

Chemical Kinetics

What is Chemical Kinetics?

Chemical kinetics is the branch of physical chemistry which deals with a study of the speed of chemical reactions. Such studies also enable us to understand the mechanism by which the reactions occur.

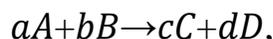
Rate of reaction:

The rate of reaction is the amount of chemical change occurring per unit time. The rate is generally expressed as the decrease in concentration of the reactant or as the increase in concentration of a product per unit time.

Consider a reaction $A \rightarrow P$, and if C_A is the concentration of reactant and C_P is the concentration of product at time t

$$rate = -dC_A/dT = dC_P/dT$$

Consider a reaction of the type



$$rate = -1/a.dC_A/dt = -1/b.dC_B/dt = 1/c.dC_C/dt = 1/d.dC_D/dt$$

Rate constant:

the rate of a reaction $A \rightarrow Product$ is experimentally found to be given by $r = kC_A$ where k is the rate constant.

For a reaction $aA + bB \rightarrow Product$

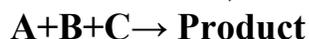
$$r = k[A]^x[B]^y$$

Order of a reaction (n):

It is the sum of the exponents of the concentration terms in the rate equation.

By stating the order of a reaction, the quantitative dependence of its rate on the concentration of a reacting substance can be indicated.

For a reaction ,



$$rate = -d[A]/dt = -d[B]/dt = -d[C]/dt$$

or, rate can also be written as $rate = k[A]^\alpha[B]^\beta[C]^\gamma$

Order of a reaction, $n = \alpha + \beta + \gamma$

eg.: $2HI = H_2 + I_2$

$rate = k[HI]^2$, here $n = 2$

If $n = 1$, reaction is said to be first order reaction

$n = 2$, it is second order reaction

$n = 0$, it is zero order reaction

Unit of rate constant:

(1) For zero order reaction : zero order reaction means rate does not depend on the concentration of the reactants $A \rightarrow P$

$$rate = -d[A]/dt = k[A]^0 = k \text{ mol L}^{-1} \text{ s}^{-1} = k$$

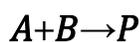
So unit of $k = \text{mol L}^{-1} \text{ sec}^{-1}$

(2) First order reaction: For a general first order reaction $A \rightarrow P$

$$rate = -d[A]/dt = k[A] \text{ mol L}^{-1} \text{ s}^{-1} = k(\text{mol L}^{-1})$$

Unit of $k = \text{sec}^{-1}$

(3) Second order reaction:



$$rate = -dx/dt = k[A][B]$$

$$\text{mol L}^{-1} \text{ s}^{-1} = k(\text{mol L}^{-1})(\text{mol L}^{-1}) \quad k = \text{L mol}^{-1} \text{ sec}^{-1}$$

Molecularity of a reaction:

The number of molecules or atoms which take part in the process of a chemical change. The reaction are said to be unimolecular, bimolecular or trimolecular according as one, two, three molecules are involved in chemical change.

For example, a reaction $2HI = H_2 + I_2$ is a bimolecular reaction

The molecularity must be an integral (1,2 ,3.....) but order may be a fractional also.

Order of a reaction is an experimental concept while molecularity is a theoretical mechanism.

For a reaction, $CH_3COOC_2H_5 + H_2O$ (excess) $\rightarrow CH_3COOH + C_2H_5OH$, Molecularity of a reaction is two, but order of a reaction is 1. The rate of reaction varies only with the concentration of ester since water is present in excess.

The difference between order and molecularity:

Molecularity	Order
The number of ions or molecules that take part in the rate-determining step is known as molecularity.	The sum of powers to which the reactant concentrations are raised in the rate law equation is known as the order of the reaction.
The molecularity of a reaction is a whole number other than zero. Its values are limited from 1 to 3.	It can either be a whole number or a fraction. Therefore, it can be 0, 1, 2, 3 or even a fraction.
The molecularity of the reaction is determined by looking at the reaction mechanism	The order of the reaction is determined by the experimental methods

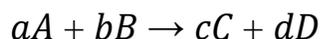
The molecularity of the reaction is obtained by the rate-determining step	The order of the reaction is obtained by the sum of the powers to which the reactant concentrations are raised in the rate law equation
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Differential and Integrated Rate Laws

Rate laws describe the progress of the reaction; they are mathematical expressions which describe the relationship between reactant rates and reactant concentrations. In general, if the reaction is:

We can write the following expression:

Where:



$$\text{rate} = k[A]^m[B]^n$$

k is a proportionality constant called *rate constant* (its value is fixed for a fixed set of conditions, specially temperature).

m and n are known as *orders of reaction*. As it can be seen from the above expression, these orders of reaction indicate the degree or extent to which the reaction rate depends on the concentration of each reactant. We can say the following about these orders of reaction:

1. In general, they are not equal to the coefficients from the balanced equation. Remember: they are determined experimentally (unless a reaction is what we call an *elementary reaction*, but they are the exception).
2. Each reactant has its own (independent) order of reaction.
3. Orders of reaction are often times a positive number, but they can also be zero, a fraction and in some instances a negative number.
4. The *overall reaction order* is calculated by simply adding the individual orders ($m + n$).

