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Chemical Kinetics

for Beginners

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1. Introduction

Reaction kinetics is the branch of physical chemistry which deals with the temporal evolution of chemical reactions. It provides explanation as to why some reactions do not take place, although their products would be much more stable thermodynamically than the reactants are; it accounts for the fact that some reactions go very fast while some other rather slowly. Furthermore, it also provides several useful tools to calculate the actual rate of reactions within a wide variety of circumstances, including *e. g.* the dependence of the rate on temperature, pressure, the solvent applied, *etc*.

The most important goal of kinetic research is the identification and characterisation of elementary molecular events which make possible the transformation of reactants into products. At the time of the beginning of reaction kinetic studies – in the second half of the 18th century when mechanical models dominated natural sciences – the scheme of these simple molecular events that constitute the overall reaction has been called as the *mechanism* of the reaction, which term survived and is still widely used. This means that the *elementary* steps of the reaction – the most simple events when typically two molecules directly encounter – are identified, and the complex reaction mechanism is constructed from these elementary steps. Most real-life chemical reactions comprise quite a number of such elementary steps; the number of them *e. g.* in gas reactions can be as much as a few hundreds. The overall rate of these reactions can successfully be calculated over a wide range of circumstances if we can calculate the rate of all the constituent elementary reactions within the given conditions, and also know the way of their connection within the reaction mechanism. This is the reason why the theory of elementary reactions has a paramount importance in chemical kinetics.

However, to explore the precise mechanism of composite reactions is not an easy task. To be able to construct a reliable mechanism, we have to identify all the components which take part in the process of the reaction, even if they are short-lived and have rather low concentration. We also have to keep track of the temporal evolution of possibly all these components, although this is not always possible. In many reactions, there are so called *intermediates* (substances formed from the *reactants* and readily removed in consecutive reactions leading to the *products*) that are rather short-lived and present only in very low concentrations, thus they easily remain unnoticed for the experimentalist. After having traced the temporal evolution of as many components of the reacting mixture as possible, the task of the kineticist is to construct a suitable mechanism that can explain all the concentration changes as a function of time. Consequently, theories of composite reactions also constitute an important topic of reaction kinetics.

To successfully model reactions the way explained above, we need an unambiguous definition of the rate of change of the amount of components taking part in the reaction. There exists an IUPAC recommendation for the definition of the *rate of reaction*. For the sake of this definition, we shall write stoichiometric equations in a special form, so that the equation is set equal to zero. The advantage of this form is that reactants and products (species on the left-hand side and on the right-hand side in the more common equation) can be treated the same way, thus simplifying the mathematical treatment. The general stoichiometric equation of this form can be written as:

$$\sum_{i=1}^{R} \nu_i A_i = 0 \tag{1.1}$$

The symbol A_i in this equation denotes the stoichiometric formula of the i-th species, and ν_i (lower case Greek "nu") is the *stoichiometric number* of this species. The index i runs over all the *reacting species* whose number is R. (Components that do not react – *e. g.* an inert solvent – should have a zero stoichiometric number, thus it is superfluous to include them in the sum.) As an example, let us write one of the possible equations of the formation of water:

$$-1\ H_2 - ½\ O_2 + 1\ H_2O = 0 \tag{1.2}$$

In this equation, $A_1 = H_2$, $A_2 = O_2$, $A_3 = H_2O$, $\nu_1 = -1$, $\nu_2 = -½$ and $\nu_3 = 1$. However, we are too much used to write stoichiometric equations in the usual left side – right side form. Thus we usually write the equation itself in the traditional form

$$H_2 + ½\ O_2 = H_2O\ , \tag{1.3}$$

but we consider the stoichiometric number ν_i of the reactants (left side) to be *negative*, while those of the products (right side) to be *positive*. In the rest of this text, we always interpret stoichiometric equations this way.

The rate of a particular reaction should be defined naturally in such a way that it should be independent from the choice of the component taking part in the reaction whose amount would be used for the temporal evolution. To formulate such definition, let us introduce the *extent of reaction* ξ also used in thermodynamics, but for use in the definition of the rate of reaction, it is sufficient to specify its change as

$$d\xi = \frac{dn_i}{\nu_i}\ . \tag{1.4}$$

The definition of the *rate of the reaction* which is written in the above explained general form (1.1) can then be written as:

$$r = \frac{d\xi}{dt} = \frac{1}{\nu_i}\frac{dn_i}{dt} \tag{1.5}$$

According to this, the SI unit of the rate of reaction is mol (stoichiometric equation) / s. In the chemical praxis, concentrations are much more convenient to measure than amounts of substances. Taking this into account, let us calculate from the above definition the rate of change of molar concentration of a species. Using the definition of the molar concentration as n_i/V, we get

$$\frac{1}{\nu_i}\frac{d(c_i V)}{dt} = \frac{1}{\nu_i}\left(V\frac{dc_i}{dt} + c_i\frac{dV}{dt}\right) \tag{1.6}$$

This equation reveals that the rate of change of the molar concentration dc_i/dt also depends on the rate of change of volume. If the volume does not change during the reaction, the rate of reaction can be obtained by multiplying dc_i/dt by the volume of the reacting system, and dividing it by the stoichiometric number. Accordingly, we can state that *in case of reactions at constant volume*, the change of molar concentration is identical to the stoichiometric number times the *rate of reaction divided by the volume*:

$$\frac{dc_i}{dt} = \frac{1}{V}\frac{dn_i}{dt} = \frac{\nu_i}{V}\frac{d\xi}{dt} \tag{1.7}$$

Within chemical kinetic context, the quantity dc_i/dt is usually called simply as the rate of reaction. However, we should be aware that this quantity is proportional only to the rate of reaction in case of constant volume reactions, when the proportionality constant is the volume V divided by the stoichiometric number ν_i. In condensed phase reactions (*e. g.* in solutions) this is typically true to a good approximation, thus the proportionality can be assumed. Further on in this text, we also consider dc_i/dt as the rate of the reaction. However, in gas phase reactions, if there is a change in number of moles during the reaction, this proportionality does not hold and the change of volume should also be taken into account. It is worth mentioning also that the latest recommendations of IUPAC suggest to use the term "*rate of conversion*" for $d\xi/dt$ and the „rate of reaction" for $\frac{1}{\nu_i}\frac{dc_i}{dt}$. However, naming of the terms does not change their relation as explained above.

As we have seen, the definition of the reaction rate (in both versions) refers to a particular stoichiometric equation as it contains the corresponding stoichiometric numbers. It is worth mentioning that even this definition is only valid if during the (composite) reaction, there won't be any accumulation of an intermediate, and no other "by-products" are formed beside those included in the stoichiometric equation. (This is never the case for elementary reactions where this definition can always be used.) Thus, in case of composite reactions it is more convenient to refer to the change of the amount (or concentration) of a *component*, or equivalently to the *rate of consumption* for reactants and the *rate of formation* for products.

