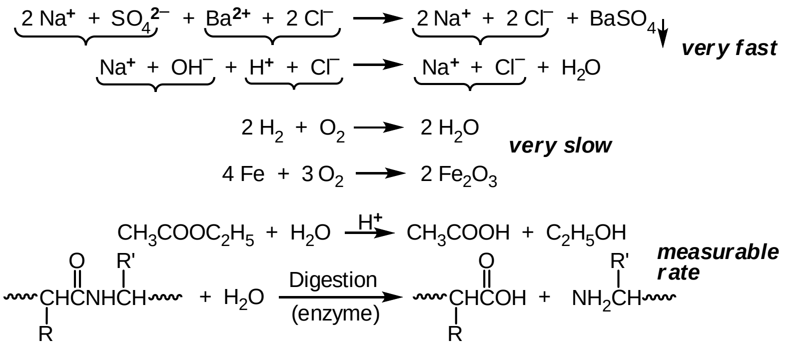
№ 11. CHEMICAL KINETICS. MOLECULARITY AND ORDER OF REACTIONS. RATE EQUATIONS.

At the molecular level, some chemical reactions go instantaneously and others take forever.

In this topic we shall develop the background needed to understand how reactions can vary so widely in their rates, even in living organisms. Enzymes will be introduced as a family of rate-controlling agents in living systems.


$$\underbrace{2\,Na^+ + SO_4^{2-}} + \underbrace{Ba^{2+} + 2\,Cl^-} \longrightarrow \underbrace{2\,Na^+ + 2\,Cl^-} + BaSO_4\downarrow$$
$$\underbrace{Na^+ + OH^-} + \underbrace{H^+ + Cl^-} \longrightarrow \underbrace{Na^+ + Cl^-} + H_2O$$
$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$
$$4\,Fe + 3\,O_2 \longrightarrow 2\,Fe_2O_3$$
$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

Thermodynamics is concerned about changes accompanying physical and chemical changes. This branch of chemistry allows conclusion on whether or not a chemical reaction can proceed spontaneously or not. **Thermodynamics cannot provide information how quickly reactions may occur.**

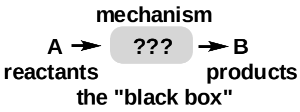
Chemical kinetics is the field of chemistry that deals with rates of chemical reactions, gives factors that affect rates, and how they work. **Kinetics study also reaction mechanism.**

The "speed" of a reaction – how long it takes to reach equilibrium – **bears no relation at all to how *spontaneous* it is** (as given by the sign and value of **ΔG°**) or **whether it is exothermic or endothermic** (given by the sign of **ΔH°**). Moreover, there is no way that reaction rates can be predicted in advance; each reaction must be studied individually. One reason for this is that the **stoichiometric equation for a reaction says nothing about its *mechanism*. It is worth noting that the concept of "time" plays no role whatsoever in thermodynamics. But kinetics is all about time.**

Reaction rate is the speed of reactants' consumption or products' formation.

Reaction mechanism is the pathway by which reactants form products describing the elemental steps involved in the transformation.

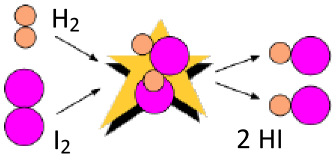
By mechanism, we mean, basically, "who does what to whom". You can think of a reaction mechanism as something that goes on in a "black box" that joins reactants to products:



$H_2\,(g) + I_2\,(g) \longrightarrow 2\,HI\,(g)$

$H_2\,(g) + Br_2\,(g) \longrightarrow 2\,HBr\,(g)$

For the reaction between hydrogen and iodine in gas phase, the experiments are consistent with the simplest imaginable mechanism: a collision between the two reactant molecules results in a rearrangement of the bonds, as the cartoon shows:



One might be tempted to suppose that the interaction between hydrogen and bromine would proceed in a similar way but experiments reveal that the mechanism of this reaction is far more complex. The reaction takes place in a succession of steps, some of which involve atomic H and Br.

The rate of any chemical reaction is affected by several factors:

- **The nature of the reactants;**
- **Physical state; interacting area (contact area);**
- **Concentration (pressure) of substances;**
- **Temperature;**
- **Presence of catalyst**

The chemical nature of the reactants is the most important factor. Wood burning in a fireplace is pleasant to the eyes. Iron rusting has noting appealing to it although both are oxidations. Clearly, **what** reacts is the first factor that determines reaction rate. **Reactions between *ionic compounds* are usually much faster than reactions between *covalent compounds***. The number of bonds cleaved and new bonds formed is also a factor, e.g.: ($KMnO_4$ + $FeSO_4$) is faster than ($KMnO_4$ + $H_2C_2O_4$) because the reducing agent in the latter case (oxalic acid) should break more bonds until oxidized to CO_2.

