

1st Order Kinetics

- The rate of a process can be empirically expressed through a ‘rate law’
- Integration of the rate law allows us to describe how concentrations change with time
- The half-life ($t_{1/2}$) is a way of quantifying how quickly the transformation happens and for a first order reaction it is related to the rate constant by $k = \ln(2)/t_{1/2}$

Kinetics is the study of the rate of change and lies at the heart of modern chemistry. Over the course of the 20th century five Nobel Prizes were *directly* awarded for work in this field. This lecture provides an introduction to 1st Order Kinetics.

“Nobody, I suppose, could devote many years to the study of chemical kinetics without being deeply conscious of the fascination of time and change: this is something that goes outside science into poetry; but science, subject to the rigid necessity of always seeking *closer approximations* to the truth, itself contains many poetical elements.”

C.N. Hinshelwood

(1956 Nobel Prize for work on the “mechanism of chemical reactions”)

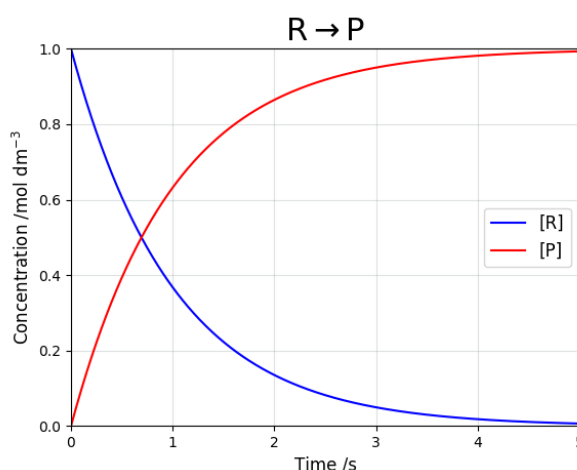


Figure 1: Example variation of the concentration of a reactant (R) and a product (P) as a function of time. The slope of the plot gives a measure of the rate of the reaction. R is defined by Eq. 11, with $k = 1 \text{ s}^{-1}$ and $c_0 = 1 \text{ mol dm}^{-3}$.

Rate of a Reaction

When we talk about the ‘rate of a reaction’, we mean the rate at which either the reactants are consumed or the rate at which the products are formed. The simplest reaction we can have is where one molecule of a reactant (R) is converted into one molecule of a Product (P), as given by:



where k is the rate constant and is a measure of how fast this process (conversion) happens. At the molecular scale we can imagine some molecule undergoing an isomerisation on its own. Fig 1 shows an example plot of how the concentrations of a reactant (R) and a product (P) may change as a function of time. As the reactant is used up the rate of the reaction slows down.

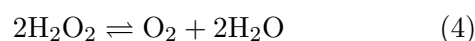
$$\text{rate} = \frac{\text{change in concentration}}{\text{change in time}} \quad (2)$$

more succinctly we can write this as:

$$\nu = \frac{dc}{dt} \quad (3)$$

where ν is the rate ($\text{mol dm}^{-3} \text{ s}^{-1}$), c is the concentration (mol dm^{-3}) and t is the time (s).

Most reactions are not as simple as the process given by equation 1. Let’s think about the more complex example of the disproportionation of hydrogen peroxide:



Here overall two molecules of peroxide lead to the formation of one molecule of oxygen and two water molecules. We could define the rate of the reaction by either monitoring the production of oxygen or the

consumption of hydrogen peroxide (assuming we are doing this reaction in an aqueous solution monitoring the production of water is not really feasible!). But due to the stoichiometry of the reaction, for every two peroxides consumed we only form one oxygen. Does this mean on the basis of equation 3 that we have two different reaction rates for one reaction? The answer to this apparent problem is straightforward: the rate of the reaction (ν) is defined as the rate of change of the reactant or product *divided* by its *stoichiometric coefficient* (v_i).

Definition: Reaction Rate

$$\nu = \frac{1}{v_i} \frac{dc_i}{dt} \quad (5)$$

So for the hydrogen peroxide example we have:

$$\nu = -\frac{1}{2} \frac{dc_{\text{H}_2\text{O}_2}}{dt} = \frac{dc_{\text{O}_2}}{dt} \quad (6)$$

NOTE: The negative sign in equation 6 is important. As the concentration of the reactant - in this case hydrogen peroxide - decreases with time (it is being used up), then the slope of the change of the reactant with time is negative. The reaction rate should be a positive value so we multiply the slope by -1 in the case of reactants.

Rate Laws

In studying the kinetics of a reaction one of the first things we want to know is how the rate of the reaction (ν) varies as a function of the concentration of the reagents, products and catalysts. This is expressed *empirically* as a rate law and many reactions are found to follow a simple rate law which has the form:

Definition: General Rate Law

$$\nu = k c_A^a c_B^b c_C^c \dots \quad (7)$$

Equation 7 says that the rate of the reaction is proportional to the concentration of the reactants (or products, or catalysts) raised to some power multiplied by a *rate constant* (k). The units of the rate constant depends upon the definition of the rate law, which often leads to some confusion (see the information box on Dimensional Analysis for more details). The *overall order* of a reaction is equal to the sum of the powers in the rate law (i.e. above the 'overall order' = $a + b + c \dots$). At this stage we are only going to consider 'simple' rate laws, examples of which are given in Table 1. Specifically, we are concerned

with the first equation in Table 1 that has the rate law $\nu = k c_A$. This is the expression for an overall first order reaction; the concentration of species A is raised to the power of 1.

