Chemical reactions vary greatly in the speed at which they occur. Some are essentially instantaneous, while others may take years to reach equilibrium. The Reaction Rate for a given chemical reaction is the measure of the change in concentration of the reactants or the change in concentration of the products per unit time.

**Definition of reaction rate**

The speed of a chemical reaction may be defined as the change in concentration of a substance divided by the time interval during which this change is observed:

\[ \text{rate} = \frac{\Delta \text{concentration}}{\Delta \text{time}} \tag{2-1} \]

For a reaction of the form \(A + B \rightarrow C\), the rate can be expressed in terms of the change in concentration of any of its components:

\[ \text{rate} = -\frac{\Delta [A]}{\Delta t} \]

\[ \text{rate} = -\frac{\Delta [B]}{\Delta t} \]

\[ \text{rate} = \frac{\Delta [C]}{\Delta t} \]

in which \(\Delta [A]\) is the difference between the concentration of A over the time interval \(t_2 - t_1\):

\[ \Delta [A] = [A]_2 - [A]_1 \tag{2-2} \]

Notice the minus signs in the first two examples above. The concentration of a reactant always decreases with time, so \(\Delta [A]\) and \(\Delta [A]\) are both negative. Since negative rates do not make much sense, rates expressed in terms of a reactant concentration are always preceded by a minus sign to make the rate come out positive.

Consider now a reaction in which the coefficients are different:

\[ A + 3B \rightarrow 2D \]

It is clear that \(\Delta [B]\) decreases three times as rapidly as \(\Delta [A]\), so in order to avoid ambiguity when expressing the rate in terms of different components, it is customary to divide each change in concentration by the appropriate coefficient.
\[ \text{rate} = -\frac{\Delta [A]}{\Delta t} = -\frac{\Delta [B]}{3\Delta t} = \frac{\Delta [D]}{2\Delta t} \tag{2-3} \]

Example 1

For the oxidation of ammonia

\[ 4 \text{NH}_3 + 3\text{O}_2 \rightarrow 2\text{N}_2 + 6\text{H}_2\text{O} \]

it was found that the rate of formation of \( \text{N}_2 \) was 0.27 mol \( \text{L}^{-1} \text{ s}^{-1} \).

a. At what rate was water being formed?

b. At what rate was ammonia being consumed?

**SOLUTION**

a) From the equation stoichiometry, \( \Delta \text{H}_2\text{O} = 6/2 \Delta \text{N}_2 \), so the rate of formation of \( \text{H}_2\text{O} \) is

\[
3 \times (0.27 \text{ mol L}^{-1} \text{ s}^{-1}) = 0.81 \text{ mol L}^{-1} \text{ s}^{-1}.
\]

b) 4 moles of \( \text{NH}_3 \) are consumed for every 2 moles of \( \text{N}_2 \) formed, so the rate of disappearance of ammonia is

\[
2 \times (0.27 \text{ mol L}^{-1} \text{ s}^{-1}) = 0.54 \text{ mol L}^{-1} \text{ s}^{-1}.
\]

Comment: Because of the way this question is formulated, it would be acceptable to express this last value as a negative number.

**Instantaneous rates**

Most reactions slow down as the reactants are consumed. Consequently, the rates given by the expressions shown above tend to lose their meaning when measured over longer time intervals \( \Delta t \). Note: Instantaneous rates are also known as differential rates.

Thus for the reaction whose progress is plotted here, the actual rate (as measured by the increasing concentration of product) varies continuously, being greatest at time zero. The *instantaneous rate* of a reaction is given by the slope of a tangent to the concentration-vs.-time curve.

An instantaneous rate taken near the beginning of the reaction (\( t = 0 \)) is known as an *initial rate* (label (1) here). As we shall soon see, initial rates play an important role in the study of reaction kinetics. If you have studied *differential calculus*, you will know that these tangent slopes are *derivatives* whose values can vary at each point on the curve, so that these instantaneous rates are really *limiting rates* defined as

\[
\text{rate} = \lim_{\Delta t \to 0} \frac{\{-[A]\}}{\Delta T}
\]

If you do not know calculus, bear in mind that the larger the time interval \( \Delta t \), the smaller will be the precision of the instantaneous rate.
Introduction