The physical state of the reactants affects rates.

Homogeneous reactions are those in which all of the reactants are in dissolved state either in a liquid solvent or in the gaseous state. **Heterogeneous reactions** involve at least one reactant that is not ultimately mixed with others. Reactions depend on the natural kinetic motion of particles, which are all atoms, molecules, or ions in homogeneous reactions. Only in a fluid state, liquid or gas, can these particles get at each other efficiently. With heterogeneous reactions, the particles of at least one component consist of huge clumps of atoms, ions, or molecules, and the sizes of these clumps are critical, as shown later. **The fastest reactions occur in gaseous state**. The molecules in it have the greatest amount of energy and are most mobile. Chemical reactions **proceed relatively easily in the liquid state also**. **Reactions between solid substances are the slowest.** The physical magnitude of **interacting area in heterogeneous reactions is important**. Smaller particles have larger combined area than bulk material. From everyday experience is known that starting camp fire is easier when wood is chopped initially into small pieces and that iron rusts faster when powdered. When the surface area is increased, the number of collisions between reacting particles is higher and the reaction is faster. There are numerous cases of explosions caused by industrial dust which can create also static electricity. $Zn\,(s) + 2\,HCl\,(aq) \longrightarrow ZnCl_2\,(aq) + H_2\,(g)$ The hydrogen bubbling in reaction between zinc and hydrochloric acid is much more with zinc dust than with lump of the metal.

Concentration (or pressure) affects reaction rate. Steel wool does not burn well in air, even when heated to red hot, but when placed hot in pure oxygen, spectacular flames result. Air is only 21% oxygen. Using pure (100%) oxygen clearly permits faster rate of interaction between iron and oxygen.

“Rate” is like “speed”, and both are always expressed as ratio, *vs.* time (the terms “velocity” or “speed” are not correct when applied to chemical reactions). Similar to the expression for velocity of a moving object, like an automobile:

$$\text{speed of travel} = \text{rate of vehicle motion} = \frac{\text{change in position}}{\text{time}} = \frac{\text{km (miles)}}{\text{hour}}$$

is the definition of chemical reaction rate.

The rate of a chemical reaction is defined as the change in concentration of a substance divided by the time interval during which this change is observed:

$$\text{rate of reaction} = \frac{\text{change in concentration}}{\text{time}} = \frac{\text{mol/L}}{\text{s}}$$

The same definition is written using symbols as: $\nu = \pm \dfrac{\Delta C}{\Delta t}$ IMPORTANT!

For a reaction of the general form **A + B → X**, the rate can be expressed in terms of the **change in concentration of any of its components:**

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} \quad \text{rate} = -\frac{\Delta[B]}{\Delta t} \quad \text{rate} = +\frac{\Delta[X]}{\Delta t}$$

where **Δ[A]** is the difference between the concentration of **A** over the time interval $t_2 - t_1$: $\Delta[A] = [A]_2 - [A]_1$

! Remember, the brackets, **[ ]**, denote moles per liter concentration, $mol.L^{-1}$; it is the same as $C_{(A)}$.

Did you notice the minus signs in first two relations above? The concentration of a reactant always decreases with time, so **Δ[A]** and **Δ[B]** are both negative (**$[A]_1 > [A]_2$**). Since negative rates don't make much sense (**the rate is always positive value**), rates expressed in terms of a reactant concentration are always preceded by a minus sign in order to make the rate come out positive. When the rate is measured by the concentration change of a reaction product, the “+” sign is obvious. **When coefficients are used in the stoichiometric equation, the change in substance’s concentration must be divided by the corresponding coefficient in order to obtain the same rate value.** For example, consider now a reaction in which the coefficients are different:

A + 3 B → 2 D It is clear that concentration of **B**, **[B]**, decreases three times as rapidly as **[A]**, so in order to avoid ambiguity when expressing the rate in terms of different components, it is customary to divide each change in concentration by the appropriate coefficient:

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = -\frac{\Delta[B]}{3\,\Delta t} = +\frac{\Delta[D]}{2\,\Delta t}$$

Problem: For the reaction of ammonia with oxygen:

$$4\,NH_3 + 3\,O_2 \longrightarrow 2\,N_2 + 6\,H_2O \qquad \textbf{rate} = \frac{\Delta[N_2]}{2\,\Delta t} = \frac{\Delta[H_2O]}{6\,\Delta t}$$

it was found that the rate of formation of N_2 was 0.27 mol.L^{-1}.s^{-1}.

a) At what rate was water being formed?

