Reaction rate is the change in the concentration of a reactant or a product with time.

Reaction rate is the change in the concentration of a reactant or a product with time.

The rate, velocity, or speed of a reaction

\[ \text{rate} = \frac{dA}{dt} \]
\[ \text{rate} = \frac{dB}{dt} \]

\( dA = \) decrease in concentration of A over time period \( dt \)
\( dB = \) increase in concentration of B over time period \( dt \)

Because \([A]\) decreases with time, \(dA\) is negative.
The Rate Expression

\[ \pm \frac{dC}{dt} \]

This expression gives the increase (+) or decrease (-) of concentration, \( C \), within a given time interval, \( dt \).

\[ A + B \rightarrow C + D \]

\[ R_f = - \frac{dA}{dt} = - \frac{dB}{dt} \]
The Rate Expression

\[ \pm \frac{dC}{dt} \]

This expression gives the increase (+) or decrease (-) of concentration, C, within a given time interval, dt.

\[ A + B \quad \longrightarrow \quad C + D \]

\[ R_f = \frac{dC}{dt} = \frac{dD}{dt} \]
The Rate Expression

\[ \pm \frac{dC}{dt} \]

This expression gives the increase (+) or decrease (-) of concentration, C, within a given time interval, dt.

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

\[ - \frac{d(A)}{dt} = - \frac{1}{2} \frac{d(B)}{dt} \]
This expression gives the increase (+) or decrease (-) of concentration, C, within a given time interval, dt.

\[ \pm \frac{dC}{dt} \]

**The Rate Expression**

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

Reaction Rate and Stoichiometry
The rate law

The rate of a chemical reaction is proportional to the product of the molar concentration of the reactants each raised to a power equal to the number of molecules of the substance undergoing reaction:
The rate law

Effect of concentration on reaction rate

\[
A + B \rightarrow C + D
\]

The rate equation can be written as:

\[
R_f = -\frac{dA}{dt} = -\frac{dB}{dt} \alpha (A)(B)
\]

In which \( k \) is known as the reaction rate constant.
The order of reaction

The overall order of a chemical reaction is the sum of the exponents of the concentration terms in a reaction kinetics equation that after integration gives a linear plot.

\[ a \ A + b \ B \rightarrow g \ G + h \ H \]

The rate equation can be written as:

\[
\begin{align*}
\frac{-1}{a} \frac{d(A)}{dt} &= -\frac{1}{b} \frac{d(B)}{dt} = \frac{1}{g} \frac{d(G)}{dt} = \frac{1}{h} \frac{d(H)}{dt} = K(A)^m (B)^n
\end{align*}
\]

reaction is \( m^{th} \) order in \( A \)

reaction is \( n^{th} \) order in \( B \)

reaction is \((m + n)^{th}\) order overall
The order of reaction

The overall order of a chemical reaction is the sum of the exponents of the concentration terms in a reaction kinetics equation that after integration gives a linear plot.

\[ a \ A + b \ B \rightarrow g \ G + h \ H \]

The rate equation can be written as:

\[
- \frac{1}{a} \frac{d(A)}{dt} = - \frac{1}{b} \frac{d(B)}{dt} = \frac{1}{g} \frac{d(G)}{dt} = \frac{1}{h} \frac{d(H)}{dt} = K(A)^m (B)^n
\]

Concentration term exponents \((m \text{ and } n)\) are usually small whole numbers but may be fractional, negative or zero.

They are unlikely to be the stoichiometric factors for the overall rate law.
Reaction Mechanisms

Simple elementary step
Elementary processes are reversible $A \leftrightarrow B$

The reactions are unimolecular or bimolecular

- Exponents for concentration terms are the same as the stoichiometric factors for the elementary process
Reaction Mechanisms

Simple elementary step

Sequence of elementary steps

• One elementary step is usually slower than all the others and is known as the rate determining step

• Intermediates are produced in one elementary process and consumed in another. They do not appear in the overall chemical equation or the rate law.
Experimental determination of rate law

\[
F_2 (g) + 2\text{ClO}_2 (g) \rightarrow 2\text{FCIO}_2 (g)
\]

\[
\text{rate} = k [F_2]^x [\text{ClO}_2]^y
\]

Double \([F_2]\) with \([\text{ClO}_2]\) constant

Rate doubles \(x = 1\)

Quadruple \([\text{ClO}_2]\) with \([F_2]\) constant

Rate quadruples \(y = 1\)

