

Determining a Rate Law

A “Sulfur Clock” Reaction

Introduction

The rate of a chemical reaction may depend on the concentration of one or more reactants, or it may be independent of the concentration of a given reactant. Exactly how the rate depends on reactant concentrations is expressed in an equation called the rate law. How can the rate law for a reaction be determined?

Concepts

- Kinetics
- Rate law
- Order of reaction
- Concentration

Background

For a general reaction of the form



the rate law can be written as

$$\text{Rate} = k[A]^m[B]^n \quad \text{Equation 2}$$

where k is the rate constant, $[A]$ and $[B]$ are the molar concentrations of the reactants, and m and n are exponents that define how the rate depends on the individual reactant concentrations. The values of m and n must be determined by experiment—they cannot be determined simply by looking at the balanced chemical equation. The rate constant for a reaction does not depend on the reactant concentrations, but it does depend on temperature. The exponents m and n are also referred to as the *order of reaction* with respect to a particular reactant. In the previous example, the reaction is said to be *m*th order in A and *n*th order in B . In general, m and n will be positive whole numbers—typical values of m and n are 0, 1, and 2.

Rate laws for different reactions take on different forms. The following reactions and their experimentally determined rate laws demonstrate that the order of reaction cannot be predicted using the coefficients in the balanced chemical equations.

Chemical Equation	Rate Law
$\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{CO}_2(\text{g})$	$\text{Rate} = k[\text{NO}_2]^2$
$2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$	$\text{Rate} = k[\text{NO}]^2[\text{O}_2]$
$2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$	$\text{Rate} = k[\text{N}_2\text{O}_5]$

The reaction order for each reactant in the rate law determines how the rate changes as the concentration of that reactant changes. If a reactant has an order of zero, the reactant does not appear in the rate law, and the rate is independent of its concentration. Increasing or decreasing the concentration of a zero-order reactant does not affect the rate of the reaction.

When a reaction is first order in a reactant, the reactant appears in the rate law with an exponent of 1—the rate is directly proportional to the reactant concentration. If the concentration of a first-order reactant is doubled, the rate will also double. For a reaction that is second order in a reactant, the reactant concentration appears in the rate law with an exponent of 2. If the concentration of a second-order reactant is doubled, the rate of the reaction will increase by a factor of four.

The general procedure in this activity may be used to determine the rate law for a reaction. First, the concentration of one reactant is held constant while the concentration of a second reactant is varied, and the reaction time is measured. Then, the first reactant's concentration is varied while the second reactant's concentration is held constant, and again the reaction time is measured. The average rate for each reaction is calculated by taking the inverse of the reaction time. The data are then analyzed to determine the reaction order for each reactant and the rate law.

Consider the reaction between nitric oxide and oxygen gas.



$$\text{Rate} = k[\text{NO}]^2[\text{O}_2] \quad \text{Equation 4}$$

The data in Table 1 were obtained by performing the reaction five times and varying the concentrations of the reactants as indicated. In each case, the reaction time was measured, then inverted to find the average rate.

Table 1.

Trial	[NO]	[O ₂]	Reaction Time (sec)	Average Rate (sec ⁻¹)
1	0.020	0.010	35.7	0.028
2	0.020	0.020	17.5	0.057
3	0.020	0.040	8.8	0.11
4	0.040	0.020	4.4	0.23
5	0.010	0.020	71.4	0.014

Lab Sulfur Clock Answers

Ray H. Boundy, J. Lawrence Amos

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Table of Contents Lab Sulfur Clock Answers

1. Understanding the eBook Lab Sulfur Clock Answers
 - The Rise of Digital Reading Lab Sulfur Clock Answers
 - Advantages of eBooks Over Traditional Books
2. Identifying Lab Sulfur Clock Answers
 - Exploring Different Genres
 - Considering Fiction vs. Non-Fiction
 - Determining Your Reading Goals
3. Choosing the Right eBook Platform
 - Popular eBook Platforms
 - Features to Look for in an Lab Sulfur Clock Answers
 - User-Friendly Interface
4. Exploring eBook Recommendations from Lab Sulfur Clock Answers
 - Personalized Recommendations

- Lab Sulfur Clock Answers User Reviews and Ratings
- Lab Sulfur Clock Answers and Bestseller Lists
- 5. Accessing Lab Sulfur Clock Answers Free and Paid eBooks
 - Lab Sulfur Clock Answers Public Domain eBooks
 - Lab Sulfur Clock Answers eBook Subscription Services
 - Lab Sulfur Clock Answers Budget-Friendly Options
- 6. Navigating Lab Sulfur Clock Answers eBook Formats
 - ePub, PDF, MOBI, and More
 - Lab Sulfur Clock Answers Compatibility with Devices
 - Lab Sulfur Clock Answers Enhanced eBook Features
- 7. Enhancing Your Reading Experience
 - Adjustable Fonts and Text Sizes of Lab Sulfur Clock Answers
 - Highlighting and Note-Taking Lab Sulfur Clock Answers
 - Interactive Elements Lab Sulfur Clock Answers
- 8. Staying Engaged with Lab Sulfur Clock Answers
 - Joining Online Reading Communities
 - Participating in Virtual Book Clubs
 - Following Authors and Publishers Lab Sulfur Clock Answers
- 9. Balancing eBooks and Physical Books Lab Sulfur Clock Answers
 - Benefits of a Digital Library
 - Creating a Diverse Reading Collection Lab Sulfur Clock Answers
- 10. Overcoming Reading Challenges
 - Dealing with Digital Eye Strain
 - Minimizing Distractions
 - Managing Screen Time
- 11. Cultivating a Reading Routine Lab Sulfur Clock Answers
 - Setting Reading Goals Lab Sulfur Clock Answers
 - Carving Out Dedicated Reading Time
- 12. Sourcing Reliable Information of Lab Sulfur Clock Answers
 - Fact-Checking eBook Content of Lab Sulfur Clock Answers

- Distinguishing Credible Sources
- 13. Promoting Lifelong Learning
 - Utilizing eBooks for Skill Development
 - Exploring Educational eBooks
- 14. Embracing eBook Trends
 - Integration of Multimedia Elements
 - Interactive and Gamified eBooks

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