Differential vs Integrated Rate Laws

Differential rate laws express the *rate of reaction as a function of a change in the concentration* of one or more reactants *over a particular period of time*; they are used to describe what is happening at the molecular level during a reaction. These rate laws help us determine the overall mechanism of reaction (or process) by which the reactants turn into products. *E.g.:*

$$\begin{aligned}\text{Rate} &= -d[A] / dt \\ &= k[A]^n\end{aligned}$$

On the other hand, **integrated rate laws** express the reaction rate as a function of the initial concentration and a measured (actual) concentration of one or more reactants after a specific amount of time (t) has passed; they are used to determine the rate constant and the reaction order from experimental data. *E.g.* (when $n = 1$):

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

Where $[A]_0$ is the initial concentration of the reactant and $[A]$ is the concentration after a time t has passed.

Integrated rate expression for zeroth order reactions ($n = 0$)

Consider a general zero order reaction $A \rightarrow P$

$$\text{Rate} = -d[A]/dt$$

$$= k[A]^0 = k$$

Rearranging, $d[A] = -kdt$

Now we can integrate both sides over the desired interval:

$$\int_{[A]_0}^{[A]_t} d[A] = -k \int_{t_0}^t dt$$

($[A]_0$ and t_0 are initial conditions, whereas $[A]$ refers to the concentration after a time t has passed)

Notice how $-k$ comes out of the integral since it is a constant. Also, recall from calculus that (you can always check a table of integrals if you don't remember):

$\int dx = x$ (a constant C is added, but we do not need it since we know the limits)

Which leads to (after evaluating over the limits, which means upper limit minus lower limit):

$$[A]_{[A]_t} - [A]_{[A]_0} = -kt \Big|_{t_0}^t$$

$$[A] - [A]_0 = -k(t - t_0)$$

We consider $t_0 = 0$, and so the equation can take the form:

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

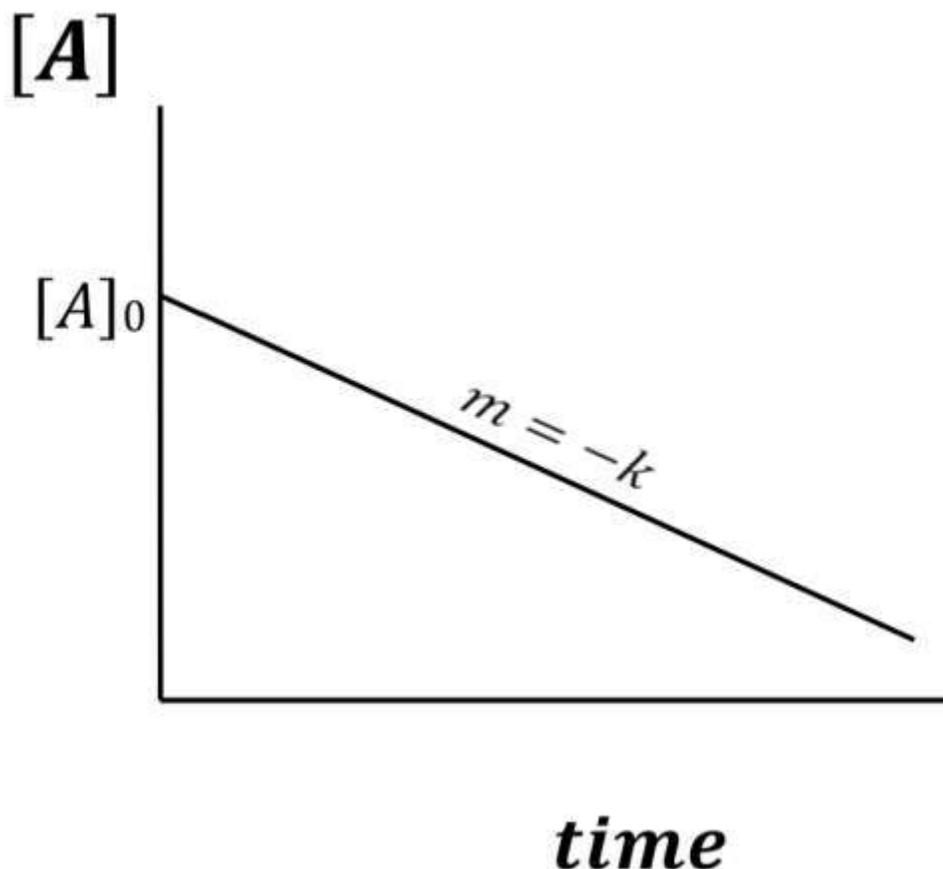
Which looks like:

