Chapter 16
Basic Principles of Kinetics

The branch of matter dynamics called *chemical kinetics* will be the topic of the next four chapters. Chemical kinetics is concerned with the temporal course of chemical reactions, meaning one investigates how fast the reactants are consumed or the products are formed. The goal of such investigations is to provide the means for predicting the rate of processes and to find the influencing factors that promote a desired reaction or inhibit an undesired one. In this introductory chapter we will first get to know the fundamental quantities *conversion rate* and *rate density* as well as different methods for measuring them in slow and fast reactions. In the last part of the chapter, it will be shown how the dependence of the rate density on the concentrations of reactants (and products) can be summarized by mathematical expressions called *rate laws*. Subsequently, the relatively simple rate laws of different types of reactions taking place in only one single step will be discussed.

16.1 Introduction

Concept of Chemical Kinetics *Chemical kinetics* or simply *kinetics* is the area of chemistry that deals with the temporal course of transformations of substances and the intermediate steps involved in it, especially the

- Recording of the *temporal course* of chemical reactions,
- Determination of (differential) *rate laws* and the corresponding *integrated rate laws* under given conditions,
- Identification of *intermediate steps* (elucidation of the reaction mechanism),
- Investigation of *temperature dependency*,
- Investigation of *facilitating* and *inhibiting influences* (catalysis, inhibition).

The goal of investigations in this area is to provide the means for predicting the rate of processes and to find the influencing factors that promote a desired reaction or inhibit an undesired one.

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Reaction Resistance We expect that the greater the drive $\mathcal{A}$ of a chemical transformation, meaning the greater the drop of potential from the reactants to the products, the faster the process will run. However, it would be a mistake to believe that the strength of the drive *alone* determines the speed, i.e., the rate at which the process runs. There are *inhibitions* in every kind of change of substances that must be overcome. They can be large or small, depending upon experimental conditions, and they influence the rate of the process as much as the drive does. In a system involving substances, the conversion in the direction of the drop in chemical potential is inhibited or even stopped by various resistances (Fig. 16.1). This is similar to an electrical circuit where the flow of charge in the direction of the drop in potential is hindered by high electrical resistance or totally stops when the circuit is interrupted. There are similar examples to be found in other fields such as mechanics. An example might be bicycling on sandy paths or stirring a thick soup. A simple idea describing the influences mentioned above would be that the rate of a transformation is directly proportional to the drive and inversely proportional to the resistance to be overcome:

$$\text{rate} = \frac{\text{drive}}{\text{resistance}}.$$

However, we do not encounter such simple circumstances very often. Ohm's law, i.e., current $I =$ voltage U/resistance R, is a well-known example of this idea, but even a lightbulb behaves differently in this case because the resistance is not constant but increases with temperature. It is not surprising, then, when in chemical processes such a simple law like Ohm's is only valid for drives $\mathcal{A} \ll RT$, meaning when equilibrium $\mathcal{A} = 0$ is almost attained.

Experiment 16.1 clarifies the concept of reaction resistance using a hydromechanical analogue for a reaction between dissolved substances A and B.

The reaction resistance can be changed analogously to the other examples (e.g., by catalysts).

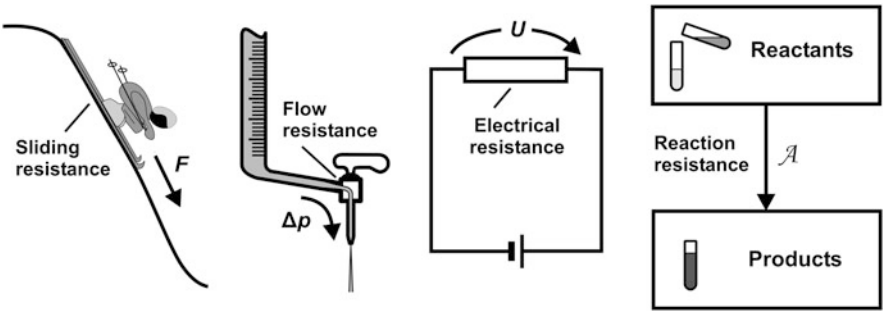
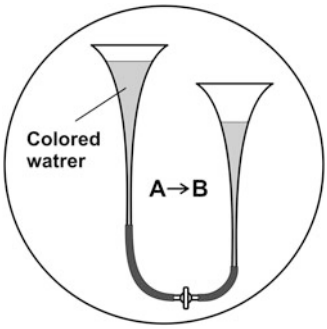


Fig. 16.1 Driving force and resistance to be overcome in different processes.

Experiment 16.1 *Hydromechanical analogue to reaction resistance*: Colored water is filled into one of the glass jars. (Their special form corresponds to the "exponential horn" in Sect. 6.7, i.e., it symbolizes the dependence of the chemical potential upon the amount of dissolved substance as in a potential diagram.) The initially closed stopcock is opened and the liquid distributes to both jars until equilibrium is established. The stopcock takes the role of reaction resistance inhibiting the reaction although it could proceed in principle.