During the course of the reaction shown below, reactants A and B are consumed while the concentration of product AB increases. The reaction rate can be determined by measuring how fast the concentration of A or B decreases, or by how fast the concentration of AB increases.

\[
\text{A + B} \rightarrow \text{AB}
\]

*Figure 1. The above picture shows a hypothetical reaction profile in which the reactants (red) decrease in concentration as the products increase in concentration (blue).*

For the stochiometrically complicated Reaction:

\[
\text{aA + bB} \rightarrow \text{cC + dD} \tag{1}
\]

\[
\text{Rate} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}
\]

Looking at Figure 1 above, we can see that the rate can be measured in terms of either reactant (A or B) or either product (C or D). Not all variables are needed to solve for the rate. Therefore, if you have the value for "A" as well as the value for "a" you can solve for the reaction rate.

You can also notice from Formula 1 above that, the change in reactants over the change in time must have a negative sign in front of them. The reason for this is because the reactants are decreasing as a function of time, the rate would come out to be negative (because it is the reverse rate). Therefore, putting a negative sign in front of the variable will allow for the solution to be a positive rate.

Rate Laws and Rate Constants

A rate law is an expression which relates that rate of a reaction to the rate constant and the concentrations of the reactants. A rate constant, \(k\), is a proportionality constant for a given reaction. The general rate law is usually expressed as:
\[ \text{Rate} = k[A]^s[B]^t \tag{2} \]

As you can see from equation 2 above, the reaction rate is **dependent** on the concentration of the reactants as well as the rate constant. However, there are also other factors that can influence the rate of reaction. These factors include temperature and catalysts. When you are able to write a rate law equation for a certain reaction, you can determine the **Reaction Order** based on the values of s and t.

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**Temperature Dependence**

**Reaction Rate**

If you were to observe a chemical reaction to occur in two different setting (one at a higher temperature than the other), you would most likely observe the reaction occurring at a higher temperature to have a higher rate. This is because as you increase the temperature, the kinetic energy of the reactants increase, allowing for more collisions between the molecules. This, therefore, allows for products to be formed faster. A simple rule of thumb that can be used is: for every 10°C increase, the reaction rate doubles.

However, increasing the temperature will not always increase the rate of the reaction. If the temperature of a reaction were to reach a certain point where the reactant will begin to degrade, it will decrease the rate of the reaction.

**Rate Constant**

As stated in the note above, the rate constant, k, is dependent on the temperature of which the reaction takes place. This can be seen through the **Arrhenius Equation** shown below:

\[ k = Ae^{-E_a/RT} \tag{3} \]

As you can see from equation 3, the rate constant \( (k) \) is dependent on the temperature (in Kelvins) and also the Activation energy, \( E_a \) (in joules). "A" in the equation represents a pre-exponential factor that has the same units as k. Finally, R is the universal gas constant.

**Catalysts**

Catalysts are a class of molecules which lower the activation energy (\( E_a \)) required for reactants to collide and form products. They are not consumed in the reaction themselves, therefore they are only there to basically assist the reaction is progressing forward. Thus, catalysts increase the rate of reaction. The most common type of catalyst is the **Enzyme Catalyst**. In chemical reactions, products are formed when reactants collide with one another. Enzymes allow for reactants to collide in perfect orientation making the reaction more effective in forming products.
Reaction Order

The reaction rate for a given reaction is a crucial tool that enables us to calculate the specific order of a reaction. The order of a reaction is important in that it enables us to classify specific chemical reactions easily and efficiently. Knowledge of the reaction order quickly allows us to understand numerous factors within the reaction including the rate law, units of the rate constant, half life, and much more. Reaction order can be calculated from the rate law by adding the exponential values of the reactants in the rate law. It is important to note that although the reaction order can be determined from the rate law, there is no relationship between the reaction order and the stoichiometric coefficients in the chemical equation.

Example 1:

\[
\text{Rate} = k[A]^s[B]^t \tag{4}
\]

\[
\text{Reaction Order} = s + t \tag{5}
\]

NOTE: The rate of reaction must be a non-negative value. It can be zero and does not need to be an integer.

As shown in Formula 5, the complete reaction order is equal to the sum of "s" and "t." But what does each of these variables by themself mean? Each variable represents the order of the reaction with respect to the reactant it is placed on. In this certain situation, s is the order of the reaction with respect to [A] and t is the order of the reaction with respect to [B].

