

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

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