Duration of Conversion The *duration of conversion*, meaning the time period $\mathcal{T}$ of substance transformations, is expressed by characteristic quantities such as half-life, lifetime, or response time. It spans many orders of magnitude in the range of $\mathcal{T} < 10^{-9}$s to $\mathcal{T} > 10^{9}$a. Compared to a usual observation period $\mathcal{T}_{\mathrm{O}}$, a transformation is

- *Inhibited*, when $\mathcal{T} \gg \mathcal{T}_{\mathrm{O}}$ (when $\mathcal{T}$ is much larger than $\mathcal{T}_{\mathrm{O}}$)
- *Slow*, when $\mathcal{T} \approx \mathcal{T}_{\mathrm{O}}$ (when $\mathcal{T}$ and $\mathcal{T}_{\mathrm{O}}$ are of similar order of magnitude)
- *Fast*, when $\mathcal{T} \ll \mathcal{T}_{\mathrm{O}}$ (when $\mathcal{T}$ is much smaller than $\mathcal{T}_{\mathrm{O}}$)

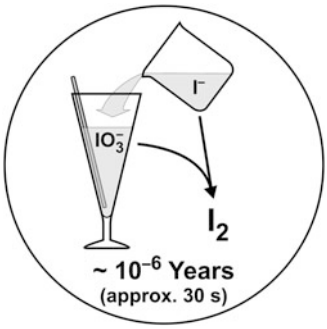
The Experiments 16.2, 16.3, 16.4, and 16.5 illustrate the large interval of durations and rates of conversion in which chemical reactions occur.

The duration of conversion increases strongly in each experiment from Experiment 16.2 to Experiment 16.5 while the rate decreases. while the rate decreases. The role played by the chosen time frame can be seen in the transition "peat → coal": Compared to how long usual laboratory experiments take, it is inhibited. Compared to geological time frames, it is not.

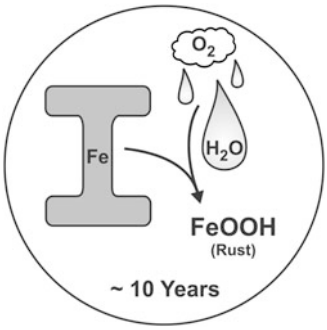
Reaction Intermediates and Reaction Mechanisms Closer examination has shown that chemical reactions are not as simple as the usual summary conversion formulas would lead us to believe, but mostly run in several steps or loops in a sequence of *reaction intermediates* quickly transforming into each other and reacting with each other. They often appear in low concentrations and remain inconspicuous and mostly undetected. These substances, appearing only in small or trace amounts, often form a "bottleneck" that limits the rate of a reaction. If it is possible to facilitate the formation of such intermediates, a reaction can be *promoted*. In contrast, it can be *hindered* by repressing production of certain intermediates. In order to approach this systematically, it is first necessary to know the steps

Experiment 16.2 *Precipitation of zinc carbonate*: If a solution containing CO_3^{2-} is added to a Zn^{2+} solution, white zinc carbonate precipitates immediately; the reaction proceeds very fast and is finished after a very short time (a period of maybe 0.3 s).

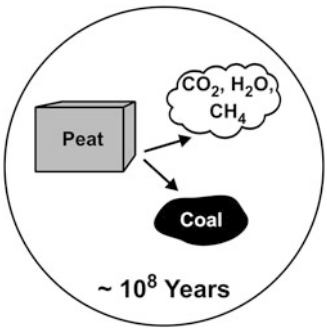
Experiment 16.3 *Reaction of iodate with iodide*: The reaction of IO_3^- and I^- in aqueous solution proceeds more slowly than the reaction of CO_3^{2-} with Zn^{2+}—the brown color of the iodine that forms makes this visible (the duration is about 30 s).



Experiment 16.4 *Rusting of iron*: Rusting of a piece of iron in humid air takes about 10 years.



Experiment 16.5 *Coal formation*: The formation of coal from peat takes millions of years.



a reaction takes. In other words, we must know the *step-by-step sequence*, meaning the *reaction mechanism*. For this reason, elucidation of *reaction mechanisms* is an important part of chemical kinetics.

16.2 Conversion Rate of a Chemical Reaction

Conversion and Conversion Rate We have already learned the terms *extent of reaction* and *conversion* in Sect. 1.7. They are necessary to know for the following. Let us take another look at the example of rusting of a piece of iron in humid air. The conversion formula for this is:

$$4\,\mathrm{Fe} + 3\,\mathrm{O_2} + 2\,\mathrm{H_2O} \rightarrow 4\,\mathrm{FeOOH}$$

or when we put all the substances on the right-hand side,

$$0 \rightarrow \underbrace{-4}_{\nu_{\mathrm{Fe}}}\,\mathrm{Fe}\ \underbrace{-3}_{\nu_{\mathrm{O_2}}}\,\mathrm{O_2}\ \underbrace{-2}_{\nu_{\mathrm{H_2O}}}\,\mathrm{H_2O}\ \underbrace{+4}_{\nu_{\mathrm{FeOOH}}}\,\mathrm{FeOOH}.$$

The coefficients ν_i represent the *conversion numbers*. The *extent of reaction* ξ can be calculated according to

$$\xi = \frac{\Delta n_i}{\nu_i} = \frac{n_i - n_{i,0}}{\nu_i} \tag{16.1}$$

[compare Eq. (1.14)], where n_i represents the instantaneous amount of substance at time t, and $n_{i,0}$ represents the amount at initial time t_0. ξ as well as *conversion* $\Delta\xi$ are then functions of time. In our example, the value of $\xi(t)$ indicates what extent the rusting process has attained at the point in time t. Think about how old automobiles rust. When the weather is dry, the reaction comes almost to a standstill, due to a lack of water. The extent of reaction ξ is constant and the conversion $\Delta\xi$ during 1 day, for example, is just about zero. When the weather is wet or the car is in a damp garage, the reaction will proceed, but slowly. The extent of reaction will gradually increase, which can be seen in the growing formation of rust. If, after being out on winter streets, there is salt sticking to the car, the reaction will proceed especially fast. The daily conversion can reach considerable values, to the annoyance of the car's owner. This observation suggests that the *conversion rate* ω of a reaction should be described by the ratio "distance"/time span like it is done in mechanics, only that "distance" as used here means the change of extent of reaction (reaction coordinate) ξ by the continuation of the reaction during the short time span Δt (Fig. 16.2). (We will avoid using the obvious name *reaction rate* for ω because it can mean different things [more about this in Sect. 16.3)].