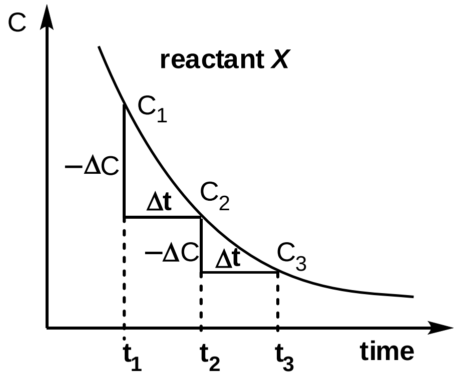
b) At what rate was ammonia being consumed?

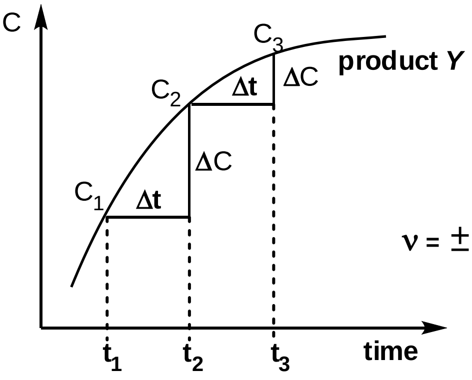
Solution: a) From the equation stoichiometry, $\Delta[H_2O] = 6/2.\Delta[N_2]$, so the rate of formation of H_2O is 3×(0.27 mol.L^{-1}.s^{-1}) = 0.81 mol.L^{-1}.s^{-1}.

b) 4 moles of NH_3 are consumed for every 2 moles of N_2 formed, so the rate of disappearance of ammonia is 2 × (0.27 mol.L^{-1}.s^{-1}) = – 0.54 mol.L^{-1}.s^{-1}.

The given definition of rate **is for the average reaction rate during the specified time interval**, **Δt**, similarly to average car speed. The car velocity is rarely constant, it depends on road conditions. Exactly the same for **chemical reactions – their rate is never constant over time**. For the transformation: **X → Y**

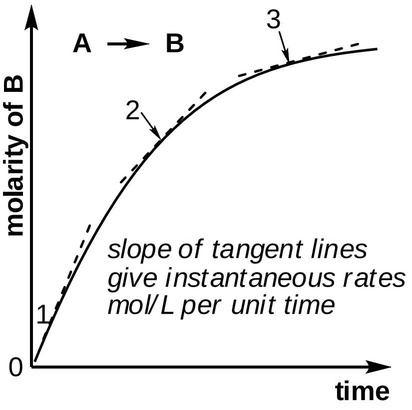
At the instant the reaction starts **[X]** is at the highest and **[Y]** is zero. As the reaction proceeds, the concentrations change; the value of **[X]** decreases and that of **[Y]** increases. Thus, **early in the reaction the rates of the disappearance of X and appearance of Y are rapid**. Later into the reaction, where the curves flatten out, further changes in concentrations take longer and longer. Hence, **the rate of a reaction decreases with time**, as illustrated in the graphics representing change of **[X]** or **[Y]** with time.





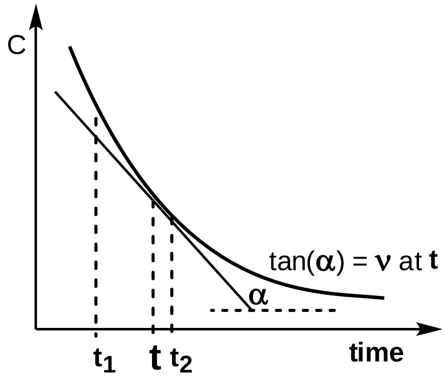
$$\nu = \pm\,\frac{\Delta C}{\Delta t}$$

Instantaneous rates, known also as differential rates. Most reactions slow down as the reactants are consumed. Consequently, the rates given by the previous expressions tend to lose their meaning when measured over longer time intervals **Δt**. Thus for the reaction whose progress is plotted in the next Figure, the actual rate (as measured by the increasing concentration of product) varies continuously, being greatest at time zero. **The *instantaneous rate* of a reaction is given by the slope of a tangent to the concentration-*vs*-time curve**. Three such rates have been identified in this plot. An instantaneous rate taken near the beginning of the reaction (**t = 0**) is known as an **initial rate** (label (1) here).