$$y = mx + b$$

Where: $y = [A]$; $m = -k$; $x = t$; $b = [A]_0$

If we keep plotting $[A]$ vs t for a longer and longer period of time, we will get to a point at which the concentration $[A]$ will become negative (since we have a negative slope); nevertheless, we are well aware of the fact that there is no such thing as a negative concentration, so,

What we can conclude is that a *zero-order reaction model can be applied to describe a reaction just for a limited amount of time*; we know the system must, at some point, change into a different kinetics model.



The half-life is defined as the time it takes for half of the initial amount of reactant to disappear (*i.e.* a reduction of 50% its original amount). If we replace this idea on the integrated rate law we get:

$$[A]_0 / 2 = -kt_{1/2} + [A]_0 ;$$

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

This means the half-life depends on the initial concentration of reactant and the rate constant.

Integrated rate expression for First order reactions ($n = 1$)

Consider a general first order reaction $A \rightarrow P$

Rearranging,

$$Rate = - d[A] / dt = k[A]$$

$$d[A]/[A] = -kdt$$

Now we can integrate both sides over the desired interval:

$$\int_{[A]_0}^{[A]_t} d[A] / [A] = -k \int_{t_0}^t dt$$

Recall from calculus that (or check a table of integrals):

$$\int 1/x dx = \ln x \text{ and } \int dx = x \text{ (definite integrals)}$$

The above formulas lead to (after evaluating over the limits):

$$\ln[A] - \ln[A]_0 = -k(t - t_0)$$

We consider $t_0 = 0$, and the equation can take the form:

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

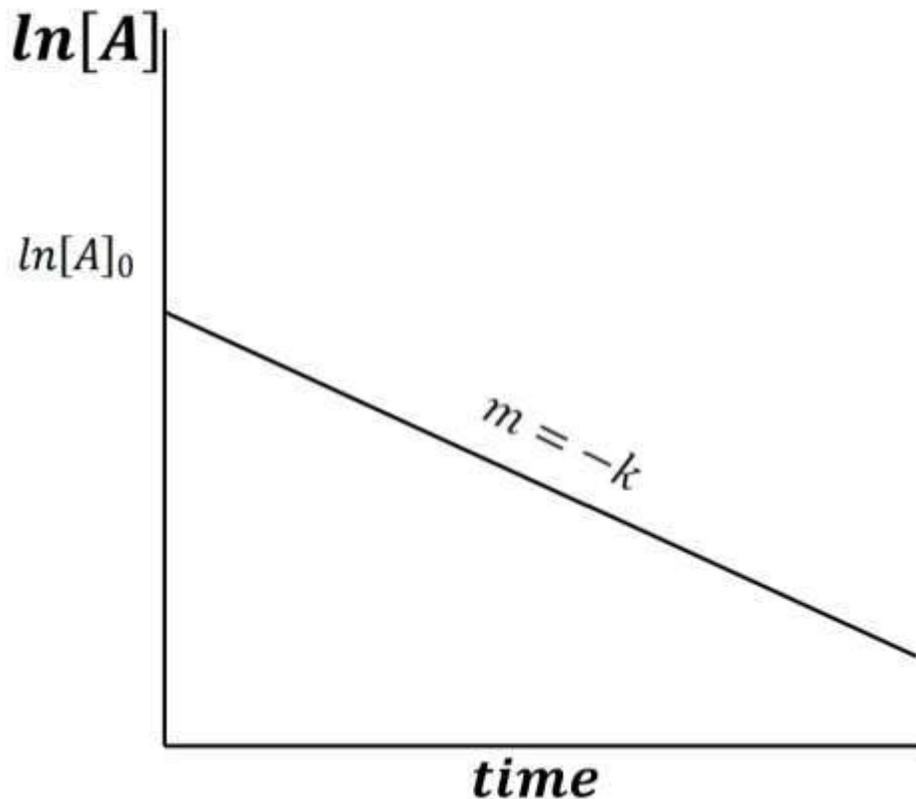
Which looks like: Where:

$$y = mx + b$$

$$y = \ln[A]; m = -k; x = t; b = \ln[A]_0$$

This means that if we plot $\ln[A]$ vs t , we get a line with a slope that is the negative of the rate constant. Also, using the laws of logarithms, we get:

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



What is the time it takes for half of the initial concentration to disappear (the half-life or $t_{1/2}$)?