Mechanical:

$$v := \frac{\Delta x}{\Delta t},$$

Chemical:

$$\omega := \frac{\Delta \xi}{\Delta t} \quad \text{Unit: mol s}^{-1}. \tag{16.2}$$

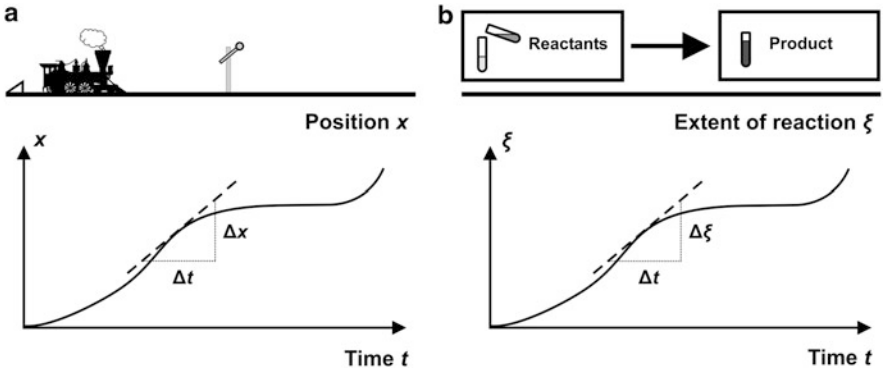
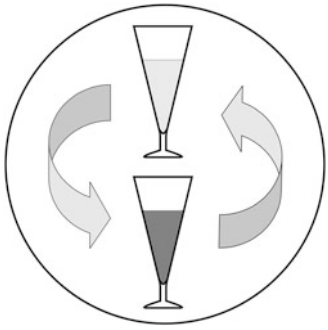


Fig. 16.2 "Distance" covered as a function of time using examples of (**a**) a locomotive and (**b**) a chemical reaction.

Experiment 16.6 *Oscillating reaction according to Briggs and Rauscher*: A solution of malonic acid, manganese sulfate, and starch as well as a solution of acidulated potassium iodate are filled into a beaker. A solution of hydrogen peroxide is then added. The color of the solution changes periodically from colorless to yellow brown, dark blue and then back to colorless, and so on and so forth



Instantaneous Rate Just as the speed of a train constantly changes by accelerating and slowing down, the speed, the rate at which the reactants are used up and the products are formed, can also change during a reaction. Let us consider the example of a periodic reaction according to Thomas S. Briggs and Warren C. Rauscher, also known as the "oscillating iodine clock" (Experiment 16.6). The repeated color changes occur due to periodic concentration oscillations whereby the reaction does not oscillate forward and backward. Instead, a complex combination of slow and fast reactions in batch mode is taking place simultaneously.

In other words, we must consider an instantaneous value: the speed at the moment in question. In order to find this *instantaneous rate,* it is necessary to move to very small time spans, as is symbolically expressed by the differential quotient dξ/dt*:*

$$v := \frac{\mathrm{d}x}{\mathrm{d}t}, \qquad \omega := \frac{\mathrm{d}\xi}{\mathrm{d}t} \quad \text{(De Donder 1929)}. \quad (16.3)$$

The instantaneous rate corresponds to the slope of the tangent to the $x(t)$ or $\xi(t)$ curve at this point. The steeper the slope, the higher the rate.

If the system in question is closed and there is only one reaction occurring inside it we can also write

$$\frac{\mathrm{d}n_i}{\mathrm{d}t} = \nu_i \underbrace{\frac{\mathrm{d}\xi}{\mathrm{d}t}}_{\omega}. \quad (16.4)$$

This is so because of $n_i = n_{i,0} + \nu_i \xi$ [compare Eq. (1.16)]. Here, $n_{i,0}$ is the (time independent) initial amount of substance. This constant term vanishes when we take the derivative. After rearranging Eq. (16.4), the following results:

$$\omega = \frac{1}{\nu_i} \frac{\mathrm{d}n_i}{\mathrm{d}t}. \quad (16.5)$$

16.3 Rate Density

Concept of Rate Density We know that chemical reactions do not take place at the same rate everywhere. For example, the flame of a candle will transform much more substance in the hot zones than in the cooler zones relative to a volume of, say, 1 mm^3 (Fig. 16.3). $\Delta\omega$ represents the contribution of a small volume ΔV of the reaction mixture to the total rate of conversion.

In order to characterize such local differences, we introduce a new quantity r that specifies conversion rate per volume (of the small volume considered) which we will call *density of conversion rate* or simply *rate density:*

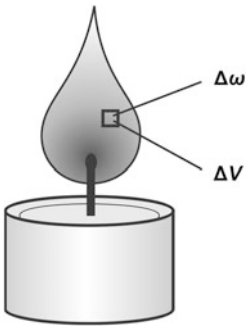


Fig. 16.3 Explanation of the concept of rate density using the example of a candle flame.

$$r := \frac{\Delta\omega}{\Delta V} \quad \text{or more precisely} \quad r := \frac{\mathrm{d}\omega}{\mathrm{d}V} \quad \text{Unit: mol s}^{-1}\,\text{m}^{-3}\,. \tag{16.6}$$

The quotient $\Delta\omega/\Delta V$ expresses the average value of the conversion $\Delta\xi$ resulting in a short time span Δt in the small volume ΔV considered here. Again, it is necessary to use a very small section when trying to find the value of the rate density r at a given point. This is characterized by the differential notation.

For future considerations, it would be practical to divide chemical reactions into certain classes and to discuss them each separately (see Sect. 16.5). For the moment, though, we will deal with some basic concepts.