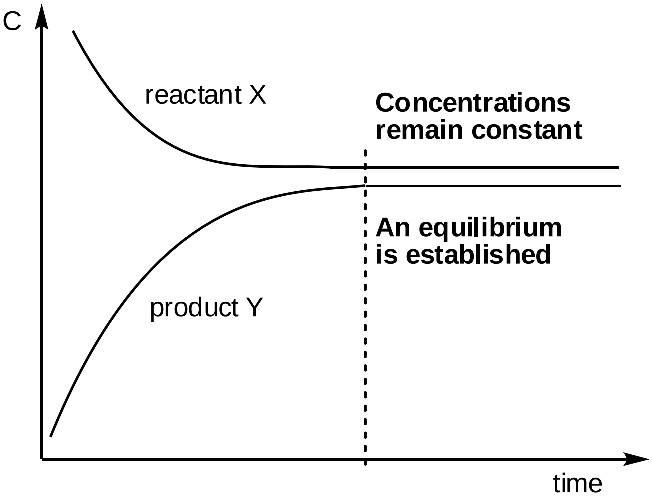


Instantaneous rate is really **limiting rate** defined as:

$$\textbf{rate}\,(t) = \lim_{\Delta t \to 0} -\frac{\Delta[X]}{\Delta t} = -\frac{d[X]}{dt}$$



In order to express the rate at any moment of time **t**, the time interval should be as short as possible, mathematically infinitesimally small. Then the concentration change is infinitesimally small and the mathematical symbol for their ratio is $\frac{d[X]}{dt}$. It gives the slope of the tangent at point **t**.



If the reaction: $X \rightleftharpoons Y$ is reversible, after long enough time no further changes in the **X** and **Y** concentrations can be observed. **An equilibrium is established. The rates of the forward and reverse reactions are equal at equilibrium state.**

For our hypothetical reaction: $X \longrightarrow Y$ the rate at which **[X]** decreases is identical to the rate at which **[Y]** increases. In more complex reactions, a relationship this simple is almost never observed.

What is found is that the rate is proportional to some mathematical combination of the molarities of two (or more) reactants, each molarity raised to some exponential power.

Let's say for the reaction of the type: $X + Y \longrightarrow Z$ when the **concentration of reactants is increased** in either gas or liquid, the reaction rate increases because of the increased probability that the moving reactant molecules will collide. The proportionality of rate to concentrations is written in general form as $\mathbf{\nu = \propto [X]^m.[Y]^n}$.

The rate of a chemical reaction depends on the concentration of the reactants. The rate is higher when concentration is higher.

Notice! The difference in the exponents in rate expression and the equilibrium constant – the latter contains stoichiometric coefficients whereas in the former, **m** and **n** have various values.

Collision theory is a major theory in chemical kinetics that explains the factors affecting rates.

Electrons and nuclei become reorganized in a chemical reaction, but for this to happen, reactant particles have to collide. Central to collision theory is the idea that a given **reaction will be faster the more frequently the reactant particles collide. Only part of the collisions, called effective, lead to chemical transformation.** If the molar concentration of one reagent is doubled, the frequency of all collisions must double because there are twice as many of its particles (in the same volume). There is analogy with moving people in city square – more people on the same area leads to increase of "excuse-me" kind of bumps and collisions. **The relation between the rate of a reaction and the concentrations of reactants is expressed by its rate law.** For example, the rate of the gas-phase decomposition of dinitrogen pentoxide has been found to be **directly proportional** to the concentration of N_2O_5: $2\,N_2O_5 \longrightarrow 4\,NO_2 + O_2$ rate = $\boldsymbol{k}\,[N_2O_5]$ **(Not squared!)**

Be very careful about confusing equilibrium constant expressions with those for rate laws. The expression for $\mathbf{K_{eq}}$ can always be written by inspecting the reaction equation, and it contains concentration terms, raised to the power equal to the stoichiometric coefficient:

$$a\,X + b\,Y \rightleftharpoons c\,Z \qquad K_{eq} = \frac{[Z]^c}{[X]^a.[Y]^b}$$

In contrast, the expression for the rate law generally bears no necessary relation to the reaction equation, and must be determined experimentally.

More generally, for a reaction of the form: $a\,X + b\,Y + \ldots\ldots \longrightarrow$ products

the rate law is written as :

$$\text{rate} = -\frac{d[X]}{dt} \propto [X]^m.[Y]^n\ldots. \;;\; \nu = \boldsymbol{k}.[X]^m.[Y]^n$$

This experimentally determined equation is called «rate expression» or «rate law». A rate law describes how fast a specific reaction proceeds and how the reaction rate depends on the concentrations of the chemical species involved. **The exponents m and n are usually integers or simple fraction (even zero) and, we must emphasize once again, bear no relation to the coefficients *a* , *b, etc*. The proportionality coefficient *k* is termed "the rate constant".**

Guldberg-Waage law (law of mass action, 1864) is applied to reaching equilibrium or **elementary reactions**.

The rate constant *k* is specific for each chemical reaction and depends on the nature of the substances, on the temperature and on the presence of catalysts. The rate constant *does not depend on the concentration of the reactants.* The meaning (and dimension) of ***k*** is reaction rate when all concentrations are equal to 1 mol/L.

In such case the rate constant has equal value as the rate of the process: $\nu = k$

For each reaction the rate constant has a specific value.

