Measuring Reaction Rates

The method for determining a reaction rate is relatively straightforward. Since a reaction rate is based on change over time, it must be determined from tabulated values or found experimentally. With the obtained data, it is possible to calculate the reaction rate either algebraically or graphically. What follows is general guidance and examples of measuring the rates of a reaction.

Introduction

Measuring time change is easy; a stopwatch or any other time device is sufficient. However, determining the change in concentration of the reactants or products involves more complicated processes. The change of concentration in a system can generally be acquired in two ways:

1. By monitoring the depletion of reactant over time, or
2. By monitoring the formation of product over time

Methods for measuring concentration

- For gases, experimenters use a buret to measure the change in volume produced at different times. They then relate these volumes to changes in concentration.
- Chemists can also remove small samples of a reaction mixture at various times and analyze the concentration using titration.
- Additional methods include the use of a spectrophotometer to determine the concentration using Beer's law. Or, more advanced techniques for very fast reactions use computers connected to advanced laser technology such as laser magnetic resonance (LMR).

For supplemental information relating to measuring reaction rates, such as the concentration of reactants, the role of catalysts, the characteristics of the rate of a chemical reaction.
Measuring Reagents Versus Product

It does not matter whether an experimenter monitors the reagents or products because there is no effect on the overall reaction. However, since reagents decrease during reaction, and products increase, there is a sign difference between the two rates. Reagent concentration decreases as the reaction proceeds, giving a negative number for the change in concentration. The products, on the other hand, increase concentration with time, giving a positive number. Since the convention is to express the rate of reaction as a positive number, to solve a problem, set the overall rate of the reaction equal to the negative of a reagent's disappearing rate. The overall rate also depends on stoichiometric coefficients.

It is worth noting that the process of measuring the concentration can be greatly simplified by taking advantage of the different physical or chemical properties (i.e., phase difference, reduction potential, etc.) of the reagents or products involved in the reaction by using the above methods. We have emphasized the importance of taking the sign of the reaction into account to get a positive reaction rate. Now, we will turn our attention to the importance of stoichiometric coefficients.

Unique Average Rate of Reaction

A reaction rate can be reported quite differently depending on which product or reagent selected to be monitored.

Given a reaction:

\[ aA + bB \rightarrow cC + dD \]

rate of reaction = \( -\dfrac{1}{a}\dfrac{\Delta[A]}{\Delta t} = -\dfrac{1}{b}\dfrac{\Delta[B]}{\Delta t} = \dfrac{1}{c}\dfrac{\Delta[C]}{\Delta t} = \dfrac{1}{d}\dfrac{\Delta[D]}{\Delta t} \)

This formula can also be written as:

rate of reaction = \( -\dfrac{1}{a}\) (rate of disappearance of A)

= \( -\dfrac{1}{b}\) (rate of disappearance of B)

= \( \dfrac{1}{c}\) (rate of formation of C)

= \( \dfrac{1}{d}\) (rate of formation of D)

Even though the concentrations of A, B, C and D may all change at different rates, there is only one average rate of reaction. To get this unique rate, choose any one rate and divide it by the stoichiometric coefficient. When the reaction has the formula:

\[ C_{R1}R_1 + \ldots + C_{Rn}R_n \rightarrow C_{P1}P_1 + \ldots + C_{Pn}P_n \]

The general case of the unique average rate of reaction has the form:

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rate of reaction = \(( - \frac{1}{C_{R1}} \frac{\Delta [R_1]}{\Delta t} = \dots = -\frac{1}{C_{Rn}} \frac{\Delta [R_n]}{\Delta t} = \frac{1}{C_{P1}} \frac{\Delta [P_1]}{\Delta t} = \dots = \frac{1}{C_{Pn}} \frac{\Delta [P_n]}{\Delta t} )\)

Example 1

For the reaction,

\(( 2A + B \rightarrow 2C + D )\)

a) find the reaction rate and b) find the reaction rate given \(( \Delta [A] ) = 0.002 \text{ M} \) and \(( \Delta [A] ) = 77 \text{ sec} \).

**SOLUTION**

a) rate of reaction = \((- \frac{1}{2} \frac{\Delta [A]}{\Delta t} = -\frac{\Delta [B]}{\Delta t} = \frac{1}{2} \frac{\Delta [C]}{\Delta t} = \frac{\Delta [D]}{\Delta t} )\)

b) rate of disappearance of A = \((- \frac{\Delta [A]}{\Delta t} = -0.000026 \text{ M per sec} )\)

rate of reaction = \((- \frac{1}{2} \frac{\Delta [A]}{\Delta t} )\) (rate of disappearance of A) \(= -0.000026 \text{ M per sec} \)

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**Average and Instantaneous Reaction Rate**

Reaction rates have the general form of (change of concentration / change of time).There are two types of reaction rates. One is called the average rate of reaction, often denoted by \(( \Delta \text{[conc.]} / \Delta t )\), while the other is referred to as the instantaneous rate of reaction, denoted as either:

\( \lim_{\Delta t \rightarrow 0} \frac{\Delta \text{[conc.]} }{\Delta t} \) or \[ \frac{d \text{[conc.]} }{dt} \]

The average rate of reaction, as the name suggests, is an average rate, obtained by taking the change in concentration over a time period, for example: \(-0.3 \text{ M / 15 minutes} \). This is an approximation of the reaction rate in the interval; it does not necessarily mean that the reaction has this specific rate throughout the time interval or even at any instant during that time. The instantaneous rate of reaction, on the other hand, depicts a more accurate value. The instantaneous rate of reaction is defined as the change in concentration of an infinitely small time interval, expressed as the limit or derivative expression above. Instantaneous rate can be obtained from the experimental data by first graphing the concentration of a system as function of time, and then finding the slope of the tangent line at a specific point which corresponds to a time of interest. Alternatively, experimenters can measure the change in concentration over a very small time period two or more times to get an average rate close to that of the instantaneous rate. The reaction rate for that time is determined from the slope of the tangent lines.

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Initial Rate of Reaction

The initial rate of reaction is the rate at which the reagents are first brought together. Like the instantaneous rate mentioned above, the initial rate can be obtained either experimentally or graphically. To experimentally determine the initial rate, an experimenter must bring the reagents together and measure the reaction rate as quickly as possible. If this is not possible, the experimenter can find the initial rate graphically. To do this, he must simply find the slope of the line tangent to the reaction curve when \( t=0 \).

Example

Determine the initial rate of the reaction using the table below.

<table>
<thead>
<tr>
<th>Time</th>
<th>[A]</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>1.55</td>
</tr>
<tr>
<td>200</td>
<td>0.99</td>
</tr>
<tr>
<td>300</td>
<td>0.67</td>
</tr>
<tr>
<td>400</td>
<td>0.45</td>
</tr>
<tr>
<td>500</td>
<td>0.34</td>
</tr>
<tr>
<td>600</td>
<td>0.24</td>
</tr>
</tbody>
</table>

**SOLUTION**

\[
\text{initial rate of reaction} = \left( \frac{-0}{(195-0) \text{ sec}} \right) = 0.0125 \text{ M per sec}
\]

Use the points \([A]=2.43 \text{ M}, t=0 \) and \([A]=1.55, t=100 \)

\[
\text{initial rate of reaction} = \left( \frac{-(1.55-2.43) \text{ M}}{(100-0) \text{ sec}} \right) = 0.0088 \text{ M per sec}
\]

References

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