Homogeneous and Heterogeneous Reactions A reaction is called *homogeneous* when it takes place in a uniform mixture. An example of this from everyday life is a cup of sweetened tea with lemon where table sugar (sucrose) is gradually split into its two component parts (glucose and fructose). A reaction is called *heterogeneous* when the substances involved are distributed over regions having differing properties. Rusting is a heterogeneous reaction because it takes place in four different regions: the metallic iron, the layer of rust, the water in the fissures of the layer of rust, and the air above. The processes of precipitation or effervescence are both heterogeneous reactions as well.

When dealing with a homogeneous reaction where the reaction takes place uniformly everywhere, the size of the section is unimportant so the entire volume V of the reaction mixture can be used for calculating the rate density:

$$r = \frac{\omega}{V} \quad \text{for reactions in a homogeneous environment at constant volume.}$$

If we insert $\omega = \Delta\xi/\Delta t$ and $\Delta\xi = \Delta n_i/\nu_i$ as well as $c_i = n_i/V$, we obtain

$$r = \frac{1}{\nu_i} \cdot \frac{\Delta c_i}{\Delta t}$$

or in the limit of very small Δt

$$r = \frac{1}{\nu_i} \cdot \frac{\mathrm{d}c_i}{\mathrm{d}t}\,. \tag{16.7}$$

The rate density describes the change of concentration of a certain substance per unit of time (under the conditions mentioned above, which are a homogeneous system having a constant volume as well as only one reaction taking place and no exchange of substances with the environment). When the reaction runs forward, the quantity r is positive for all the substances participating—whether they are reactants or products. This is so because the concentration of the reactants decreases ($\mathrm{d}c_i < 0$) and we divide by $\nu_i < 0$. r is negative when the reaction runs backward.

Let us take a look at one final example of this, ammonia synthesis, which is very important to industrial applications. We assume a closed system at constant volume:

$$N_2 + 3\,H_2 \rightarrow 2\,NH_3 \quad \text{or} \quad 0 \rightarrow -1\,N_2 - 3\,H_2 + 2\,NH_3.$$

We then obtain for rate density r

$$r = -\frac{dc_{N_2}}{dt} = -\frac{1}{3}\frac{dc_{H_2}}{dt} = +\frac{1}{2}\frac{dc_{NH_3}}{dt}.$$

The procedures for heterogeneous reactions are less uniform. Depending upon the application, the conversion rate can be related to various quantities, for example, for processes related to membranes

- To the membrane surface,
- To the amount of bound enzyme there,
- To the amount of pores in the membrane,
- To the amount of available carrier molecules, etc.

In closing, a few words about the concept of "reaction rate." Because homogeneous reactions at almost constant volume—possibly a reaction in a beaker or flask where the volume of solution remains almost unchanged in a reaction process—often get the most attention, the difference quotient $\Delta c_i/\Delta t$ or the differential quotient dc_i/dt for a product i or the quotient $-\Delta c_i/\Delta t$ or $-dc_i/dt$ for a chosen reactant i is defined as the reaction rate. These quantities are closely related to our rate density, differing only by the factor $1/|\nu_i|$, but due to this difference they are dependent upon the substances and therefore not useful for our purposes. This quantity does not come into question as a general measure for conversion rate because, for example, in reactions between pure substances such as $Fe + S \rightarrow FeS$ the concentrations of all substances remain constant even though the amounts vary, or in reactions between gases the concentrations can vary as a result of compression or expansion alone without any conversion taking place at all. For this reason, we will avoid the ambiguous term "reaction rate" and use the quantities introduced above.

16.4 Measuring Rate Density

Introduction When making a kinetic investigation of a reaction, its stoichiometry must first be determined and possible side reactions must be identified. Because the rate density is proportional to temporal change of concentration of the substances involved in the reaction, at least when the reaction is homogeneous and the volume is constant, the concentrations of reactants and products must be determined at various times during the course of the reaction. Because the rates of disappearance and formation of chemical species are related to each other, the measurement of the

change of concentration of one of the reactants or products suffices. The temperature of a reaction mixture must be kept constant during the entire time of reaction due to the temperature dependence of chemical reactions (think of the slowing of biochemical processes of food in a freezer).

As we have seen, chemical reactions take place in time intervals that range from a fraction of a second to millions of years. The speed interval to be considered is just as great. For this reason, the experimental methods for determining rate density can vary greatly from case to case. The basic problem in analyzing reacting systems is that their composition is constantly changing and we do not have unlimited time to carry out an analysis. Depending upon the speed at which a reaction runs and the method used for analysis, there are different approaches for acquiring kinetic data.

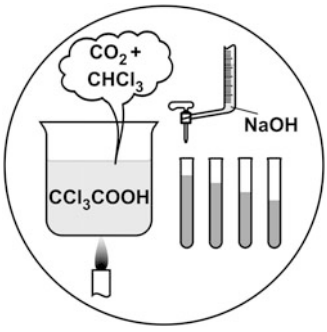
Slow Reactions When investigating a *slow* reaction, a small sample of the reacting mixture can be taken to instantly determine the concentration of the reaction partners chemically by, for example, titration or gravimetry. This is called *real-time analysis*. As an example, we will investigate the decomposition of trichloroacetic acid by decarboxylation into chloroform according to

$$CCl_3{-}COOH|w \rightarrow CCl_3H|g + CO_2|g.$$

(see Experiment 16.7).