For heterogeneous reactions, the concentration of a solid is constant, and it is not included in the rate law.

$$Zn\,(s) + H_2SO_4\,(aq) \longrightarrow ZnSO_4\,(aq) + H_2\,(g)\uparrow$$

$$\nu = k.[H_2SO_4]$$

REACTION ORDER

In chemical kinetics, **the order of a reaction with respect to certain reactant, is defined as the exponent to which its concentration term in the rate equation is raised.**

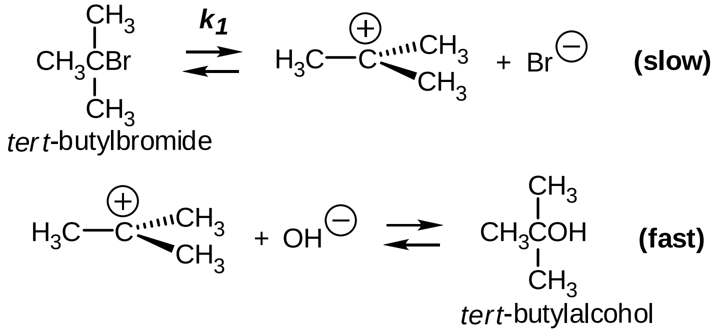
For example, given a chemical reaction $2\,X + Y \longrightarrow Z$ with a rate equation $\nu = k.[X]^2.[Y]$

The reaction order with respect to **X** in this case is 2 and with respect to **Y** is 1, **the overall reaction order would be 2 + 1 = 3**. It is not necessary that the order of a reaction be a whole number – zero and fractional values of order are possible but they tend to be rare. **Reaction orders can be determined only by experiment**. Their knowledge allows conclusions about the reaction mechanism.

The alkaline hydrolysis of ethyl acetate is a complex reaction with the following rate equation:

$$CH_3COOC_2H_5 + OH^- \longrightarrow CH_3COO^- + C_2H_5OH \qquad \nu = k.[CH_3COOC_2H_5].[OH^-]$$

Reactions of zero order. Zero-order means that the rate is independent of the concentration of a particular reactant. But of course enough of it must be present to allow the reaction or equilibrium mixture to form. Typical example is a nucleophilic substitution reaction, after finding its monomolecular mechanism **– S_N1** reaction:



$$\nu = k_1.[(CH_3)_3CBr] \quad \textbf{zero order with respect to } OH^-$$

As the rate law (based on the mechanism) demonstrates, the reaction is of zero order with respect to the hydroxide anions' concentration.

The order of a complex reaction reflects the experimental data – it is **experimental quantity**. Determination of reaction order requires also knowledge of the mechanism.

Reactions of first order. In such reactions the rate depends on the concentration of the reactant to the first power.

Second order reaction – the rate depends on the concentration of the reactant to the second power.

Third order reactions, or higher are rare.

For some reactions the determined order can be equal to the number of particles, as indicated by the stoichiometric coefficients, e.g. alkaline hydrolysis of an ester and the reaction:

$$H_2\,(g) + I_2\,(g) \longrightarrow 2\,HI\,(g) \qquad \nu = k.[H_2].[I_2]$$

Such cases are usual for reactions taking place in an elementary step.

The order of a reaction can also be a fraction.

$$H_2\,(g) + Br_2\,(g) \longrightarrow 2\,HBr\,(g) \qquad \nu = k.[H_2].[Br_2]^{1/2}$$

The rate expression shows that the reaction is first order with respect to hydrogen and **1/2 order with respect to bromine**. The total order of the reaction is (1 + 1/2 = 3/2), which cannot be obtained from the balanced chemical equation. It can only be obtained by experiment.

MOLECULARITY OF A REACTION

Molecularity in chemical kinetics is the number of colliding molecular entities that are involved in a single reaction step. While the order of a reaction is derived experimentally, the molecularity is a theoretical concept and can only be applied to elementary reactions. Most reactions do not take place in a single step. They occur in consecutive individual steps. **Reaction mechanism is the step by step sequence of elementary reactions by which overall chemical change occurs**. The number of particles colliding and reacting in each individual step is called the *molecularity of the elementary process*. **The number of particles involved in the rate-determining step of a reaction (the slowest step) is defined as the molecularity of this reaction.**

A reaction involving one molecular entity is called unimolecular, e.g. **S_N1** (**S**ubstitution **n**ucleophilic, **1**:unimolecular), and all such as: $X \longrightarrow \text{product(s)} \qquad v = \boldsymbol{k_1}.[X]$

(Only one reacting species produces product(s).)

A reaction involving two molecular entities in the rate determining step is called bimolecular, for example:

$$X + X \longrightarrow \text{product(s)} \qquad v = \boldsymbol{k_2}.[X]^2$$

$$X + Y \longrightarrow \text{product(s)} \qquad v = \boldsymbol{k_2'}.[X].[Y]$$

A reaction involving three molecular entities is called termolecular. Termolecular reactions in solutions or gas mixtures are very rare, because of the improbability of three molecular entities simultaneously colliding. (In all rate laws expressions above, some term may have the exponent equals to zero or fraction!)

