

Determination of Reaction Order and Half-life Time

1- A **zeroth-order reaction** is one whose rate is independent of concentration.



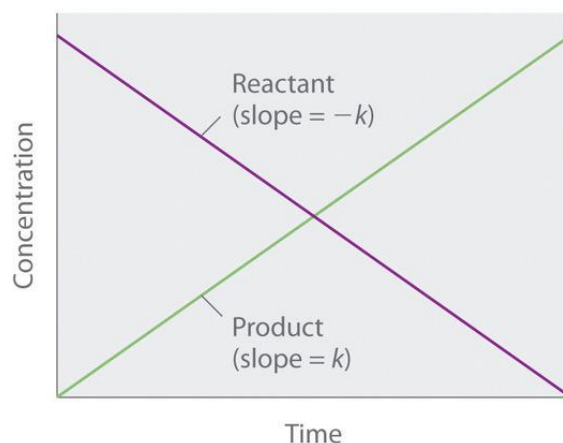
$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = k[\text{reactant}]^0 = k(1) = k$$

The integrated rate law for a zeroth-order reaction also produces a straight line and has the general form

$$[A] = [A]_0 - kt$$

where $[A]_0$ is the initial concentration of reactant A. Equation above has the form of the algebraic equation for a straight line, $y = mx + b$, with $y = [A]$, $mx = -kt$, and $b = [A]_0$. In a zeroth-order reaction, k (the rate constant) must have the same units as the reaction rate, typically moles per liter per second.

Because rate is independent of reactant concentration, a graph of the concentration of any reactant as a function of time is a straight line with a slope of $-k$. The value of k is negative because the concentration of the reactant decreases with time. Conversely, a graph of the concentration of any product as a function of time is a straight line with a slope of k , a positive value.



The graph of a zeroth-order reaction. The change in concentration of reactant and product with time produces a straight line.

- **Half-life for Zero Order Reactions:**

The half-life is a timescale in which each half-life represents the reduction of the initial population to 50% of its original state. We can represent the relationship by the following equation:

$$[A] = \frac{1}{2}[A]_o$$

$$\frac{1}{2}[A]_o = [A]_o - kt \frac{1}{2}$$

$$t_{1/2} = \frac{[A]_o}{2k}$$

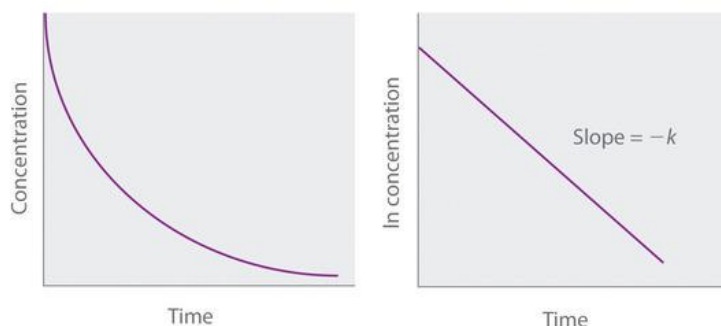
2- In a **first-order reaction**, the reaction rate is directly proportional to the concentration of one of the reactants. For the reaction $A \rightarrow P$:

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

The integrated rate law for a first-order reaction can be written in two different ways:

$$\ln[A] = \ln[A]_0 - kt$$

Because Equation above has the form of the algebraic equation for a straight line, $y = mx + b$, with $y = \ln[A]$ and $b = \ln[A]_0$, a plot of $\ln[A]$ versus t for a first-order reaction should give a straight line with a slope of $-k$ and an intercept of $\ln[A]_0$.



Graphs of a first-order reaction. The expected shapes of the curves for plots of reactant concentration versus time (top) and the natural logarithm of reactant concentration versus time (bottom) for a first-order reaction.

- **Half-life for First Order Reactions:**

$$\ln \frac{[A]_0}{2} = \ln[A]_0 - kt_{\frac{1}{2}}$$

$$t_{\frac{1}{2}} = \frac{\ln(2)}{k}$$

3- The simplest kind of **second-order reaction** is one whose rate is proportional to the square of the concentration of one reactant. These generally have the form $2A \rightarrow$ products. A second kind of second-order reaction has a reaction rate that is proportional to the product of the concentrations of two reactants. Such reactions generally have the form $A + B \rightarrow$ products.

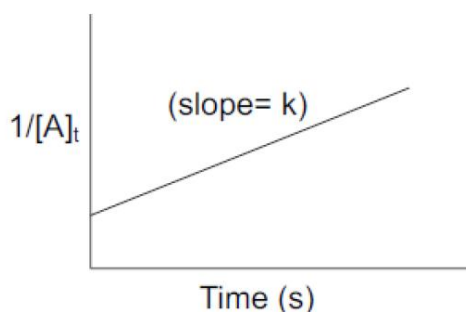
The differential rate law for the simplest second-order reaction in which $2A \rightarrow P$ is as follows:

$$\text{rate} = -\frac{\Delta[A]}{2\Delta t} = k[A]^2$$

The following integrated rate law describes the concentration of the reactant at a given time:

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$$

Because Equation above has the form of an algebraic equation for a straight line, $y = mx + b$, with $y = 1/[A]$ and $b = 1/[A]_0$, a plot of $1/[A]$ versus t for a simple second-order reaction is a straight line with a slope of k and an intercept of $1/[A]_0$.



- **Half-life for Second Order Reactions:**

$$\frac{1}{\frac{[A]_0}{2}} = \frac{1}{[A]_0} + kt$$

$$\frac{2}{[A]_0} = \frac{1}{[A]_0} + kt$$

$$t_{\frac{1}{2}} = \frac{1}{k[A]_0}$$

4- **3rd order**...doubling concentration leads to 23 (or 8 times) the rate.

5- extremely rare.