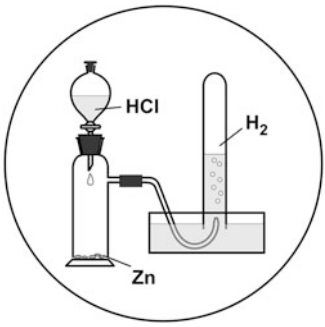
Physical analytic methods such as optical or electric measurement methods can be used as well. One must always make certain, though, that the total volume of a mixture does not change much. The sampling and analysis must also take place quickly in relation to how long the conversion takes. If this is not possible, the reaction continuing to take place in the sample must be stopped in some way, possibly by diluting or cooling.

Direct measurement of concentration by utilizing some physical characteristic of the reaction mixture is much more practical than taking and analyzing small samples. If, for example, one of the reaction partners is a gas, the total volume can change during the reaction taking place in a container under constant pressure (possibly air pressure). The progress of the reaction can be followed by measuring the change in volume over time. Let us consider the reaction of zinc with an acid (Experiment 16.8), where hydrogen is produced and zinc is dissolved:

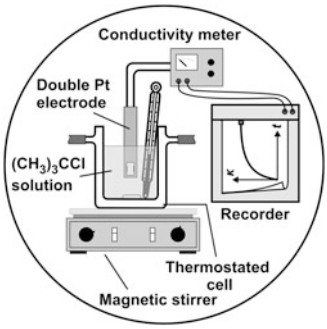


Experiment 16.7 *Measuring rate density by titration*: A trichloroacetic acid solution is poured into slightly alkalized boiling water. The concentration of the acid left in the reaction mixture after a certain time interval can be determined by titrating a sample with a sodium hydroxide solution. When the titrated solution is transferred into test tubes, the reaction process can be followed by observing the fill level. As the acid concentration decreases, so does the amount of sodium hydroxide that needs to be added.

Experiment 16.8 *Volumetric determination of conversion*: Hydrochloric acid is trickled onto zinc granules. The hydrogen gas produced by this is caught pneumatically in a measuring cylinder or eudiometer. Water is used to trap the gas in the cylinder, and the graduation allows the change of gas volume to be measured.



Experiment 16.9 *Conductometric determination of conversion*: A conductivity meter with a double platinum electrode is used for measuring conductivity. (We will go into conductivity and measuring it in more detail in Chap. 21.) Conductivity is temperature dependent so the use of a thermostat is recommended. To start the reaction, a known amount of tertiary butyl chloride is pipetted into the demineralized water in the measuring cell to start the reaction.



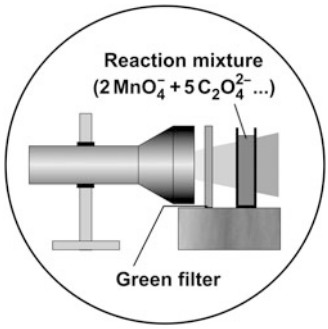
$$\mathrm{Zn|s + 2\,H^+|w \rightarrow Zn^{2+}|w + H_2|g.}$$

The volume of the hydrogen gas can be measured easily.

Other useful characteristics for analysis are the pressure in a gas reaction at constant volume, the refraction index, or the electric conductivity. If a reaction changes the number or type of ions in a solution, its progress can be monitored utilizing conductivity. As a result of hydrolysis of tertiary butyl chloride for example, tertiary butanol is produced along with H^+ and Cl^- ions. The H^+ ions, in particular, strongly raise the solution's conductivity (Experiment 16.9):

$$\mathrm{(CH_3)_3C-Cl|l + H_2O|l \rightarrow (CH_3)C-OH|w + H^+|w + Cl^-|w.}$$

A disadvantage of the methods mentioned above is their lack of specificity because, for one thing, all particles in the gas phase contribute to the change in volume. Therefore, *molecular specific* characteristics are better suited than characteristics related to the entire system. One method of measurement that is often applied in kinetics is *photometry*, the measurement of the absorption intensity of light in a given spectral range. The strength of absorption or transparency for light at a certain wavelength is a measure for the concentration of the reaction partner in



Experiment 16.10 *Photometric monitoring of the progress of a reaction*: A green filter is placed in front of a flashlight and the light is allowed to fall through a cuvette containing the reaction mixture. At first, the light can hardly be seen because it is almost totally absorbed by the intensely violet permanganate ions. Only as the reaction progresses, does the light eventually turn bright green. This is because the solution gradually loses its color. A spectrophotometer is necessary for quantitatively recording the changes of concentration.

question. When, for example, the reaction of a potassium permanganate solution with oxalic acid in a sulfuric acid solution is investigated (Experiment 16.10),

$$2\ MnO_4^-|w + 5\ C_2O_4^{2-}|w + 16\ H^+|w \rightarrow 2\ Mn^{2+}|w + 10\ CO_2|g + 8\ H_2O|l,$$

its progress can be followed by measurement of absorption in the visible range because the permanganate ion is colored.

Fast Reactions Chemists have lately become interested in especially fast reactions and great progress has been made in investigating them. We consider a reaction to be fast when the complete process takes less than about 1 s to occur. Special methods have been developed for these kinetic analyses. In the *flow method*, the reaction mixture does not remain in the reaction vessel over a longer time, as it does with the static methods discussed above, but flows through the reaction volume. The moment the reactants enter a mixing chamber, they are very quickly and thoroughly mixed. At that point the reaction starts; it progresses while the mixture is flowing through the outlet tube.

The distance covered by the reaction mixture in the tube is a measure of the time elapsed since the start of the reaction. If we observe the reaction at different positions along this tube using, for example, a moveable spectrophotometer, we see the mixture at different times of the reaction. The temporal coordinate of the reaction process is thereby mapped onto the spatial coordinate along the flow tube. When highly efficient mixing chambers are used, the flow tube technique is applicable for fast reactions with reaction times down to the millisecond range.