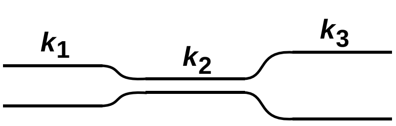
$$X + X + X \longrightarrow \text{product(s)} \qquad v = \boldsymbol{k_3}.[X]^3$$

$$X + X + Y \longrightarrow \text{product(s)} \qquad v = \boldsymbol{k_3'}.[X]^2.[Y]$$

$$X + Y + Z \longrightarrow \text{product(s)} \qquad v = \boldsymbol{k_3''}.[X].[Y].[Z]$$

A reaction mechanism in chemistry is a series of consecutive elementary steps. Their sum is the overall balanced reaction equation. Mechanisms describe in a stepwise manner the exact collisions and events that happen during the conversion of reactants into products. In order to derive the rate law from a mechanism is necessary to find first the **rate-determining (rate-limiting) step. The rate limiting step determines the rate of the overall reaction because it is the slowest step**. The number of molecules involved in the rate-determining step is called the molecularity of the reaction. In some reactions, the rate-determining step involves only one molecule. Hence, the molecularity is one although other elementary processes in the same mechanism involve more molecules. The rate equation for the overall reaction is written for its rate-determining step. In the example of decomposition of dinitrogen pentoxide, two molecules N_2O_5 are in balanced equation, however, it has been determined experimentally that the rate depends on first power of N_2O_5 concentration, *i.e. reaction is monomolecular*: $2\,N_2O_5 \longrightarrow 4\,NO_2 + O_2 \qquad v = \boldsymbol{k}\,[N_2O_5]$

The rate-determining step might be compared to set of tubes with different diameters with a fluid pushed through; the maximum amount of fluid going per unit time depends on the narrowest tube $\boldsymbol{k_2}$ with smallest diameter.



The majority of biochemical reactions, including enzyme catalyzed, also comprise several connected elementary reactions, that is, they are complex reactions. In such complex reactions, to account for the kinetic data, reaction mechanisms are also formulated. For a mechanism of many steps (including their reverse), the construction of the overall rate law is quite difficult, requiring an approximation or a computer for a numerical analysis. **The rate law** for a complex reaction cannot be predicted from the stoichiometry of the reaction; **it must be determined experimentally**. The goal of a kinetics experiment is to measure the concentration of a species at a particular time during a reaction so that a rate law can be determined.

Elementary reactions that proceed through only one step have order equals to the molecularity, e.g. :

$$H_2\,(g) + I_2\,(g) \longrightarrow 2\,HI\,(g) \qquad v = \boldsymbol{k}.[H_2].[I_2]$$

The order is 1 + 1 = 2, which is same as the number of molecules in the stoichiometric equation, that collide in an elementary step. This reaction is therefore first order with respect to each reactant and is second order overall; in this particular reaction ***Molecularity = Order***.

Unimolecular reaction are by necessity of 1st order. Not all 1st order reactions need to be unimolecular.

MOLECULARITY *vs* REACTION ORDER comparison

Molecularity	Order
Molecularity is the number of molecules, ions or atoms involved in the elementary step of a chemical reaction.	**Order is the sum of the exponents on the concentration terms in the rate equation.**
It is a theoretical concept based on the elementary step.	**It is experimentally determined.**
It is always an integer.	**It may be integer or a fraction.**
It is never zero.	**It can be zero for some reactions.**
It provides no information on reaction mechanism.	**The slowest step in the reaction can be found by the order and this gives further information about the mechanism.**
Molecularity usually does not exceed 3.	**Order usually does not exceed 3.**

Differential and integral rate laws

Measuring instantaneous rates is the most direct way of determining the rate law of a reaction, but is not always convenient or possible. If the reaction is very fast, its rate may change more rapidly than the time for measurement (finished before an initial rate observation). In the case of very slow reactions, observable changes in concentrations occur so slowly that the observation of a truly "instantaneous" rate becomes impractical. **The ordinary rate law** (more precisely known as the *instantaneous* or *differential* rate law) **tells us how the rate of a reaction depends on the concentrations of the reactants**. But for many practical purposes, **it is more important to know how the concentrations of reactants (*and of products*) change with time.** For example, in industry is important to know how long it will take for, say, 95% of the reactants to be converted into products. **The answer is obtained from an *integrated rate law*.**