2. Formal kinetic description of elementary reactions

Theories of elementary reactions suggest that the traditional form of kinetic equations describing the rate of reactions – dating back as early as the middle of the 19th century – is always valid for elementary reactions, *i. e.* for the simplest molecular events comprising only a few molecules and proceeding by the formation of only one transition state between the reactants and the products. Thus, if the elementary reaction is the decomposition of an (non-thermally) activated species, then the rate equation can be written as $R = k\,N_{\mathrm{A}}$, where R is the reaction rate, N_{A} the number density (concentration) of the reacting species A. Similarly, for the reaction of two molecules A and B we can write the rate equation as $R = k\,N_{\mathrm{A}}N_{\mathrm{B}}$. The only other – much less frequent – possibility is the reaction of three molecules (A, B and C) after their encounter, when the rate equation has the form $= k\,N_{\mathrm{A}}N_{\mathrm{B}}N_{\mathrm{C}}$. We can generalise this result by writing one single equation. Replacing the number density by the more common molar concentration and writing the reaction rate also in terms of this concentration, the rate equation has the form

$$-\frac{1}{\nu_i}\frac{dc_i}{dt} = k\prod_{i=1}^{n} c_i \,, \tag{2.1}$$

where ν_i is the stoichiometric number of the i-th component in the stoichiometric equation, and c_i is its actual molar concentration. The rate coefficient k in this equation is somewhat different from the one in the rate equations containing number densities N (usually in molecules/cm^3 unit). Let us ignore here to use another notation for the rate coefficient when the concentration has the unit mol/dm^3, and interpret it further on as referring to the molar concentration. (The relation between the two contains the Avogadro constant and 1000 to convert cm^3 to dm^3.) The negative sign of the time derivative reflects the fact that reactants disappear in the course of the reaction. (If we consider the stoichiometric number as being negative for the reactants, this negative sign can be dropped.) The quantity denoted by n is of course the number of molecules participating in the reaction.

Rate equations having the form of Eq. (2.1) are called *mass action kinetic* equations. If we consider the stoichiometry of the reaction, we can readily realise that the concentration of the n different reactants do not change independently – which will help a lot to solve the kinetic equation. This form of the kinetic equation is typically classified according to the number of molecules participating in the molecular event of the reaction. Let us write the three stoichiometric and rate equations in the form of Eq. (2.1) for the actual cases of one, two and three molecules:

Reaction: $$\mathrm{A} \rightarrow \text{products} \qquad (2.2)$$

Rate equation: $$-\frac{dc}{dt} = kc \qquad (2.3)$$

Reaction: $$\mathrm{A} + \mathrm{B} \rightarrow \text{products} \qquad (2.4)$$

Rate equation: $$-\frac{dc_\mathrm{A}}{dt} = -\frac{dc_\mathrm{B}}{dt} = kc_\mathrm{A}c_\mathrm{B} \qquad (2.5)$$

Reaction: $$\mathrm{A} + \mathrm{B} + \mathrm{C} \rightarrow \text{products} \qquad (2.6)$$

Rate equation: $$-\frac{dc_\mathrm{A}}{dt} = -\frac{dc_\mathrm{B}}{dt} = -\frac{dc_\mathrm{C}}{dt} = kc_\mathrm{A}c_\mathrm{B}c_\mathrm{C} \qquad (2.7)$$

Observing these equations we can see the coupling between concentration changes due to the stoichiometry, and that derivatives at the left side of the rate equations are expressed at the right side by a product, where the variables to be multiplied are not independent. Equations having this form are called *first order homogeneous ordinary differential equations of degree* n. It is *ordinary*, as it contains the derivative of a function $c(t)$ of one single variable only. It is *first order*, as the only derivative is a first derivative. It is *homogeneous of degree* n, as there is a single function in it (apart from the derivative), which is the product of n variables; thus a polynomial of n-th degree. However, in chemistry, we call the reaction characterised by these equations as *n-th order reaction*. (This name dates back to ancient times when the degree of polynomials in mathematics was also called order. This term is no more used for the degree of polynomials.) According to this naming tradition, the three reactions listed above are *first order*, *second order* and *third order* reactions, respectively.

The examples discussed above were related to molecular events happening via formation of one transition state only from the reactants and its consecutive decomposition into products. Such events are called *elementary reactions*. Their rate equation always follows the mass action kinetic law (2.1), and the number of molecules taking part in the reaction is called their *molecularity* – which, in the case of the elementary reactions – is identical to their *order*. From the point of view of molecularity, the first reaction is a *unimolecular*, the second one a *bimolecular*, and the third one a *termolecular* reaction. (The latter is sometimes also called a *trimolecular* reaction, but we shall not use this term in this text.) It is worth to emphasise that the order and molecularity of the reaction are not identical categories. We shall later deal with composite reactions whose rate equation can sometimes have the form of an integer order, but molecularity is not meaningful for composite reactions which consist of several elementary reactions. We can also find composite reactions which have an order that is not an integer number, while molecularity always refers to integers.

It is worth mentioning why termolecular reactions are not frequent. The probability of simultaneous encounter (or, in gas phase, of simultaneous collision) of three molecules is much less frequent than that of two molecules. For this reason, the termolecular process is extremely slow, and in many cases, there is an equivalent route with a complex mechanism which is faster, and largely masks an eventual termolecular process.

2.1. Solution of rate equations of integer order reactions

As we have seen, rate equations of elementary reactions are always of integer order; thus, the title of this section might well have been also “solution of rate equations of elementary reactions”. However, this would exclude the possibility for composite reactions to be of integer order, though there are plenty of examples for this behaviour. One of the possible forms of a general integer order reaction is the case when the initial concentrations of the reactants are identical. (This is necessarily the case if, for example, two reacting molecules are identical.) In this case, the relevant rate equation has the form

$$-\frac{dc}{dt} = kc^n \ , \tag{2.8}$$

if the concentration *c* refers to a component with unit stoichiometric number. In mathematics, this kind of differential equation is called *separable* as the dependent variable *c* and the independent variable *t* can be separated to the opposite sides of the equation, then both sides can readily be integrated to get an implicit function of the independent variable. The above differential equation can be written in the separated form

$$-\frac{1}{c^n} dc = kdt \ . \tag{2.9}$$

Integrating both sides we can get the solution as

$$-\int \frac{1}{c^n} dc = \int kdt \ . \tag{2.10}$$

Evaluating the integrals, we can determine the primitive functions up to an undetermined additive constant. (It is enough to write one single constant; the two constants arising from the two integrations can be combined.) To find the primitive function, we can realise that the integrands at both sides are simple power functions. On the right side – after factoring out *k* from the integration – we get $1 = t^0$, while on the left side, we get $\frac{1}{c^n} = c^{-n}$. Substituting their primitive functions in place of the integrals, the *general solution* is