A disadvantage of the flow method is that relatively large volumina of the reaction mixture are necessary. Consumption of substances is especially great in very fast reactions because the flow rate needs to be very high so that the reaction process can be spread over a long enough length of the outlet tube. The "*stopped-flow method*" lets us avoid this disadvantage. Here, as well, the reactants are mixed

very quickly and then let flow into a flow tube. However, this flow tube contains a piston that can abruptly stop the flow as soon as a given volume (mostly around 1 cm^3) is injected. The reaction then continues in the resting, well-mixed solution and can be followed from outside spectrometrically. The filling of the observation chamber corresponds to the sudden taking of a small initial sample of the reaction mixture, so the "stopped-flow" technique is much more economical than the flow method. It is especially useful in investigating biochemical reactions.

When reactions with durations of conversion shorter than 10^{-3} s are to be investigated, the *mixing methods* we have introduced no longer apply. *Relaxation methods* let us avoid the time-consuming mixing of reaction partners. Instead, they allow us to observe how a system in equilibrium reacts to an external perturbation of equilibrium. If, for example, parameters such as pressure or temperature are suddenly changed, a chemical reaction must take place in order to once again establish equilibrium. This time, however, pressure or temperature takes new values (pressure-jump or temperature-jump method). The reaction's return to equilibrium, called relaxation, can be followed spectroscopically.

16.5 Rate Laws of Single-Step Reactions

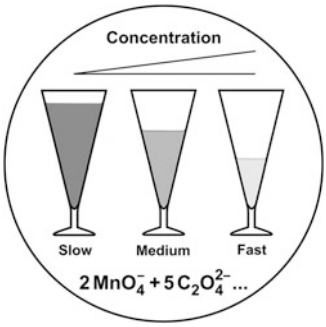
Basic Principles When investigated in detail, most chemical reactions can be broken down into different steps occurring either in sequence or in parallel. These kinds of reactions are called *multistep* or *composite* reactions. The smallest units involved in such an analysis are called *single-step* or *elementary* reactions. Such reactions take place in one single step. This means that all the particles appearing in a conversion formula react *simultaneously* with each other. We use the word *molecularity* to indicate the number of particles of reactants involved in a single-step reaction. When one, two, three, ... particles interact, we speak of *mono-*, *di-*, *tri-*, ... *molecular* reactions.

For the beginning, it will suffice to limit our investigation to only simple types of homogeneous reactions. We are most interested in what influence

- The concentrations (and types) of reaction partners B, B′, ... and
- The temperature, as well as
- The presence and types of substances not appearing in the conversion formula (catalysts, inhibitors, solvents)

have upon the rate density r. Let us take a closer look at concentration dependency using the example of decoloration of a potassium permanganate solution by oxalic acid in a sulfur acid solution at various dilutions (Experiment 16.11). (The reaction itself was presented already in Experiment 16.10.)

The higher the dilution, meaning the lower the concentration of reactants, the more slowly the reaction proceeds. Obviously, the rate density depends directly upon the concentration.



Experiment 16.11 *Concentration dependency of rate of conversion*: The same amount of acidulated oxalic acid is poured into each of three conical cups (goblets). Potassium permanganate solution along with a larger amount of water is added to the first goblet. The same amount of potassium permanganate solution is added to the second goblet but with less water. The third goblet receives only potassium permanganate solution. The three solutions decolorize from violet to wine red and then yellow brown until they are colorless. At the same time, some bubble formation due to the generation of carbon dioxide can be observed. The decolorizing appears just after a short time in the third goblet, while the reaction in the first goblet takes the most time.

The equation $r = f(c_B, \ldots, T)$ describing the relations above is called the *rate law* of the reaction. Most reactions take place in many steps, so the various dependencies can be rather complicated. However, under certain circumstances (certain ranges of concentration, moving away from equilibrium, etc.), there are simple relations that allow us to write the rate law in the form of a power function,

$$r = k(T) \cdot c_B^b \cdot c_{B'}^{b'} \ldots \ ., \tag{16.8}$$

where the concentrations of reactants are usually found on the right-hand side (in rare cases, those of a product or another type of substance not found in the conversion formula are used). We call the exponents $b, b', \ldots$ the *order* of a reaction with respect to the individual reactants B, B′, ... Usually, the numbers 1 and 2 appear as exponents, rarely fractions like $\frac{1}{2}$ or $\frac{1}{3}$ and even more rarely negative numbers. If, for example, the exponent is $b = 1$, the reaction is said to be first order with respect to substance B. If $b = 2$ or $b = 0$, which can also occur, we speak of second- or zero-order reactions with respect to B. Moreover, it is usual to introduce an *overall order* of a reaction which is given by the sum $b + b' + \ldots$ of the exponents of all concentrations present. It is important to note that the exponents often do *not* agree with the conversion numbers. There are several relations, such as the mass action law where conversion numbers actually appear as exponents so that they might also be expected to appear in the rate law. However, this is not generally the case.

The proportionality factor, i.e., the *rate coefficient k*, generally depends strongly upon the conditions of the reaction, especially temperature, but also upon the types of reactants and the reaction medium. The usual name "*rate constant*" does not seem appropriate here because k is not a constant. The units of k are dependent upon the form of the rate law, as we will see.

Finally, we will take a brief look at the relation between the order of a reaction and the molecularity mentioned above. Reaction orders are experimentally determined quantities while molecularity (of a reaction step) is a theoretical quantity essential for the elucidation of a reaction mechanism. In single-step reactions, molecularity and reaction order (as well as conversion number sum) agree with each other because all the particles react *simultaneously* with each other according to their appearance in the conversion formula. Conversely, it is not necessarily possible to infer the molecularity of an arbitrary reaction from its order. This is because in complex reaction processes made up of several single-step reactions, simple rate laws might still be valid.