$[A]$

$$@ t = t_{1/2} \Rightarrow [A] = [A]_0/2$$

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

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

$$kt_{1/2} = \ln 2$$

$$t_{1/2} = 0.693/k$$

the equation above means the half-life or $t_{1/2}$ for a first order reaction is a constant.

Integrated rate expression for Second order reactions ($n = 2$)

$$\begin{aligned} \text{Rate} &= -d[A]/dt \\ &= k[A]^2 \end{aligned}$$

Rearranging and integrate over the interval:

Now we can integrate both sides over the desired interval:

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} = -k \int_{t_0}^t dt$$

From calculus (or check a table of integrals):

$$\int x^n dx = x^{n+1}/(n+1) \text{ (definite integral) ; where } n = -2, \text{ so: } \int x^{-2} dx = x^{-1}(-1)$$

The above formulas lead to (after evaluating over the limits):

$$1/[A]_0 - 1/[A] = -k(t - t_0)$$

If $t_0 = 0$ then

$$1/[A] = kt + 1/[A]_0$$

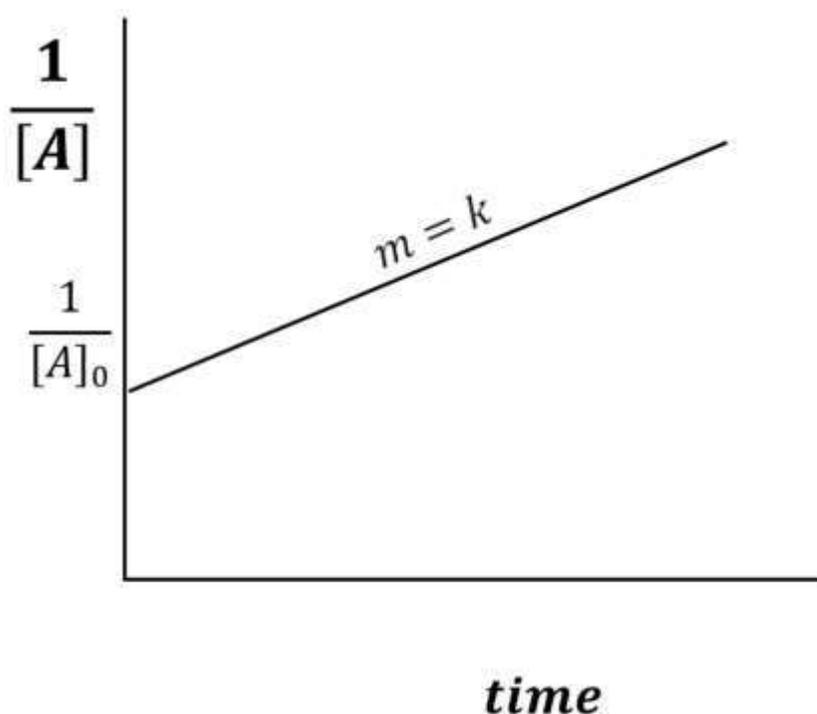
Which is similar to

$y = mx + b$ where

$y = 1/[A]$; $m = k$; $x = t$;

$b = 1/[A]_0$

Which means if we plot $1/[A]$ vs t , we get a line with a slope that is the rate constant itself.



What is the time it takes for half of the initial concentration to disappear (the half-life or $t_{1/2}$)?

At $t=t_{1/2}$, $[A]/[A]_0/2$

Therefore, $1/[A]_0/2=kt_{1/2} + 1/[A_0]$

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

Notice that, as it was the case with the half-life for the zeroth order reaction, the half-life for the second order reaction also depends on the initial concentration of the reactant (as well as on the rate constant); for this reason, the concept of half-life for second (and zeroth order) reactions are far less useful. However, the inverse relation of the half-life on the initial concentration suggests the following:

Integrated rate expression for Second order reactions ($n = 2$)

1. With a high initial concentration of reactant, we have a higher probability of the two reactant molecules interacting to form product; consequently, the reactant will be consumed in a shorter period of time.
2. Since the half-life is longer when initial concentrations are low, species following a second order kinetics may exist for a longer period of time if their initial concentrations are small