$$-\frac{c^{1-n}}{1-n} = kt + I \ \ , \tag{2.11}$$

where the left side can be re-written in a more transparent form:

$$\frac{1}{(n-1)\,c^{n-1}} = kt + I \tag{2.12}$$

From this general solution, we can get the *particular solution* by determining the undetermined integration constant I with the help of the *initial conditions*. For the first-order ordinary differential equation, one initial condition is sufficient; the most convenient in this case is to give the value of the concentration at the very beginning of the reaction. Let us denote this concentration at $t = 0$ by c_o. (Further on we will call this concentration as the *initial concentration*.) Substituting $t = 0$ and $c = c_o$, we readily get the value of the integration constant as

$$I = \frac{1}{(n-1)c_o^{n-1}} \tag{2.13}$$

Let us write this result into the general equation:

$$\frac{1}{(n-1)\,c^{n-1}} = \frac{1}{(n-1)c_o^{n-1}} + kt \tag{2.14}$$

Multiplying both sides by $(n - 1)$ we can get a somewhat simpler form

$$\frac{1}{c^{n-1}} = \frac{1}{c_o^{n-1}} + (n-1)kt \;, \tag{2.15}$$

from which it is straightforward to express the explicit solution $c\,(t)$:

$$c = \sqrt[n-1]{\frac{1}{\frac{1}{c_o^{n-1}} + (n-1)kt}} \tag{2.16}$$

We can also rewrite the $(n - 1)$-th root in a power expression form equivalent to the above:

$$c = \left(\frac{1}{\frac{1}{c_o^{n-1}} + (n-1)kt}\right)^{\frac{1}{n-1}} \tag{2.17}$$

It is worth noting that there is also an alternative method to solve the differential equation by evaluating *definite integrals* in accordance with the initial condition. To do this, we evaluate the right side integral in Eq. (2.10) over the limits from the time of the initial condition 0 to an arbitrary final time t_f, and the left side integral with respect to c from $c(0)$ to $c(t_f)$:

$$-\int_{c(0)}^{c(t_f)} \frac{1}{c^n}\,dc = \int_0^{t_f} k\,dt \tag{2.18}$$

Evaluating the integral we get the result

$$\frac{1}{(n-1)}\left(\frac{1}{[c(t_f)]^{n-1}} - \frac{1}{c_o^{n-1}}\right) = kt_f \tag{2.19}$$

As this solution is valid for any final time t_f and the corresponding concentration $c(t_f)$, we can substitute t in place of t_f and c in place of $c(t_f)$, thus getting the same form of the solution as before:

$$\frac{1}{(n-1)\,c^{n-1}} - \frac{1}{(n-1)c_o^{n-1}} = kt \tag{2.20}$$

Some textbooks and research papers commit a severe formal error while using the definite integration by not making a difference between the dummy integration variable and the limit of the integration; in the above example they would write incorrectly

$$-\int_{c_o}^{c} \frac{1}{c^n} dc = \int_0^t k dt\,. \tag{2.21}$$

We can easily see that this *should not* and *cannot* give the correct result we want to have, as the limit of integration always changes with the value of the integration variable. However, with the correct notation of using a different symbol for the dummy integration variable and the limit of the integration, the pencil work (especially the keyboard work) is not really simpler than in the case of evaluating the indefinite integrals and then calculating the integration constant. This procedure has the advantage that the possibility of introducing incorrect notation (and result) is avoided. Thus we shall follow the way to get the general solution first and then evaluating the integration constant to get the particular solution for the initial value problem.

Let us return to the solution as expressed in Eq. (2.16). It is readily seen that this solution is not applicable for all values of the reaction order n; for $n = 1$, the time dependence disappears and the fraction $1/0$ cannot be interpreted either. This frequently happens in the practice of natural sciences; the solution of a mathematical model does not always give meaningful result within all physically possible conditions. Another related interesting property is that, though the function itself can be interpreted and gives mathematically meaningful results (in case $n \neq 1$) for times $t < 0$, this does not have any physical (or chemical) meaning either, as no reaction occurs before the start of the reaction, *i. e.* before $t = 0$; thus, the solution in this time region cannot be interpreted either. We shall return to the case of $n = 1$, but let us first explore the properties of the function given in Eq. (2.16).

The disappearance of reactants is traditionally characterized by the so called *half-life*. By definition, this is the instant $t = t_{1/2}$, when the concentration of the reactants becomes $c = c_o/2$. It can readily be calculated by writing $c_o/2$ in place of c in the implicit solution (2.15):

$$\frac{2}{c_o^{n-1}} = \frac{1}{c_o^{n-1}} + (n-1)kt_{1/2}\ , \tag{2.22}$$

By rearranging we get the half-life $t_{1/2}$ as:

$$t_{1/2} = \frac{2^{n-1}-1}{(n-1)k}\frac{1}{c_o^{n-1}} \tag{2.23}$$

Observing this result it is obvious that – not surprisingly – this formula of the half-life is not meaningful for first order reactions, *i. e.* $n = 1$. For any $n \neq 1$ it can be seen that the sign of the first and the second coefficient is always the same, and the second coefficient depends on the initial concentration. According to this, reactions having an order greater than 1 "slow down" while proceeding, in the sense that the second time period needed to reduce the concentration by half is longer, than the first time period necessary to halve the initial concentration, etc. Conversely, reactions having an order less than 1 "accelerate" while proceeding, in the sense that successive half-lives during the reaction become less and less due to the reduction of the concentration.

It is worth discussing an aspect of the solution of the rate equations that is typically generously treated in older textbooks. Before powerful computers we use nowadays would have been widely accessible, it was much easier to determine the parameters of functions (which are c_0, n and k in case of the solution of n-th order reaction rate equations) using graphical methods. The simple and easy-to-use tool to fit functions was the (straightedge) ruler. However, as the ruler enabled only to draw straight lines, for this purpose, functions had to be "linearized". The linearized version of the solution of n-th order reaction rate equation is the implicit solution in the form of Eq. (2.15):

$$\frac{1}{c^{n-1}} = \frac{1}{c_0^{n-1}} + (n-1)kt \tag{2.24}$$

We can see that plotting the transformed $\frac{1}{c^{n-1}}$ of the concentration as a function of time t we would get a straight line whose intercept (its value at $t = 0$) were $\frac{1}{c_0^{n-1}}$ and its slope $(n-1)k$. If we apply the ruler to draw a line across the measured points in this plot, the intersection of this line with the vertical axis (at $t = 0$) is theoretically $\frac{1}{c_0^{n-1}}$ and its slope $(n-1)k$. Knowing the value of n, we could determine k from the slope.