We will limit the following to homogeneous single-step reactions in a closed container at constant volume. Side reactions and exchange of substances with the environment are excluded (ξ', ξ'', $\ldots = \xi_{\text{other}} = \text{const}$).

First-Order Reactions Consider a single-step reaction

$$\text{B} \rightarrow \text{products},$$

which comes about through random transformations of individual particles (meaning their decomposition or internal rearrangement) and is therefore *monomolecular*. Assuming that almost no backward (reverse) reaction takes place, it obeys a rate law in which the rate density r is directly proportional to the concentration c of the substance B at the time t:

$$r = k \cdot c_{\text{B}}. \tag{16.9}$$

This simply means that the more particles there are, the greater the number that transform per unit time. In this case, the rate coefficient k has the unit s^{-1} and therefore the characteristic of a decay frequency. Because the exponent of the concentration c_{B} equals 1, we have a reaction of first order in B. Moreover, the overall order of the reaction is equal to 1. Under the conditions that apply here ($V = \text{const}$, $\xi_{\text{other}} = \text{const}$), we also have (see Sect. 16.3):

$$r = -\frac{\text{d}c_{\text{B}}}{\text{d}t}. \tag{16.10}$$

In summary, we obtain the differential rate law

$$-\frac{\text{d}c_{\text{B}}}{\text{d}t} = kc_{\text{B}}. \tag{16.11}$$

The rate density at a given time corresponds to the (negative) slope of the experimentally determined $c_{\text{B}}(t)$ curve (Fig. 16.4). The rate density at the beginning of the reaction ($t = 0$; initial concentration $c_{\text{B},0}$) is at its maximum value and approaches zero as substance B is used up.

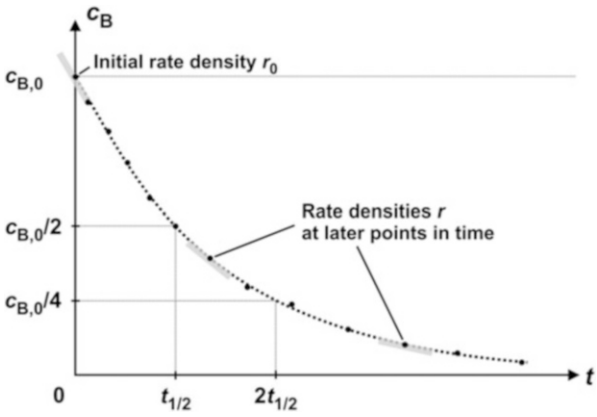


Fig. 16.4 Decrease in concentration of the reactant over time in a first-order reaction. The rate density at a given time can be determined from the slope of the tangent (*light gray*). $t_{1/2}$ illustrates the half-life (the time it takes to reduce the concentration of the reactant to half of its initial value).

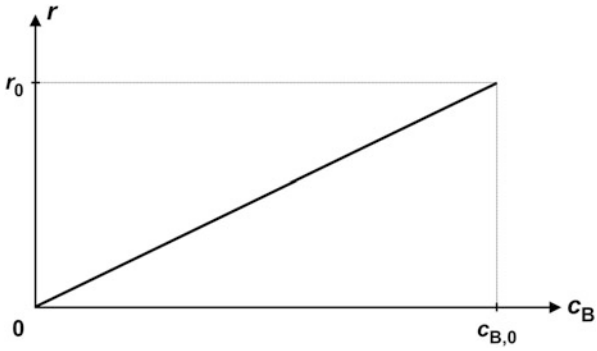


Fig. 16.5 Rate density as a function of the corresponding concentration of substance B.

If the rate densities r are plotted as functions of the concentration c_B (Fig. 16.5), we obtain straight lines as can be expected according to Eq. (16.9). The slope corresponds to the rate coefficient k.

Rate densities are, however, rarely determined directly because slopes can only be determined inexactly. It is, therefore, desirable to know the mathematical relation between the measureable quantities, i.e., concentration and time. Important parameters such as rate coefficient and half-life can be calculated using them. Moreover, if we have a relation for the concentration as a function of time, and if the initial concentration $c_{B,0}$ is given, we can predict the concentration of the substance for any point in time. This is of great importance for industrial processes.

The starting point of our considerations is Eq. (16.11) which, mathematically speaking, is a so-called differential equation. It is necessary to find a function $c_B(t)$ that satisfies this equation. The following relation shows a solution,

$$\ln\frac{c_{B,0}}{c_B} = kt, \tag{16.12}$$

that establishes the desired connection between concentration and time. An alternative form of Eq. (16.12) is obtained by applying the quotient rule of logarithms

[see Eq. (A.1.2) in the Appendix]. However, it should be kept in mind that the argument of a logarithmic function must be dimensionless. This means that we have to divide by an arbitrary reference value $c^\dagger$ having the same dimension as c_B (e.g., the standard concentration $c^\ominus = 1\,\mathrm{kmol\,m^{-3}}$):

$$\ln\left(c_\mathrm{B}/c^\dagger\right) - \ln\left(c_{\mathrm{B},0}/c^\dagger\right) = -kt.$$

In order to avoid unnecessarily complicated looking formulas, we will indicate division by a reference value with curly brackets from now on; we then obtain

$$\ln\{c_\mathrm{B}\} = \ln\{c_{\mathrm{B},0}\} - kt. \tag{16.13}$$

An alternative way of expressing this is

$$c_\mathrm{B} = c_{\mathrm{B},0} \cdot \mathrm{e}^{-k\,t}. \tag{16.14}$$

The solution's correctness can be easily confirmed by taking the derivative:

$$\frac{\mathrm{d}c_\mathrm{B}}{\mathrm{d}t} = -c_{\mathrm{B},0} \cdot k e^{-kt} = -k c_\mathrm{B}.$$

This corresponds to the differential equation (16.11) from which we started.