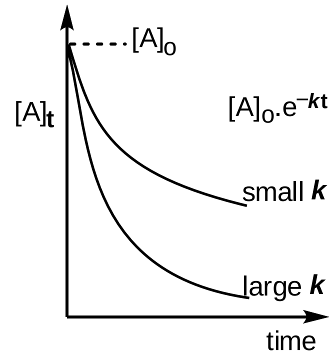
First-order reactions are governed by the law of exponential change

The rate at which a reactant is consumed in a first-order process is proportional to its concentration at that time. This general relationship, in which a quantity changes at a rate that depends on its instantaneous value, is said to follow an **exponential law**. The integrated rate law for a first-order reaction

$$\mathbf{A} \longrightarrow \text{products} \qquad \textbf{rate} = -\frac{\mathbf{d[A]}}{\mathbf{dt}} = \boldsymbol{k}.\mathbf{[A]}$$

is a common example of the law of exponential change. For a reactant **A**, **its concentration $[A]_t$ at time *t*** is given by:

$$[A]_t = [A]_o.e^{-kt}$$



in which **$[A]_o$** is its initial concentration, **e** is the base of natural logarithm, ~ 2.718, and ***k*** is the first-order rate constant. The Figure shows how the initial concentration, **$[A]_o$** , falls with time in two different reactions possessing different rate constants ***k*** . A more convenient form of the integrated rate law

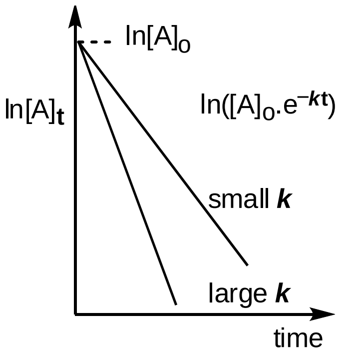
$$[A]_t = [A]_o.e^{-kt}$$

is obtained by taking the natural logarithm of both sides:

$$\ln[A] = -k.t + \ln[A]_o$$

IMPORTANT!

This expression has the form of an equation for a straight line ***y = ax + b*** in which **the slope *a* corresponds to the rate constant *k***. This means that, **for a first-order reaction, a plot of ln[A] as a function of time gives a straight line with a slope of –*k***.



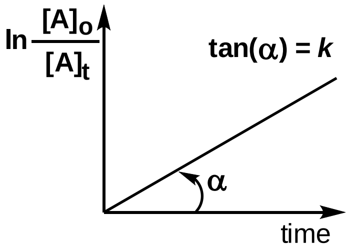
The next Figure illustrates two such logarithmic and linear plots corresponding to the cases in previous graph:

After rearrangement of the integral rate law we obtain:

$$\ln[A]_t = -k.t + \ln[A]_o$$

$$\ln[A]_o - \ln[A]_t = k.t$$

Then, useful is the integral form: $\ln \frac{[A]_o}{[A]_t} = k.t$



Plotting the natural logarithm of the ratio between initial and current (at time **t**) concentration *vs.* time gives straight line with slope ***k*** , as shown in the graph:

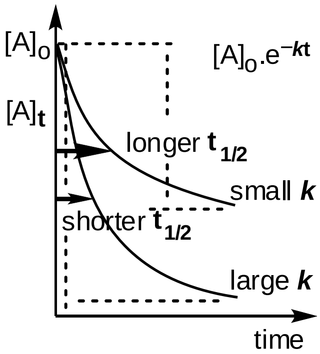
The half-life of a reaction (reactant)

Instead of trying to identify the time required for the reaction to become completed, it is far more practical to specify its half-life (half-time). **The time required for the concentration of a reactant to fall to half of its initial value is known as the *half-life* (or half-time) of the reaction (reagent, radioisotope decay)**. **After a period of one half-life, t = $t_{1/2}$** and we can write: $\frac{[A]_{1/2}}{[A]_o} = \frac{1}{2} = e^{-kt_{1/2}}$

(in which we express the exponential as a function in order to make it stand out more prominently). Taking logarithms of both sides yields: $\ln 0.5 = -k.t_{1/2}$

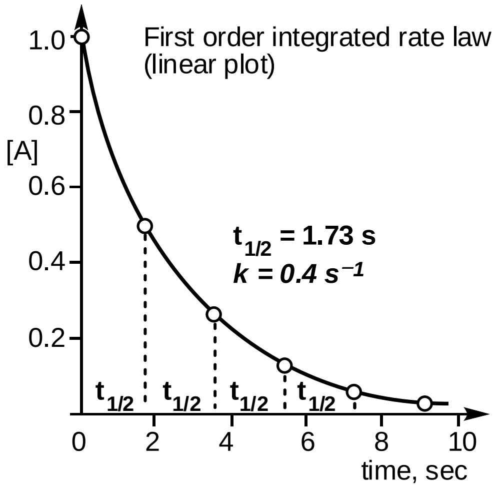
Solving for the half-life, we obtain the simple relation: $t_{1/2} = \frac{0.693}{k}$