Moreover, the order of the reaction can also be determined by the same technique of fitting a straight line with the ruler. Returning to the n-th order rate equation (2.8), let us write in place of the derivative on the left side its absolute value in the equation:

$$\left|\frac{dc}{dt}\right| = kc^n \tag{2.25}$$

Let us take the logarithm of both sides:

$$\log\left|\frac{dc}{dt}\right| = \log k + n\log c \tag{2.26}$$

We can see that plotting the transformed values $\log\left|\frac{dc}{dt}\right|$ as a function of the transformed values $\log c$, these points will be aligned along a straight line whose intercept (its value at $\log c = 0$) will be $\log k$, while its slope n. (This way, not only n but – in principle – $\log k$ could also be determined. This is the reason that this method is called the *differential method* to determine the rate coefficient.[1]) If we want to have a quick and simple picture concerning the order of reaction, the differential method may be a suitable choice. However, we should realize that numerical derivation of the discrete experimental data of the function $c(t)$ is needed, along with the logarithmic transformation of the function itself and its derivative. Furthermore, a difficulty also arises when we should allocate the derivatives (reaction rates) calculated from adjacent discrete data to some intermediate time between the two data points. These procedures thus contain some arbitrariness, and the transformations (sometimes quite heavily) distort the experimental errors. In addition, numerical derivation always increases errors. As a consequence, kinetic parameters determined this way are necessarily charged with high uncertainty.

All the problems mentioned above can easily be avoided if we do not insist using the straightedge method but perform a (nonlinear) parameter estimation based on the untransformed measured data and the explicit solution of the rate equation. Therefore, we shall only briefly mention the usual linearization tricks of the concentration functions enabling (a typically inaccurate and distorted) parameter estimation with a graphical procedure using a straightedge. The knowledge of this outdated method can help to properly understand and interpret kinetic parameters and their limitations reported in older publications, determined with graphical methods. Nowadays, with the availability of powerful computers and a great choice of suitable statistical and numerical software packages we should prefer direct nonlinear methods to get more reliable, less distorted kinetic parameters.

Up to now, we only explored the solution of the rate equation of the reaction of order n for the case of equal initial concentration of the reactants. Let us find solutions for different initial conditions as well, and also for different values of the reaction order n. Further on in this text we shall see that there exist some special reactions that are zeroth-order. (*E. g.* heterogeneous catalytic reactions.) The solution of their rate equation can easily be derived from the solution of the n-th order reaction discussed above. Let us begin the detailed analysis with this reaction type.

2.1.1. Zeroth-order reactions

The rate equation for a reaction which is zeroth-order can be written as

$$-\frac{dc}{dt} = k \,, \qquad (2.27)$$

for the value of the power function c^0 is always 1, independently of the actual value of c. The solution of this rate equation can easily be written by substituting $n = 0$ into the general solution of the n-th order reaction:

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[1] In addition to this name, it is also called the *van't Hoff method*, from Jacobus Henricus van't Hoff (1852-1911), the Dutch chemist who first described it. He was the first Nobel Prize winner in 1901 “for his discovery of the laws of chemical dynamics and osmotic pressure in solutions”.

$$c = c_{\mathrm{o}} - kt \tag{2.28}$$

It is obvious that this function cannot be interpreted without limitations either. Following the start of the reaction at $t = 0$, after the elapsed time $t = c_{\mathrm{o}}/k$, the reactant is completely consumed and the reaction will halt; thus, negative c values after that do not have any physical meaning. To emphasize this condition, the concentration function can be given as $c = c_{\mathrm{o}} - kt$, if $0 < t < c_{\mathrm{o}}/k$, and zero, if $t > c_{\mathrm{o}}/k$. We can also see that the unit of the rate coefficient k for a zeroth-order reaction is mol dm^{-3} s^{-1} in terms of molar concentration and seconds as time units – in accordance with the condition that the unit of the ratio c_{o}/k should be seconds. The half-life of reaction – in addition to a substitution of $n = 0$ into the general expression of the n-th order reaction – can be calculated easily by realising that the decrease of the reactant concentration is proportional to time until it reaches zero at the instant c_{o}/k, thus it is $t_{1/2} = c_{\mathrm{o}}/2k$. Obviously, consecutive half-life periods decrease by 50% each time after the concentration becomes half of the previous one. The plot of the concentration of the reactant is a straight line between c_{o} at $t = 0$ and zero at $t = c_{\mathrm{o}}/k$.

The concentration as a function of time for the product(s) of the reaction can be obtained from the above solution relying on the stoichiometry. If the stoichiometric number of the reactant is 1 and that of a product is ν_{P} in the reaction reactant → products, then the concentration of the product as a function of time can be given as:

$$c_{\mathrm{P}} = \begin{cases} \nu_{\mathrm{P}} kt\,, & \text{ha } 0 < t < c_{\mathrm{o}}/k \\ \nu_{\mathrm{P}} c_{\mathrm{o}}\,, & \text{ha } t > c_{\mathrm{o}}/k \end{cases} \tag{2.29}$$

This is easy to justify based on the relation that ν_{P} moles of the product are produced from 1 mol of the reactant. Thus $c_{\mathrm{P}} = \nu_{\mathrm{P}}[c_{\mathrm{o}} - (c_{\mathrm{o}} - kt)] = \nu_{\mathrm{P}} kt$.

2.1.2. First-order reactions

The rate equation for a first-order reaction is

$$-\frac{dc}{dt} = kc\ . \tag{2.30}$$

It is readily seen that the unit of the rate coefficient k is simply s^{-1}. The solution of this equation cannot be given by substituting $n = 1$ into the solution obtained for the general n-th order reaction, as it does not provide a meaningful result. In such cases, we should solve the actual rate equation. As this equation is also separable, after separation and insertion of the integrals we get:

$$-\int \frac{1}{c}\, dc = \int k dt \tag{2.31}$$

Writing the primitive functions of both sides, the general solution is the following:

$$-\ln c = kt + I \tag{2.32}$$

Substituting the plausible initial condition ($c = c_0$ when $t = 0$), the integration constant can be obtained as $I = -\ln c_0$. Let us plug this into the above equation, and multiply it by – 1 to get

$$\ln c = \ln c_0 - kt \, . \tag{2.33}$$

The explicit solution is readily obtained as

$$c = c_0 e^{-kt} \, . \tag{2.34}$$

The concentration function of the product(s) of the reaction can be obtained again relying on the stoichiometry. If ν_P moles of the product are produced from 1 mol of the reactant, based on the relation $c_P = \nu_P(c_0 - c)$, we can write

$$c_P = \nu_P c_0 (1 - e^{-kt}) \tag{2.35}$$

which gives the concentration of a product with stoichiometric number ν_P as a function of time.

