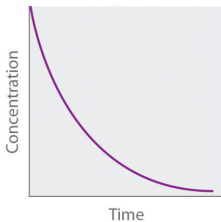
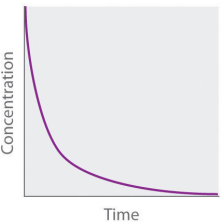
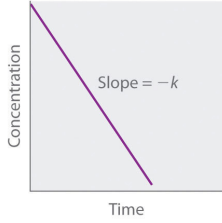

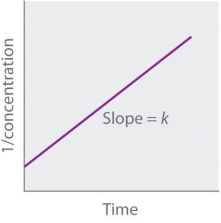
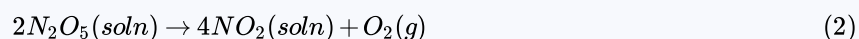
	Zeroth Order	First Order	Second Order																								
Differential rate law	Rate = $-\frac{\Delta[A]}{\Delta t} = k$	Rate = $-\frac{\Delta[A]}{\Delta t} = k[A]$	Rate = $-\frac{\Delta[A]}{\Delta t} = k[A]^2$																								
Concentration vs. time																											
Integrated rate 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																											
Relative rate vs. concentration	<table border="1"> <thead> <tr> <th>[A], M</th> <th>Rate, M/s</th> </tr> </thead> <tbody> <tr><td>1</td><td>1</td></tr> <tr><td>2</td><td>1</td></tr> <tr><td>3</td><td>1</td></tr> </tbody> </table>	[A], M	Rate, M/s	1	1	2	1	3	1	<table border="1"> <thead> <tr> <th>[A], M</th> <th>Rate, M/s</th> </tr> </thead> <tbody> <tr><td>1</td><td>1</td></tr> <tr><td>2</td><td>2</td></tr> <tr><td>3</td><td>3</td></tr> </tbody> </table>	[A], M	Rate, M/s	1	1	2	2	3	3	<table border="1"> <thead> <tr> <th>[A], M</th> <th>Rate, M/s</th> </tr> </thead> <tbody> <tr><td>1</td><td>1</td></tr> <tr><td>2</td><td>4</td></tr> <tr><td>3</td><td>9</td></tr> </tbody> </table>	[A], M	Rate, M/s	1	1	2	4	3	9
[A], M	Rate, M/s																										
1	1																										
2	1																										
3	1																										
[A], M	Rate, M/s																										
1	1																										
2	2																										
3	3																										
[A], M	Rate, M/s																										
1	1																										
2	4																										
3	9																										
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 2: Properties of Reactions That Obey Zeroth-, First-, and Second-Order Rate Laws

Example 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/concentration versus *t* and then determine the rate law and calculate the rate constant.

Time (s)	[N ₂ O ₅] (M)	ln[N ₂ O ₅]	1/[N ₂ 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



Time (s)	[N ₂ O ₅] (M)	ln[N ₂ O ₅]	1/[N ₂ O ₅] (M ⁻¹)
3600	0.00640	-5.051	156

Given: balanced chemical equation, reaction times, and concentrations

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

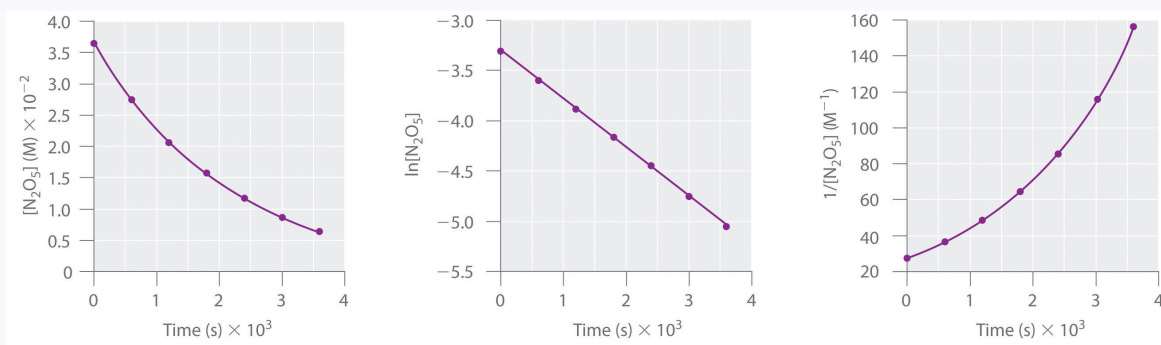
Strategy:

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 1 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 [N₂O₅] versus *t*, ln[N₂O₅] versus *t*, and 1/[N₂O₅] versus *t*:



The plot of ln[N₂O₅] versus *t* gives a straight line, whereas the plots of [N₂O₅] versus *t* and 1/[N₂O₅] versus *t* do not. This means that the decomposition of N₂O₅ is first order in [N₂O₅].

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[N₂O₅] versus *t*. Using the points for *t* = 0 and 3000 s,

$$\text{slope} = \frac{\ln[\text{N}_2\text{O}_5]_{3000} - \ln[\text{N}_2\text{O}_5]_0}{3000 \text{ s} - 0 \text{ s}} = \frac{(-4.756) - (-3.310)}{3000 \text{ s}} = -4.820 \times 10^{-4} \text{ s}^{-1} \quad (3)$$

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

Exercise 1

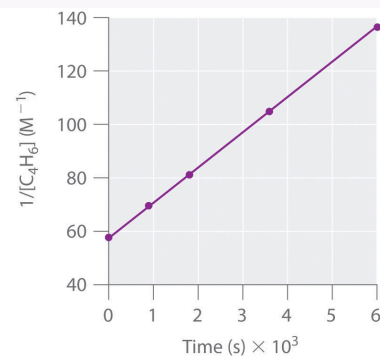
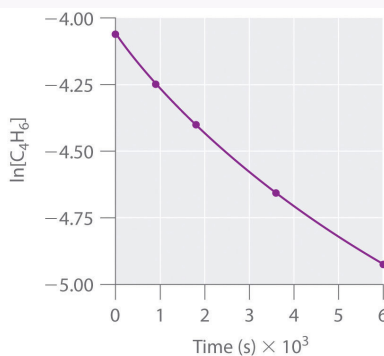
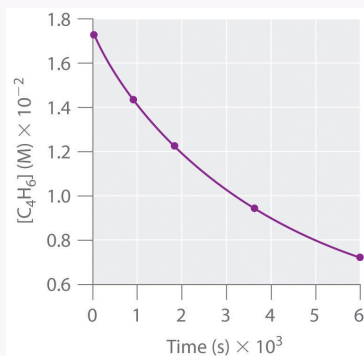
1,3-Butadiene (CH₂=CH—CH=CH₂; C₄H₆) is a volatile and reactive organic molecule used in the production of rubber. Above room temperature, it reacts slowly to form products. Concentrations of C₄H₆ as a function of time at 326°C are listed in the following table along with ln[C₄H₆] and the reciprocal concentrations. Graph the data as concentration versus *t*, ln concentration versus *t*, and 1/concentration versus *t*. Then determine the reaction order in C₄H₆, the rate law, and the rate constant for the reaction.

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



Time (s)	[C ₄ H ₆] (M)	ln[C ₄ H ₆]	1/[C ₄ H ₆] (M ⁻¹)
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 .