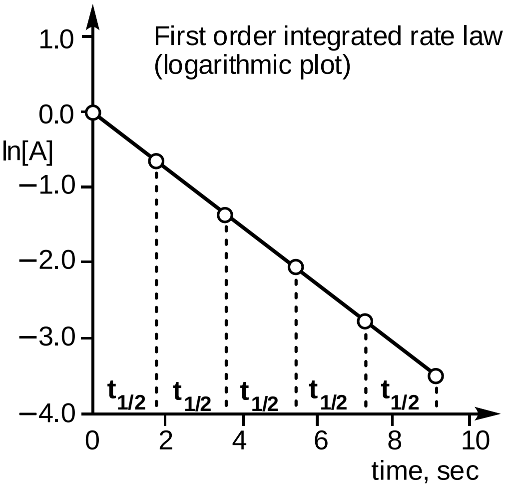
which tells us that the half-life of a first-order reaction is a constant. This means that 100,000 molecules of a reactant will be reduced to 50,000 in the same time interval needed for ten molecules to be reduced to five.



It should be clear that the rate constant and the half life of a first-order process are inversely related, as is indicated in the Figure. **Radioactivity is one very frequent example of exponential decay**. Useful isotope for dating of samples is ^{14}C. It has a half-life of 5730 years allowing age determination of very old materials. Positron emission tomography (PET) scans use labeled with ^{18}F glucose – half-life of 110 min. The artificial listed element Ununhexium, ^{293}Uuh, has half-life 5.3×10^{-2} s.

Illustrations of a reaction half-life using linear (left) and logarithmic (right) plots are shown below. When the half-time of a reagent is determined experimentally, the value of ***k*** is easily calculated.





Zero-order processes In some reactions, the rate is apparently independent of the reactant concentration. There are two general conditions that can give rise to zero-order rates:

1) Only a small fraction of the reactant molecules are in a location (as in heterogeneous catalysis) or state in which they are able to react, and this fraction is continually replenished from the larger pool. **Enzyme-catalyzed reactions in organisms** begin with the attachment of the substrate to the active site on the enzyme, leading to the formation of an **enzyme-substrate complex**. If the number of enzyme molecules is limited in relation to substrate molecules, then the reaction may appear to be zero-order. The notion of steady state is necessary in order to describe enzyme kinetics.

2) When two or more reactants are involved, the concentrations of some are much greater than those of others. Thus if the reaction $A + B \longrightarrow \text{product(s)}$ is first-order in both reactants so that: **rate** = $\boldsymbol{k}$.[A].[B] , then **if B is present in great excess**, the reaction **will appear to be zero order in B** (and first order overall). This commonly happens when **B** is H_2O and the reaction is carried out in aqueous solution.

Pseudo unimolecular reactions Hydrolysis of table sugar (sucrose or saccharose) in very dilute solution, catalyzed by an acid is bimolecular. However, water concentration is very high in relation to sucrose. The molar concentration [H_2O] does not change much during the hydrolysis and is assumed ≈ constant. Therefore, when one of the reactants in the rate equation is present in great excess over the other in the reaction mixture, its concentration term is not included in the rate equation.

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6} \qquad \nu = \boldsymbol{k}.[\text{sucrose}]$$

This hydrolysis reaction is bimolecular but appears as pseudo unimolecular and of first order with respect to sucrose (zero order in water).

The steady state approximation, occasionally called the **stationary-state approximation, involves setting the rate of change of a reaction intermediate in a reaction mechanism equal to zero**. Kinetics of enzyme catalyzed reactions is mathematically derived using steady state model. Steady state in physiology is called homeostasis. It is the property of a living organism that regulates its internal environment and tends to maintain a stable, constant condition of properties such as temperature or pH, e.g. glucose blood level in humans should remain about constant.

Mammals regulate their blood glucose with the hormones insulin and glucagon. The human body maintains glucose levels constant most of the day. Insulin, secreted by the beta cells of the pancreas, effectively transports glucose to the body's cells by instructing those cells to keep more of the glucose for their own use. **If the glucose inside the liver cells is high, the cells will convert it to the insoluble glycogen** to prevent the soluble glucose from interfering with cellular metabolism. Ultimately this lowers blood glucose levels, and **insulin prevents hyperglycemia**. When insulin is deficient or cells become resistant to it, diabetes occurs.

Glucagon, secreted by the alpha cells of the pancreas, encourages cells to break down stored glycogen or convert non-carbohydrate carbon sources to glucose, thus **preventing hypoglycemia**.

The **kidneys are used to remove excess water and ions from the blood**. These are then expelled as urine. The kidneys perform a vital role in homeostatic regulation in mammals, removing excess water, salt, and urea from the blood. These are the body's main waste products.