The validity of the above concentration functions are – in principle – not limited for times greater than zero. However, it is worth to consider that if the reactant concentration multiplied by the volume results in a value inferior to the inverse of the Avogadro constant, there should be less than one reactant molecule in the reaction vessel. Obviously, this does not have a physical meaning; thus, in this sense, the validity of the concentration function is limited also in case of a first-order reaction. (However, the concentration would not become negative, only decrease monotonously; thus the concentration function would predict an ever smaller fraction of the last molecule if the amount of the reactant is divided by the Avogadro constant.)

The half-life of the first-order reaction has a unique property. We can calculate it by substituting $c_0/2$ in place of c:

$$\frac{c_0}{2} = c_0 e^{-kt_{1/2}} \tag{2.36}$$

Dividing both sides by c_0 and taking logarithms we get the result:

$$t_{1/2} = \frac{\ln 2}{k} \tag{2.37}$$

As can be seen, the unique property is that the half-life is independent of the initial concentration c_0. Accordingly, the concentration of the reactant for a given first-order reaction is reduced by 50 % within the same time intervals, also in the case of consecutive time periods. In other words, the reactant is consumed always at the same pace, thus the reaction does not speed up nor slow down during the reaction. (It could be foreseen from the behaviour of the half-life of the n-th order reactions; below $n = 1$, the half-life decreases, above 1 it increases with decreasing initial concentration. Approaching 1 either from below or from above would lead to the same result.)

We can also notice that the implicit solution (2.33) is already appropriate for the estimation of kinetic parameters using a graphical plot and a ruler; plotting the measured $\log c - t$ data in a diagram, the discrete points are found along a straight line. The slope of this line is k and its intercept $\ln c_0$.

2.1.3. Second-order reactions

The rate equation for a second-order reaction *if the concentrations of the reactants are identical* can be written in the form

$$-\frac{dc}{dt} = kc^2 \, . \tag{2.38}$$

We can see that the SI unit of the rate coefficient k is $\mathrm{dm^3\,mol^{-1}\,s^{-1}}$. The solution of this equation can be given by substituting $n = 2$ into the solution obtained for the general n-th order reaction:

$$c = \frac{1}{\frac{1}{c_0} + kt} \tag{2.39}$$

The concentration function of the product(s) of the reaction can be obtained as usual, relying on the stoichiometry. If ν_P moles of the product are produced from 1 mol of the reactant, *i. e.* $c_P = \nu_P(c_0 - c)$, we can write

$$c_P = \nu_P c_0 \left(1 - \frac{1}{1 + c_0 kt}\right) \tag{2.40}$$

for the concentration function of the product.

It is worth noting here as well that, if the reactant concentration multiplied by the volume results in a value inferior to the inverse of the Avogadro constant, there would remain less than one reactant molecule in the reacting system; thus the validity range of the solution is limited also in this case. However, negative concentrations would never result from the concentration function.

As we have already stated, the half-life of the reactant of a second-order reaction depends on the initial concentration. Substituting $c_0/2$ in place of c, we get

$$\frac{c_0}{2} = \frac{1}{\frac{1}{c_0} + kt_{1/2}} \, , \tag{2.41}$$

from which we can express the half-life:

$$t_{1/2} = \frac{1}{k\,c_0} \tag{2.42}$$

This reveals that the half-life of second order reactions is inversely proportional to the initial concentration c_0. Accordingly, each consecutive reduction by 50 % of the concentration takes twice as much time as the previous reduction by half. As the half-life increases during the reaction, we can say that – in this sense – the reaction "slows down" as it proceeds. A plot of the reactant concentration as a function of time clearly reflects this tendency.

To get a formula for using the ruler to estimate kinetic parameters, we can start from Eq. (2.39). Taking the reciprocal of both sides we can get the following equation:

$$\frac{1}{c} = \frac{1}{c_0} + kt \tag{2.43}$$

We can see that the inverse of the concentration as a function of time results in a plot where the discrete $\frac{1}{c} - t$ data points are aligned along a straight line. The slope of the line is the rate coefficient k and the intercept gives $\frac{1}{c_0}$.

Those who paid close attention to the above derivation might have noticed that the obtained solution of the rate equation applies only for the case when the concentrations of the two reactants are identical, but *not the reactants themselves.* When the two reacting molecules are the same, the rate equation (2.38) slightly changes, and so does its solution. Let us begin with the relevant stoichiometric equation:

$$2\mathrm{A} \rightarrow \mathrm{Products} \tag{2.44}$$

The proper rate equation is the following:

$$-\frac{dc_\mathrm{A}}{dt} = 2kc_\mathrm{A}^2 \tag{2.45}$$

For the sake of simplicity, let us drop the subscript A further on:

$$-\frac{dc}{dt} = 2kc^2 \tag{2.46}$$

It is worth noting that the factor 2 appears in the rate equation as the reaction rate always *refers to the stoichiometric equation*; while the rate relative to "one mol *equation*" is proportional to kc^2, the rate relative to one mol *reactant* is twice as large: $2kc^2$. (We would get the same result by adding two rate equations (2.38) which refer only for one mol reactant.) We should remember this property of the rate equation; to get the rate of change of a component, the product of the rate coefficient and the relevant concentration(s) *should be multiplied by the stoichiometric number of the component.*

It is readily seen that this change results only in a replacement of k by $2k$. Accordingly, the relevant solution has the form

$$c = \frac{1}{\frac{1}{c_0} + 2kt}, \tag{2.47}$$

and the half-life will also change accordingly:

$$t_{1/2} = \frac{1}{2kc_0} \tag{2.48}$$

Compared to when two different molecules react in a second-order reaction, in case of two identical molecules, the half-life is reduced by a factor of two. This is not surprising as it follows from the fact that the rate of disappearance is twice as fast in the latter case than in the former.

The concentration of the product(s) of the reaction as a function of time can be obtained in this case by replacing the stoichiometric number ν_P by $\nu_P/2$, and writing $2k$ in place of k in Eq. (2.40).