Here is an example of how you can look at this: If a reaction order with respect to [A] was 2 (s = 2) and [B] was 1 (t = 1), then that basically means that the concentration of reactant A is decreasing by a factor of 2 and the concentration of [B] is decrease by a factor of 1.

So if you have a reaction order of Zero (s + t = 0), this basically means that the concentration of the reactants does not affect the rate of reaction. You could remove or add reactants to the mixture but the rate will not change.

A list of the different reaction rate equations for zero-, first-, and second-order reactions can be seen in Table 1. This table also includes further equations that can be determine by this equation once the order of the reaction is known (Half life, integrated rate law, etc.)

**Table 1.** The table below displays numerous values and equations utilized when observing chemical kinetics for numerous reactions types

<table>
<thead>
<tr>
<th></th>
<th>Zero-Order</th>
<th>First-Order</th>
<th>Second-Order</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Rate Law</strong></td>
<td>( \text{Rate} = k )</td>
<td>( \text{Rate} = k[A] )</td>
<td>( \text{Rate} = k[A]^2 )</td>
</tr>
<tr>
<td><strong>Integrated Rate Law</strong></td>
<td>( \frac{[A]_t}{[A]_0} = -kt + \ln[A]_0 )</td>
<td>( \ln[A]_t = -kt + \ln[A]_0 )</td>
<td>( \frac{1}{[A]_t} = -kt \frac{1}{[A]_0} )</td>
</tr>
</tbody>
</table>
### Units of Rate Constant (k):

<table>
<thead>
<tr>
<th>Units of Rate Constant (k):</th>
<th>( \text{mol} \text{ L}^{-1} \text{ s}^{-1} )</th>
<th>( \text{s}^{-1} )</th>
<th>( \text{L} \text{ mol}^{-1} \text{ s}^{-1} )</th>
</tr>
</thead>
</table>

### Linear Plot to Determine (k):

<table>
<thead>
<tr>
<th>Linear Plot to Determine (k):</th>
<th>( [A] ) versus time</th>
<th>( \ln [A] ) versus time</th>
<th>( \dfrac{1}{[A]} ) versus time</th>
</tr>
</thead>
</table>

### Relationship of Rate Constant to the Slope of Straight Line:

<table>
<thead>
<tr>
<th>Relationship of Rate Constant to the Slope of Straight Line:</th>
<th>( \text{slope} = {-k} )</th>
<th>( \text{slope} = {-k} )</th>
<th>( \text{slope} = {k} )</th>
</tr>
</thead>
</table>

### Half-life:

<table>
<thead>
<tr>
<th>Half-life:</th>
<th>( \dfrac{[A]_0}{2k} )</th>
<th>( \dfrac{\ln 2}{k} )</th>
<th>( \dfrac{1}{k[A]_0} )</th>
</tr>
</thead>
</table>

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### Sample Problems

1. Define Reaction Rate

2. TRUE or FALSE: Changes in the temperature or the introduction of a catalyst will affect the rate constant of a reaction

For sample problems 3-6, use **Formula 6** to answer the questions

\[
H_2O \longrightarrow 2H_2 + O_2 \tag{6}
\]

*Assume the reaction occurs at constant temperature*

3. For the given reaction above, state the rate law.

4. State the overall order of the reaction.

5. Find the rate, given \( k = 1.14 \times 10^{-2} \) and \([H_2O] = 2.04\text{M}\)

6. Find the half-life of the reaction.

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### Answers

1. **Reaction Rate** is the measure of the change in concentration of the disappearance of reactants or the change in concentration of the appearance of products per unit time.

2. FALSE. The rate constant is not dependant on the presence of a catalyst. Catalysts, however, can effect the total rate of a reaction.

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3. \( \{ \text{Rate} \} = \{ k[H_2O] \} \) 

4. First Order 

5. \( 2.33 \times 10^{-2} \text{ s}^{-1} \) 

6. 29.7 s 

References 


Contributors 

- Florence-Damilola Odufalu, Pamela Chacha, Galaxy Mudda, Andrew Iskandar (UCD) 
- Stephen Lower, Professor Emeritus (Simon Fraser U.) Chem1 Virtual Textbook