The reaction order is the relationship between the concentrations of species and the rate of a reaction.

Introduction

The order of a rate law is the sum of the exponents of its concentration terms. Once the rate law of a reaction has been determined, that same law can be used to understand more fully the composition of the reaction mixture. More specifically, the reaction order is the exponent to which the concentration of that species is raised, and it indicates to what extent the concentration of a species affects the rate of a reaction, as well as which species has the greatest effect. For the N$_2$O$_5$ decomposition with a rate law of $k[N_2O_5]$, this exponent is 1 (and thus is not explicitly shown); this reaction is therefore a first order reaction. It can also be said that the reaction is "first order in N$_2$O$_5$". For more complicated rate laws, the overall reaction order and the orders with respect to each component are used. As an example, consider the following reaction,

\[ A + 3B + 2C \rightarrow \text{products} \]

whose experimental rate law is given by:

\[ \text{rate} = k[A][B]^2 \]

This reaction is third-order overall, first-order in A, second-order in B, and zero-order in C.

Zero-order means that the rate is independent of the concentration of a particular reactant. Of course, enough C must be present to allow the equilibrium mixture to form.

Relation to Rate Law

For the reaction:

\[ aA + bB \rightarrow P \]

The rate law is as follows:

\[ \text{rate}=k[A]^x[B]^y \]

where

- $[A]$ is the concentration of species A,
- $x$ is the order with respect to species A.
- $[B]$ is the concentration of species B,
- $y$ is the order with respect to species B.
- $k$ is the rate constant.
- $n$ is the reaction order for the whole chemical reaction. This can be found by adding the reaction orders with respect
Simple Rules

The order of a reaction is not necessarily an integer. The following orders are possible:

- Zero: A zero order indicates that the concentration of that species does not affect the rate of a reaction.
- Negative integer: A negative order indicates that the concentration of that species inversely affects the rate of a reaction.
- Positive integer: A positive order indicates that the concentration of that species directly affects the rate of a reaction.
- Non-integer: Non-integer orders, both positive and negative, represent more intricate relationships between concentrations and rate in more complex reactions.

Example 1

The rate of oxidation of bromide ions by bromate in an acidic aqueous solution,

$$6H^+ + BrO_3^- + 5Br^- \rightarrow 3 Br_2 + 3 H_2O$$

is found to follow the following rate law:

$$\text{rate} = k[Br^-][BrO_3^-][H^+]^2$$

What happens to the rate if, in separate experiments, (a) $[BrO_3^-]$ is doubled; (b) the pH is increased by one unit; (c) the solution is diluted to twice its volume, with the pH held constant using a buffer?

SOLUTION

a. Because the rate is first-order in bromate, doubling its concentration doubles the reaction rate.

b. Increasing the pH by one unit decreases the $[H^+]$ by a factor of 10. Because the reaction is second-order in $[H^+]$, this decreases the rate by a factor of 100.

c. Dilution reduces the concentrations of both $Br_2$ and $BrO_3^-$ to half their original values. Doing this to each concentration alone would reduce the rate by a factor of 2, so reducing both concentration reduces the rate by a factor of 4, to $(\frac{1}{2}) \times (\frac{1}{2}) = \frac{1}{4}$ of its initial value.

Methods to Determining Reaction Order

For chemical reactions that require only one elementary step, the values of $x$ and $y$ are equal to the stoichiometric coefficients of each reactant. For chemical reactions that require more than one elementary step, this is not always the case. However, there are many simple ways of determining the order of a reaction. One very popular method is known as the differential method.
The Differential Method

The differential method, also known as the initial rates method, uses an experimental data table to determine the order of a reaction with respect to the reactants used. Below is an example of a table corresponding with the following chemical reaction:

\[ A + B \rightarrow P \]

<table>
<thead>
<tr>
<th>Experiment</th>
<th>[A] M</th>
<th>[B] M</th>
<th>Rate M Min^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.100</td>
<td>0.100</td>
<td>1.0 x 10^{-3}</td>
</tr>
<tr>
<td>2</td>
<td>0.200</td>
<td>0.100</td>
<td>1.0 X 10^{-3}</td>
</tr>
<tr>
<td>3</td>
<td>0.100</td>
<td>0.200</td>
<td>2.0 x 10^{-3}</td>
</tr>
</tbody>
</table>

When looking at the experiments in the table above, it is important to note factors that change between experiments. In order to determine the reaction order with respect to A, one must note in which experiment A is changing; that is, between experiments 1 and 2. Write a rate law equation based on the chemical reaction above.

This is the rate law:

\( \text{rate} = k[A]^x[B]^y \)

Next, the rate law equation from experiment 2 must be divided by the rate law equation for experiment 1. Notice that the \([B]^y\) term cancels out, leaving "x" as the unknown variable. Simple algebra reveals that \(x = 0\).

The same steps must be taken for determining the reaction order with respect to B. However, in this case experiments 1 and 3 are used. After working through the problem and canceling out \([A]^x\) from the equation, \(y = 1\).

Finding the reaction order for the whole process is the easy addition of \(x\) and \(y\): \(n = 0 + 1\). Therefore, \(n = 1\)

After finding the reaction order, several pieces of information can be obtained, such as half-life.

Other methods

Other methods that can be used to solve for reaction order include the integration method, the half-life method, and the isolation method.
Problems

1. Define "reaction order."

Use the following information to solve questions 2 and 3:

Given the rate law equation:

\[
\text{rate} = k[A]^1[B]^2
\]

2. Determine: a) the reaction order with respect to A, b) the reaction order with respect to B, and c) the total reaction order for the equation.

3. Assuming the reaction occurs in one elementary step, propose a chemical equation using P as the symbol for your product.

Use the data table below to answer questions 4 and 5:

<table>
<thead>
<tr>
<th>Experiment</th>
<th>[A] M M</th>
<th>[B] M M</th>
<th>Rate M Min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.100</td>
<td>0.100</td>
<td>1.0 x 10⁻³</td>
</tr>
<tr>
<td>2</td>
<td>0.400</td>
<td>0.100</td>
<td>2.0 x 10⁻³</td>
</tr>
<tr>
<td>3</td>
<td>0.100</td>
<td>0.150</td>
<td>2.0 x 10⁻³</td>
</tr>
</tbody>
</table>

4. Use the differential method to determine the reaction order with respect to A (x) and B (y). What is the total reaction order (n)?

5. What is the rate constant, k?

Answers

1. The relationship between the concentrations of species and the rate of a reaction
2. a) x = 1, b) y = 2, and c) n = 3
3. \( A + 2B \rightarrow P \)
4. x = 0.5 and y = 1.7. n = 2.2
5. k = 0.10 M min⁻¹

References

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• Stephen Lower, Professor Emeritus (Simon Fraser U.) Chem1 Virtual Textbook