Those who paid close attention to the above derivations might also have noticed that the solution of the rate equation was applied only for the cases when the initial concentrations of the two reactants were the same, and when the two reactants were chemically identical. We still not discussed the case of two different reactants with non-identical initial concentrations. Let us recall the relevant stoichiometric equation

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{Products}\ , \tag{2.49}$$

along with the corresponding rate equation

$$-\frac{dc_\mathrm{A}}{dt} = -\frac{dc_\mathrm{B}}{dt} = kc_\mathrm{A}c_\mathrm{B}\ . \tag{2.50}$$

Seemingly, there are two variables on the right side, but the stoichiometry reduces this to one underlying variable; the same amount of reactant A will always be consumed as that of the reactant B. If the volume does not change during the reaction, this relation also applies for the concentrations. Let us denote the decrease in concentration (the *progress variable*) by x, and the (different) initial concentrations of the reactants by $c_{\mathrm{A,o}}$ and $c_{\mathrm{B,o}}$, respectively. Using this notation, the rate equation can be written as

$$-\frac{d(c_{\mathrm{A,o}}-x)}{dt} = -\frac{d(c_{\mathrm{B,o}}-x)}{dt} = k(c_{\mathrm{A,o}}-x)(c_{\mathrm{B,o}}-x) \tag{2.51}$$

We can simplify the two time-derivatives by realising that $c_{\mathrm{A,o}}$ and $c_{\mathrm{B,o}}$ do not depend on time:

$$-\frac{d(c_{\mathrm{A,o}}-x)}{dt} = -\frac{dc_{\mathrm{A,o}}}{dt} + \frac{dx}{dt} = \frac{dx}{dt} \tag{2.52}$$

We get a similar result for B as well. The differential equation to solve thus simplifies in the following form:

$$\frac{dx}{dt} = k(c_{\mathrm{A,o}}-x)(c_{\mathrm{B,o}}-x)\ . \tag{2.53}$$

This differential equation is also a separable one. After separation, we get the two sides of the equation ready to integrate:

$$\int \frac{1}{(c_{\mathrm{A,o}}-x)(c_{\mathrm{B,o}}-x)}\, dx = \int k\, dt \tag{2.54}$$

The right side provides the well-known primitive function of a zeroth-order power function, while we get a *rational algebraic fraction* to integrate on the left side. We can recall that the integration of this fraction can be done by resolving it into the sum of *partial fractions*:

$$\int \frac{1}{(c_{\mathrm{A,o}}-x)(c_{\mathrm{B,o}}-x)}dx = \int \left(\frac{1}{(c_{\mathrm{B,o}}-c_{\mathrm{A,o}})(c_{\mathrm{A,o}}-x)} + \frac{1}{(c_{\mathrm{A,o}}-c_{\mathrm{B,o}})(c_{\mathrm{B,o}}-x)} \right) dx \qquad (2.55)$$

The integration can readily be performed resulting in the following primitive function:

$$-\ln\frac{(c_{\mathrm{A,o}}-x)}{(c_{\mathrm{B,o}}-c_{\mathrm{A,o}})} - \ln\frac{(c_{\mathrm{B,o}}-x)}{(c_{\mathrm{A,o}}-c_{\mathrm{B,o}})} + constant \qquad (2.56)$$

The solution of the differential equation including the integration constant *I*, after some rearrangement can be written as:

$$\frac{1}{(c_{\mathrm{A,o}}-c_{\mathrm{B,o}})}\ln\frac{(c_{\mathrm{A,o}}-x)}{(c_{\mathrm{B,o}}-x)} = kt + I \qquad (2.57)$$

Upon substitution of the initial condition ($x = 0$ at $t = 0$) the integration constant *I* becomes

$$I = \frac{1}{(c_{\mathrm{A,o}}-c_{\mathrm{B,o}})}\ln\frac{c_{\mathrm{A,o}}}{c_{\mathrm{B,o}}}.$$

If we plug this in the solution and make use of the identities of the logarithm function we get:

$$\frac{1}{(c_{\mathrm{A,o}}-c_{\mathrm{B,o}})}\ln\frac{c_{\mathrm{B,o}}(c_{\mathrm{A,o}}-x)}{c_{\mathrm{A,o}}(c_{\mathrm{B,o}}-x)} = kt \qquad (2.58)$$

Let us rewrite now the original symbols c_{A} and c_{B} in place of $c_{\mathrm{A,o}} - x$ és $c_{\mathrm{B,o}} - x$, and we already have the implicit solution:

$$\frac{1}{(c_{\mathrm{A,o}}-c_{\mathrm{B,o}})}\ln\frac{c_{\mathrm{B,o}}\,c_{\mathrm{A}}}{c_{\mathrm{A,o}}\,c_{\mathrm{B}}} = kt \qquad (2.59)$$

This result is already appropriate for the estimation of kinetic parameters using a graphical plot and a ruler; plotting the left-side transform of the concentrations as a function of time, discrete experimental points are found along a straight line across the origin, which has a slope of *k*.

To find the explicit solution, we should express the concentrations c_{A} and c_{B} from this equation. To do so, let us first make use of the relation $c_{\mathrm{A}} = c_{\mathrm{A,o}} - x$, and add the difference $c_{\mathrm{A,o}} - c_{\mathrm{A,o}}$ to $c_{\mathrm{B}} = c_{\mathrm{B,o}} - x$. This results in $c_{\mathrm{B}} = c_{\mathrm{B,o}} - x = c_{\mathrm{B,o}} - c_{\mathrm{A,o}} + (c_{\mathrm{A,o}} - x)$, which is identical to $c_{\mathrm{B}} = c_{\mathrm{B,o}} - c_{\mathrm{A,o}} + c_{\mathrm{A}}$. This way we have eliminated c_{B}, and the remaining variable in the solution (2.59) is c_{A}. After some rearrangement and applying inverse logarithm (exponentiation) we can get the following result:

$$c_{\mathrm{A}} = \frac{c_{\mathrm{A,o}}-c_{\mathrm{B,o}}}{1-\frac{c_{\mathrm{B,o}}}{c_{\mathrm{A,o}}}e^{(c_{\mathrm{A,o}}-c_{\mathrm{B,o}})kt}} \qquad (2.60)$$

It is easy to see that – for symmetry reasons (the role of A and B can be interchanged) – the time-dependence of the concentration of B is similar to this:

$$c_{\mathrm{B}} = \frac{c_{\mathrm{B,o}} - c_{\mathrm{A,o}}}{1 - \frac{c_{\mathrm{A,o}}}{c_{\mathrm{B,o}}} e^{(c_{\mathrm{B,o}} - c_{\mathrm{A,o}})kt}} \tag{2.61}$$

The above two equations provide the solution for the rate equation in general of second-order reactions.

However, this solution cannot be used within all circumstances. If the initial concentrations of A and B are identical, we get an expression 0/0 for the concentration functions that cannot be interpreted. Luckily, we have the previous solutions (2.39) or (2.47) for this case.

It is worth noting that the half-life of the reaction is not unique in this case nor can it be defined within all initial conditions. What is always meaningful is the half-life of the reactant whose initial concentration is inferior with respect to the other reactant. This reactant can namely be completely consumed during the reaction. The reactant with higher initial concentration can only be reduced by half if its initial concentration is less than twice the concentration of the other reactant.