Mechanism	Rate Law	Overall Order	Order w.r.t. A
$A \rightarrow B$	$\nu = k c_A$	1	1
$A + A \rightarrow B$	$\nu = k c_A^2$	2	2
$A + B \rightarrow C$	$\nu = k c_A c_B$	2	1

Table 1: Example elementary reaction mechanisms and the associated rate laws, orders and orders with respect to species A

Elementary reactions

In chemistry we have 'elementary' and 'complex' (aka multi-step) reactions. In an elementary reaction one or more chemical species react directly to form products in a single reaction step and with a single transition state. Generally elementary reactions only involve one (uni-) or two (bi-) molecules. A unimolecular reaction is where only one molecule reacts on its own to form the product(s), an example being the decomposition of azomethane to form nitrogen and ethane. Elementary reactions often follow simple rate laws like those given in table 1, where the rate law can be inferred from the stoichiometry of the process. As a general rule for multi-step or 'complex' reactions the rate law can not be guessed from the stoichiometry of the reaction.

Calculus

Kinetics is about studying the rate of physical processes; calculus is the maths we use to describe change. The main mathematical result we need for 1st order kinetics is a definition of the natural logarithm:

$$\frac{d}{dx} \ln x = \frac{1}{x}$$

Furthermore, remember that the natural logarithm is the inverse of the exponential:

$$\ln(e^x) = x$$

and that,

$$\ln \frac{A}{B} = \ln A - \ln B$$

Looking Forward: Multi-Step Reactions

From a chemical standpoint one of the main reasons we are interested in the rate law of a reaction is because it can give insight into a reaction mechanism, thereby revealing information about how a complex chemical process works. If you're interested perhaps look ahead to the Lindemann-Hinshelwood mechanism and Michaelis-Menten Enzyme Kinetics (see Topic 17F, *Atkins Physical Chemistry, 11 Ed.* for more details).

1st Order Integrated Rate Law

Having defined the rate law, the next thing we want to know is how the concentration of a reactant (or product) varies during the course of a reaction. To solve this problem we need to employ a little maths; see the Information Box on Calculus if you need a reminder.

If we take the rate law (Eq. 7) and express the reaction rate (ν) as a derivative as defined in eq. 5, then we have the following differential equation for a first order reaction:

$$\frac{dc_A}{dt} = -kc_A \quad (8)$$

We can solve this differential equation to find out how the concentration of A changes with time. Rearranging the equation gives the integral:

$$\int_{c_{A,0}}^{c_{A,t}} \frac{1}{c_A} dc_A = - \int_0^t k dt \quad (9)$$

where $c_{A,0}$ is the concentration of A at $t=0$, and $c_{A,t}$ is the concentration of A after time t .

$$\ln \frac{c_{A,t}}{c_{A,0}} = -kt \quad (10)$$

Hence, the concentration of A decreases exponentially as a function of time as given by:

$$c_{A,t} = c_{A,0}e^{-kt} \quad (11)$$

Eq. 11 is the blue line plotted in Fig. 1, where k has been given a value of 1 s^{-1} and the initial concentration of c has been taken to be 1 mol dm^{-3} .

Now that we know how the concentration of A varies with time, we can ask the question 'how long does it take for the concentration of A to decrease to half of its initial value'? This is known as the half-life ($t_{1/2}$) of the reaction and is found by setting $c_{A,t} = \frac{1}{2}c_{A,0}$ and substituting this equality into Eq. 10. From this we get:

Definition: First Order half-Life

$$t_{1/2} = \frac{\ln 2}{k} \quad (12)$$

Q. For the first order reaction plotted in Fig 1, which has 1:1 stoichiometry between the reactant and product, what is the equation that defines the change in concentration of the product as a function of time (red line)?

LINK What *analytical* chemistry techniques might you use to monitor a reaction, so as to measure the reaction kinetics?

Suggested Reading:

Physical Chemistry, P. W. Atkins

Reaction Kinetics, M. J. Pilling and P. W. Seakins

Chemical Kinetics, K. J. Laidler

Dimensional Analysis

The units associated with rate constants tend to lead to some confusion. The reaction rate (ν) always has units of quantity per time, for most of our chemistry examples this corresponds to it having units of $\text{mol dm}^{-3} \text{ s}^{-1}$. 'k' is the rate constant - however, its units differ depending on the definition of the rate law! The most important thing to remember is that **any physically meaningful equation will have the same dimensions (units) for both the left and right-hand side expressions**. Comparing two values with different units is not meaningful; we cannot ask if a mile equals one kilogram.

For a first order reaction the rate law is

$$\nu = kc_A$$

If we write this equation in terms of its units we have

$$(\text{mol dm}^{-3} \text{ s}^{-1}) = [k](\text{mol dm}^{-3})$$

where $[k]$ means the units of k . Rearranging this expression we find that the units of the first order rate constant, $[k]$, are s^{-1} .

Q. Use this technique of equating the units on both sides of a rate law to find the units of a) a second order reaction and b) a reaction of 3/2 order.