

Reaction Rate

chemical kinetics deals with the study of reaction rate.

In order for two or more substances to react, their molecules must "collide". The probability of a collision increases with increasing temperature, pressure, and concentration of substances.

"Reaction rate (v)" can be defined as the rate of "decrease of reactants" or the rate of "increase of products", i.e. for the reaction $a A + b B \rightarrow c C + d D$:

$$v = -\frac{1}{a} \cdot \frac{d[A]}{dt} = -\frac{1}{b} \cdot \frac{d[B]}{dt} = \frac{1}{c} \cdot \frac{d[C]}{dt} = \frac{1}{d} \cdot \frac{d[D]}{dt}$$

Let's take a closer look at the relationship between reaction rate and reactant concentration. Consider a simple reaction $X \rightarrow Y$. Its rate will be proportional to $[X]$ according to the equation:

$$v = -\frac{d[X]}{dt} = k \cdot [X] \quad (15)$$

where k is the **rate constant**.

In some cases, the rate may be proportional to $[X]^2$, may depend more complexly on $[X]$, or conversely may not depend on $[X]$ at all (in which case the reaction proceeds at a constant rate). The exact relationship between the reaction rate and the concentration of the reactants is an ``empirical fact *and - especially if we consider reactions with more complex reaction mechanisms - cannot be derived only from the stoichiometry of the observed transformation.*

Chemists define the ``kinetic order of a reaction *by the number of terms whose concentrations affect the rate. If the speed does not depend on the concentration, and therefore the equation $v = k$ applies, we speak of the zeroth order. If the rate is directly proportional to the concentration of one of the reactants, it is first-order kinetics (as in the case of the above-mentioned reaction (15)). If the rate is affected by the concentration of two reactants or if it is an exponential relationship of one reactant ($v = k \cdot [X] \cdot [Y]$ or $v = k \cdot [X]^2$), we speak of second-order kinetics etc.*

Sometimes we want to predict how much reactant X will remain unreacted after a time t from the start of the reaction, or how long it will take for $[X]$ to halve. For zero-order reactions, the calculation is simple, but for higher orders it gets complicated.

For a *first-order* reaction:

$$-\frac{d[X]}{dt} = k \cdot [X] \quad (16)$$

Integrating equation (16) we get:

$$\begin{aligned} -\frac{1}{[X]} \cdot \frac{d[X]}{dt} &= k \cdot [X] \\ -\int \frac{1}{[X]} \cdot \frac{d[X]}{dt} &= \int k \cdot [X] \\ -\ln[X] &= k \cdot t + c \end{aligned} \quad (17)$$

By solving for the beginning of the reaction, i.e. for $t = 0$ (while we denote the initial concentration of substance X at this time as $[X]_0$), we get

$$c = -\ln[X]_0 \quad (18)$$

$$-\ln[X] = k \cdot t - \ln[X]_0$$

$$-\ln[X] + \ln[X]_0 = k \cdot t$$

$$-\ln \frac{[X]}{[X]_0} = k \cdot t$$

$$\frac{[X]}{[X]_0} = e^{-k \cdot t}$$

$$[X] = [X]_0 \cdot e^{-k \cdot t} \quad (19)$$

This equation describes the **exponential decay of X concentration over time**. **A useful parameter of exponential decay is the time required to reduce the initial concentration (or amount) of substance X by half. It is called the "half-time" ($t_{1/2}$).** From equation (19), we can express the half-time as:

$$t_{1/2} = \frac{\ln 2}{k}$$