2.1.4. Third-order reactions

The rate equation of a third-order reaction for *three different reactants with identical initial concentration* can be written in the following form:

$$-\frac{dc}{dt} = kc^3 \tag{2.62}$$

We can see that the SI unit of the rate coefficient k is $\mathrm{dm}^6\ \mathrm{mol}^{-2}\ \mathrm{s}^{-1}$. The solution of this rate equation can be obtained by substituting $n = 3$ into the solution of the general n-th order rate equation with the plausible initial condition $c = c_{\mathrm{o}}$ at $t = 0$:

$$c = \sqrt{\frac{1}{\frac{1}{c_{\mathrm{o}}^2} + 2kt}} \tag{2.63}$$

The concentration function of the product(s) of the reaction can be obtained as usual, taking into account the stoichiometry. If ν_{P} moles of the product are produced from 1 mol of the reactant, *i. e.* $c_{\mathrm{P}} = \nu_{\mathrm{P}}(c_{\mathrm{o}} - c)$, we can write

$$c_{\mathrm{P}} = \nu_{\mathrm{P}} c_{\mathrm{o}} \left(1 - \sqrt{\frac{1}{1 + \frac{2kt}{c_{\mathrm{o}}^2}}} \right). \tag{2.64}$$

The half-life of the reaction can be calculated by solving the equation

$$\frac{c_0}{2} = \sqrt{\frac{1}{\frac{1}{c_0^2} + 2kt_{1/2}}} \,. \tag{2.65}$$

After both sides are squared and their reciprocals taken, we get the result

$$t_{1/2} = \frac{3}{2kc_0^2} \,. \tag{2.66}$$

This shows that the half-life of second order reactions is inversely proportional to the square of the initial concentration c_0. Accordingly, each consecutive reduction by 50 % of the concentration takes four times as much time as the previous reduction by half. Thus the half-life of third-order reactions increases quite largely during the reaction, which means that – in this sense – the reaction “slows down” significantly as it proceeds. A plot of the reactant concentration as a function of time reveals this tendency.

To estimate kinetic parameters using a graphical plot and a ruler, we can derive the necessary linearized relation by starting from Eq. (2.63). After both sides are squared and their reciprocals taken, we get the following equation:

$$\frac{1}{c^2} = \frac{1}{c_0^2} + kt \tag{2.67}$$

Thus, plotting the inverse square of the concentration as a function of time, discrete experimental points are found along a straight line of slope of k and intercept $\frac{1}{c_0^2}$.

It is clear that there are reactions with different initial conditions than the above one, and we can also imagine that three identical molecules react and the reaction rate is proportional to the third power of their concentration. In the latter case we can follow the procedure we have discussed with second-order reactions. Starting with the relevant stoichiometric equation

$$3\mathrm{A} \rightarrow \mathrm{Products}\,, \tag{2.68}$$

a factor of 3 will appear in the corresponding rate equation:

$$-\frac{dc_\mathrm{A}}{dt} = 3kc_\mathrm{A}^3 \tag{2.69}$$

The solution of this differs also from the previous case only that it contains $3k$ in place of k. Dropping the subscript A from the symbol of the concentration, the proper solution reads as follows:

$$c = \sqrt{\frac{1}{\frac{1}{c_0^2} + 6kt}} \tag{2.70}$$

The half-life of the reaction can be obtained in a similar manner:

$$t_{1/2} = \frac{3}{6kc_{\mathrm{o}}^2} \tag{2.71}$$

If the initial concentration of the reactants is not identical, we can still discern two cases. One is when three different reactants take part in the reaction having different initial concentrations, and the other is when two identical reactant molecules and a third, different one have different initial concentrations. Let us begin the description of the second case by writing the related stoichiometric equation:

$$2\mathrm{A} + \mathrm{B} \rightarrow \mathrm{Products} \tag{2.72}$$

The corresponding rate equation has the following form:

$$-\frac{1}{2}\frac{dc_{\mathrm{A}}}{dt} = -\frac{dc_{\mathrm{B}}}{dt} = kc_{\mathrm{A}}^2 c_{\mathrm{B}} \tag{2.73}$$

The two variables on the right side can also be reduced to one by realising that the amount of reactant A consumed will always be twice as much as that of the reactant B. If the volume does not change during the reaction, this relation also applies for the concentrations. Let us denote the decrease in concentration (the progress variable) by x, and the (different) initial concentrations of the reactants by $c_{\mathrm{A,o}}$ and $c_{\mathrm{B,o}}$, respectively. Using this notation, the rate equation can be written as

$$-\frac{1}{2}\frac{d(c_{\mathrm{A,o}}-x)}{dt} = -\frac{d(c_{\mathrm{B,o}}-x)}{dt} = k(c_{\mathrm{A,o}} - x)^2(c_{\mathrm{B,o}} - x) \tag{2.74}$$

We can simplify the two time-derivatives by taking advantage that $c_{\mathrm{A,o}}$ and $c_{\mathrm{B,o}}$ do not depend on time:

$$\frac{1}{2}\frac{dx}{dt} = k(c_{\mathrm{A,o}} - x)^2(c_{\mathrm{B,o}} - x) \tag{2.75}$$

The other differential equation differs only by a factor of 2 from this one. The implicit solution of this differential equation can be obtained by the method of partial fractions (similar to the second-order case) and – by substituting the initial condition ($x = 0$ at $t = 0$) and re-substituting the original time-dependent concentrations c_{A} and c_{B} – yields

$$\frac{1}{(c_{\mathrm{A,o}}-2c_{\mathrm{B,o}})}\left(\frac{1}{c_{\mathrm{A,o}}} - \frac{1}{c_{\mathrm{A}}}\right) + \frac{1}{(c_{\mathrm{A,o}}-2c_{\mathrm{B,o}})^2}\ln\frac{c_{\mathrm{B,o}}\, c_{\mathrm{A}}}{c_{\mathrm{A,o}}\, c_{\mathrm{B}}} = kt\ . \tag{2.76}$$

This result is already appropriate for the estimation of kinetic parameters using a graphical plot and a ruler; plotting the left-side transform of the concentrations as a function of time, discrete experimental points are found along a straight line across the origin, with a slope of k. Unfortunately, the explicit solution is not known for this case. Thus, if we want to estimate kinetic parameters without relying on the graphical method, we should use numerical methods including numerical inversion of the implicit solution, or numerical integration to get time-dependent concentration values.