**Table 13.2** Rate Data for the Reaction between \(F_2\) and \(\text{ClO}_2\)

<table>
<thead>
<tr>
<th>(<a href="M">F_2</a>)</th>
<th>(<a href="M">\text{ClO}_2</a>)</th>
<th>Initial Rate (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 0.10</td>
<td>0.010</td>
<td>(1.2 \times 10^{-3})</td>
</tr>
<tr>
<td>2. 0.10</td>
<td>0.040</td>
<td>(4.8 \times 10^{-3})</td>
</tr>
<tr>
<td>3. 0.20</td>
<td>0.010</td>
<td>(2.4 \times 10^{-3})</td>
</tr>
</tbody>
</table>

\[
F_2 (g) + 2\text{ClO}_2 (g) \rightarrow 2\text{FCIO}_2 (g)
\]

\[
\text{rate} = k [F_2][\text{ClO}_2]^1
\]
I. Zero Order Reaction: 

Are reactions, in which the rate of reaction is independent of the concentration of the reactants.

The velocity of the reaction is constant.
I. Zero Order Reaction:  

**Zero-order reactions** are typically found when a material that is required for the reaction to proceed, such as a surface or a **catalyst**, is saturated by the reactants.

1) occurs in a closed system
2) there is no net build-up of intermediates
3) there are no other reactions occurring
I. Zero Order Reaction:

Zero-order reactions are typically found when a material that is required for the reaction to proceed, such as a surface or a catalyst, is saturated by the reactants.

Haber Process

Decomposition of multi-sulfa drugs
I. Zero Order Reaction:

\[
\text{rate} = - \frac{d(C)}{dt}
\]

\[
\text{rate} = k (C)^0 = k
\]

\[
- \frac{d(C)}{dt} = K
\]

The rate equation is a differential equation. It can be integrated to obtain an integrated rate equation that links concentrations of reactants or products with time.
I. Zero Order Reaction:

rate = \(- \frac{d(C)}{dt}\)

rate = \(k \ (C)^0 = k\)

\(- \frac{d(C)}{dt} = K\)

\(- dC = K \ dt\)

\(C_t = C_0 - Kt\)

On Integration

\([C_t] \) is the concentration of C at any time \(t\)

\([C]_0 \) is the concentration of C at time \(t=0\)

Intercept = \(C_0\)

Slope = - \(K\)
We can also calculate the constant of reaction by rearranging the linear equation:

\[ C_t = C_0 - Kt \]

\[ k = \frac{C_0 - C_t}{t} \]

UNITS?

\[ \frac{d(C)}{dt} = K_0 \]

\[ \frac{Conc.}{time} \]

\[ \frac{mole/liter}{Second} = mole \cdot liter^{-1} \cdot S^{-1} \]
I. Zero Order Reaction:

The half-life \((t_{1/2})\) the time required for a quantity to fall to half its value as measured at the beginning of the time period.

\[ t_{1/2} = t \text{ when } C_t = \frac{1}{2} C_0 \]
I. Zero Order Reaction:

The half-life \((t_{1/2})\)

Putting \(C_t = \frac{1}{2}C_o\) in the linear equation:

\[
C_t = C_o - k \cdot t
\]

\[
t = \frac{C_o - C_t}{k}
\]

\[
t_{1/2} = \frac{C_o - \frac{1}{2}C_o}{k}
\]

\[
t_{1/2} = \frac{\frac{1}{2}C_o}{k}
\]
I. Zero Order Reaction:

The shelf life \( t_{90\%} \) is the time required for 10% of the drug to decompose. In other word 90% of the drug remains.

Putting \( C_t = 0.9 C_0 \) in the linear equation:

\[
t_{90\%} = \frac{C_0 - 0.9C_0}{k}
\]

\[
t_{90\%} = \frac{0.1C_0}{k}
\]
I. Zero Order Reaction:

**Time life** \( (t_{life}) \) is the time required for 100% of the drug to decompose. Time for a drug to decompose completely.

Putting \( C_t = \text{zero} \) in the linear equation:

\[
 t_{life} = \frac{C_o - 0}{k}
\]

\[
 t_{life} = \frac{C_o}{k}
\]
Example

The decomposition of a multi-sulfa compound, was found to follow zero order kinetics. If its concentration was 0.47 mole/liter, when freshly prepared, and after 473 days its concentration reached 0.225 mole/liter, calculate its degradation rate constant and $t_{1/2}$. 
The decomposition of a multi-sulfa compound, was found to follow zero order kinetics. If its concentration was 0.47 mole/liter, when freshly prepared, and after 473 days its concentration reached 0.225 mole/liter, calculate its degradation rate constant and $t_{1/2}$.
Solution

\[ k = \frac{C_o - C_t}{t} \quad \therefore k = \frac{0.470 - 0.225}{473} \]

\[ = 0.00052 \text{ mole/liter . days}^{-1} \]

\[ t^{1/2} = \frac{C_o}{2K} = \frac{0.47}{2 \times 0.00052} = 452 \text{ days} = 15 \text{ months} \]
II. 1st Order Reaction:

The speed of the reaction depends on the concentration of only one reactant, raised to the first power.