Finally, let us discuss the general third-order reaction with three different initial concentrations $c_{\mathrm{A,o}}$, $c_{\mathrm{B,o}}$, and $c_{\mathrm{C,o}}$, respectively. Starting from the relevant stoichiometric equation

$$\mathrm{A} + \mathrm{B} + \mathrm{C} \rightarrow \mathrm{Products}\,, \tag{2.77}$$

we can write the corresponding rate equation in the following form:

$$-\frac{dc_{\mathrm{A}}}{dt} = -\frac{dc_{\mathrm{B}}}{dt} = -\frac{dc_{\mathrm{C}}}{dt} = kc_{\mathrm{A}}c_{\mathrm{B}}c_{\mathrm{C}} \tag{2.78}$$

If the volume does not change during the reaction, we can express time-dependent concentrations again with the help of a single progress variable x. Using this notation, the rate equation can be re-written as

$$-\frac{d(c_{\mathrm{A,o}}-x)}{dt} = -\frac{d(c_{\mathrm{B,o}}-x)}{dt} = -\frac{d(c_{\mathrm{C,o}}-x)}{dt} = k(c_{\mathrm{A,o}} - x)(c_{\mathrm{B,o}} - x)(c_{\mathrm{C,o}} - x) \tag{2.79}$$

We can simplify the time-derivatives by making use of the time-independence of the initial concentrations and get the differential equation to solve:

$$\frac{dx}{dt} = k(c_{\mathrm{A,o}} - x)(c_{\mathrm{B,o}} - x)(c_{\mathrm{C,o}} - x) \tag{2.80}$$

The solution of this differential equation can also be obtained by the method of partial fractions. After integration, substitution of the initial condition ($x = 0$ at $t = 0$) and re-substitution of the original time-dependent concentrations – we get the implicit solution

$$\frac{\ln\frac{c_{\mathrm{A}}}{c_{\mathrm{A,o}}}}{(c_{\mathrm{B,o}}-c_{\mathrm{A,o}})(c_{\mathrm{A,o}}-c_{\mathrm{C,o}})} + \frac{\ln\frac{c_{\mathrm{B}}}{c_{\mathrm{B,o}}}}{(c_{\mathrm{A,o}}-c_{\mathrm{B,o}})(c_{\mathrm{B,o}}-c_{\mathrm{C,o}})} + \frac{\ln\frac{c_{\mathrm{C}}}{c_{\mathrm{C,o}}}}{(c_{\mathrm{A,o}}-c_{\mathrm{C,o}})(c_{\mathrm{C,o}}-c_{\mathrm{B,o}})} = kt\,. \tag{2.81}$$

This result is also appropriate for the estimation of kinetic parameters using a graphical plot and a ruler; plotting the left-side transform of the concentrations as a function of time, discrete experimental points are found along a straight line across the origin, with a slope of k. Unfortunately, the explicit solution is not known for this case either. Thus, if we want to estimate kinetic parameters without relying on the graphical method, we should use numerical methods including numerical inversion of the implicit solution, or numerical integration to get time-dependent concentration values.

2.2. Generalisation and extension of the order of reaction; pseudo-order

As it is mentioned in the introductory part of this chapter, there exist composite reactions which do have an order but this order is not an integer. (For elementary reactions, the order is always a positive integer.) Accordingly, we can generalise the order of reaction for any empirical rate equation which can be written in the form

$$-\frac{dc_j}{dt} = \nu_j k \prod_{i=1}^{r} c_i^{\alpha_i}\,. \tag{2.82}$$

In this equation, r is the number of reactants, c_j and c_i are concentrations, ν_j is the stoichiometric number, and the symbol α_i is called the *order of the reaction with respect to the i-th component* (or component A_i in Eq. (1.1)). The sum of the orders $\sum_{i=1}^{r} \alpha_i = n$ is called the *overall order* of the reaction. In relation to this name, α_i is also called the *partial order* of A_i. In a general (composite) reaction, the partial order of components as well as the overall order should not be a positive integer; it may be a negative integer or a rational nonintegral number. It is worth noting that a nonintegral order always implies a composite reaction.

As we shall see further (when discussing composite reactions), the rate equation of the majority of composite reactions cannot be written in the form of Eq. (2.82). At this point we could ask why such a generalisation of the reaction order should be considered. We can have the answer also at the discussion of composite reactions; when studying unknown reactions, the notion of reaction order can help to explore kinetic properties. Kineticists often begin this exploration by "forcing" the reaction to behave as if its rate equation would have the form of Eq. (2.82), thus at least one of its reactants would have a genuine – mostly integer – order. The simplest way of forcing this behaviour is to add all but one reactant in such great excess that their concentrations during the progress of the reaction remain constant to a good approximation. (This technique is sometimes referred to as *flooding*, or as *isolation*.) A frequently applied example is the case of two reactants, when the concentration of one reactant is many times that of the other.

Let us consider the case when the rate equation of the reaction of components A_1 and A_2 can be written in the second-order form

$$-\frac{dc_1}{dt} = -\frac{dc_2}{dt} = kc_1c_2 \ . \tag{2.83}$$

For example, in case of $c_2 = 100c_1$ it is easy to see that, even after the reaction is completed, the concentration of A_2 only changes by 1 percent. The typical error of time-dependent concentration measurements being in this order of magnitude, we do not make a big mistake by considering c_2 as a constant throughout the reaction. In that case, the product $k' = kc_2$ can also be considered constant, thus we can rewrite the rate equation as

$$-\frac{dc_1}{dt} = k'c_1 \ . \tag{2.84}$$

We can see that it is formally identical to a first-order rate equation. However, not being a genuine first-order reaction, it is called a *pseudo-first-order* reaction[1].

The pseudo-first-order rate coefficient has an interesting property; its usual unit is *not* s^{-1}, but $dm^3\ mol^{-1}\ s^{-1}$, according to the rate equation (2.83) or the product kc_2. Formerly, when parameter estimation had been performed using graphical methods and a ruler, it was common practice to

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[1] The Greek prefix *ψευδο-* has the meaning *false*, or *not a real one*.

apply the pseudo-first-order results to determine a second-order rate constant. To do so, calculated linearized (ln $c_1 - t$) transformed values have been plotted at different concentrations c_2. From these diagrams, the slopes of the lines from different diagrams were determined, as discussed in section 2.1.2. Pseudo-first-order rate coefficients obtained this way were plotted as a function of the corresponding concentrations c_2 , and a staraight line was fitted to the data points in the diagram. The slope of this line was the (graphically) estimated value of the second-order rate coefficient, according to the relation $k' = kc_2$.

In case of the graphical parameter estimations described, there is no suitable method to determine the uncertainty of the rate coefficients. Performing the described line fittings using appropriate statistical methods, we could calculate correct uncertainties of the pseudo-first-order rate coefficients, as well as the resulting second-order rate coefficient. However, it is pointless to follow this tedious method for two reasons. The first one is that the distortion of the errors due to the transformation of the original data would lead to biased results. The second one is that the statistical properties of the results obtained after the two stages (*e. g.* the number of the degrees of freedom of the probability distribution of the second-order rate coefficient) were unfavourable. A more simple, more precise and statistically more favourable method is to fit the concentration function (2.60) to all measured points (obtained by measuring both concentrations) and estimate the second-order rate coefficient as a parameter of this function, along with its uncertainty.

However, the method of flooding (or isolation) is a usual way to study unknown reactions. If it turns out for example, that – in case of two reactants – the reaction has a pseudo-first-order kinetics for both reactants, it is a reasonable conclusion that the overall reaction is a second-order one, and we can put up a suitable experimental design to determine the second-order rate coefficient using proper non-linear parameter estimation methods.

Suggested literature

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