There can be other reactants present in the reaction, but their concentrations do not affect the rate.

First-order equations are often seen in decomposition reactions. Absorption, metabolism, distribution and elimination (not linked with a carrier or a carrier with unsaturable state).
II. 1st Order Reaction:

The speed of the reaction depends on the concentration of only one reactant, raised to the first power.

\[- \frac{d (C)}{dt} = K_1 C\]
II. 1<sup>st</sup> Order Reaction:

\[- \frac{d (C)}{dt} = K_1 C\]

Integrating the previous equation between \(C_0\) at time \(t = 0\) and concentration \(C\) at some later time \(t\) gives:

\[\ln C = \ln C_0 - k t\]

Converting to common logarithms yields:

\[\log C = \log C_0 - \frac{k t}{2.303}\]
II. 1\textsuperscript{st} Order Reaction:

\begin{align*}
\ln C &= \ln C_0 - k t \\
\log C &= \log C_0 - \frac{k t}{2.303}
\end{align*}

- Intercept = \ln C_0
- Slope = -k

- Intercept = \log C_0
- Slope = \frac{-k}{2.303}
II. 1\textsuperscript{st} Order Reaction:

\[
\ln C = \ln C_0 - k t
\]

\[
\log C = \log C_0 - \frac{k t}{2.303}
\]

The reaction rate constant

\[
k = \frac{\ln C_0 - \ln C}{t}
\]

\[
k = \frac{2.303}{t} \log \frac{C_0}{C}
\]

UNITS?

\[- \frac{d(C)}{dt} = K_1(C)\]

\[\frac{1}{\text{time}}\]

\[\frac{\text{mole/liter}}{\text{Sec (mole/liter)}} = S^{-1}\]
II. 1\textsuperscript{st} Order Reaction:

The relation between concentration and time is exponential:

\[ C_t = C_0 e^{-kt} \]

\[ C_t = C_0 10^{-kt/2.303} \]
II. 1st Order Reaction:

The Half Life “t½”

half life when \( C = \frac{1}{2} C_o \)

\[
k = \frac{2.303}{t} \log \frac{C_o}{C}
\]

\[
t = \frac{2.303}{k} \log \frac{C_o}{C}
\]

\[
= \frac{2.303}{k} \log \frac{C_o}{\frac{1}{2} C_o} = \frac{2.303}{k}. \log 2 = \frac{0.693}{k}
\]

\( T_{1/2} \)
II. 1st Order Reaction:

The Shelf Life \((t_{90\%})\)

The shelf life when \(C = 0.9 \ C_o\)

\[
\begin{align*}
  k &= \frac{2.303}{t} \log \frac{C_o}{C} \\
  t &= \frac{2.303}{k} \log \frac{C_o}{C}
\end{align*}
\]

\[
\begin{align*}
  t_{90\%} &= \frac{2.303}{k} \log \frac{C_o}{0.9 \ C_o} = \frac{2.303}{k} \cdot (0.0457) = \frac{0.105}{k}
\end{align*}
\]
II. 1st Order Reaction:

**Time life** \((t_{life})\) is the time required for 100% of the drug to decompose.

Putting \(C_t = 0\) in the linear equation:

?
II. 1st Order Reaction:

A solution of a drug contained 500 units per ml when prepared. It was analyzed after a period of 40 days and was found to contain 300 units per ml. Assuming that the decomposition is first order, at what time will the drug have decomposed to one–half of its original concentration?

Solution:

\[
K = \frac{2.303}{t} \log \frac{C_0}{C_t} = \frac{2.303}{40} \log \frac{500}{300} = 0.0128 \text{ day}^{-1}
\]

\[
t_{\frac{1}{2}} = \frac{0.693}{K} = \frac{0.693}{0.0128} = 54 \text{ days}
\]
What is the half-life of $\text{N}_2\text{O}_5$ if it decomposes with a rate constant of $5.7 \times 10^{-4}$ s$^{-1}$?

$$t_{\frac{1}{2}} = \frac{0.693}{k} = \frac{0.693}{5.7 \times 10^{-4} \text{ s}^{-1}} = 1200 \text{ s} = 20 \text{ minutes}$$