Solving a differential equation—finding a formula for the desired function—simply means transforming it so that all the derivatives disappear. This requires using integral calculus. When we do this, we speak of the *integrated rate law*. Let us consider this method step by step. First, we "separate" the variables in the initial equation

$$-\frac{\mathrm{d}c_\mathrm{B}}{\mathrm{d}t} = k c_\mathrm{B};$$

this means we rearrange the equation so that all terms with the independent variable appear on one side and all terms with the dependent variable on the other,

$$-\frac{1}{c_\mathrm{B}}\,\mathrm{d}c_\mathrm{B} = k\mathrm{d}t.$$

We then integrate on both sides of the equation between the limits $t = 0$ with corresponding initial concentration $c_{\mathrm{B},0}$, and an arbitrary later time t with corresponding concentration c_B:

$$-\int_{c_{\mathrm{B},0}}^{c_\mathrm{B}} \frac{1}{c_\mathrm{B}}\,\mathrm{d}c_\mathrm{B} = k\int_0^t \mathrm{d}t.$$

Here, the following elementary indefinite integral that we have already applied in Sect. 5.5 serves us well:

$$\int \frac{1}{x}\,\mathrm{d}x = \ln x + \text{constant}.$$

This way we can directly obtain Eq. (16.12),

$$\ln \frac{c_{\mathrm{B},0}}{c_{\mathrm{B}}} = kt,$$

which is the desired integrated rate law.

Equation (16.14) illustrates a characteristic of first-order reactions: the concentration of the reactant decreases *exponentially* with time (compare dashed curve in Fig. 16.4). The paradigm for this kind of process is radioactive decay, but all monomolecular elementary reactions such as the rearrangement of cyclopropane into propane in the gas phase are included in this. There are many further decomposition reactions to be found in "classical chemistry," such as decomposition of dinitrogen pentaoxide N_2O_5 in the gas phase according to

$$2\ \mathrm{N_2O_5|g} \rightarrow 4\ \mathrm{NO_2|g} + \mathrm{O_2|g}$$

that follow a first-order rate law even if they proceed according to a complex mechanism, i.e., even if they are not monomolecular reactions.

With the help of relation (16.14) we can check whether we are actually dealing with a first-order reaction. However, the logarithmic relation (16.13) is more suitable in this case. If we do have a first-order reaction, we will obtain a straight line when $\ln\{c_{\mathrm{B}}\}$ is plotted as a function of t (Fig. 16.6). Its slope gives us the rate coefficient k.

Another important quantity characterizing the rate of a reaction is the *half-life* $t_{1/2}$ (Fig. 16.4). It gives the time that elapses until the concentration of the reactant has been reduced by half of its initial value. Now, if $c_{\mathrm{B}} = c_{\mathrm{B},0}/2$ and $t = t_{1/2}$ are inserted into Eq. (16.12), it follows that

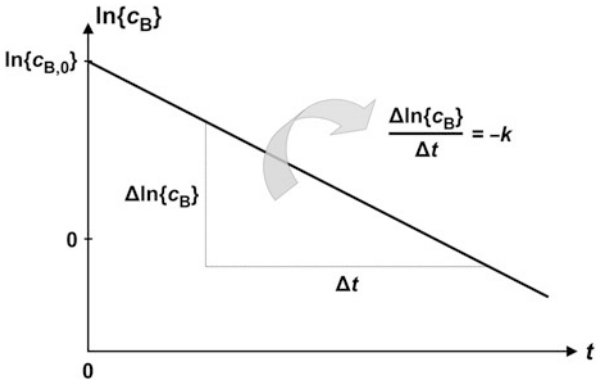


Fig. 16.6 Determining the rate coefficient k of a first-order reaction by drawing the logarithm of the concentration of the reactant as a function of time.

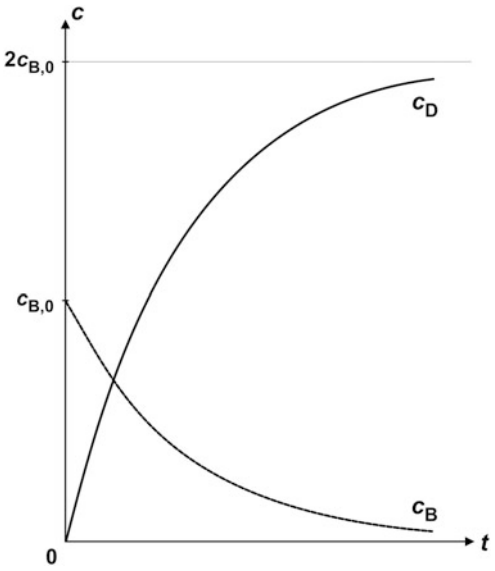


Fig. 16.7 Temporal change of concentration of reactant and product in a first-order reaction of type B → 2 D.

$$t_{1/2} = \frac{\ln 2}{k}. \tag{16.15}$$

The half-life for a first-order reaction is therefore independent of the initial concentration of the reactant.

There is an increase in the concentration of the reaction product that corresponds to the exponential decrease of the reactant concentration. It is equal to the product of the ratio of the conversion numbers and the decrease of concentration ($c_{B,0} - c_B$). Let us consider the reaction

$$B \rightarrow 2\,D$$

(see Fig. 16.7). The concentration c_D of the reaction product D is:

$$c_D = 2(c_{B,0} - c_B).$$

When Eq. (16.14) is used instead of c_B, it follows that:

$$c_D = 2\left(c_{B,0} - c_{B,0}e^{-kt}\right) = 2c_{B,0}\left(1 - e^{-kt}\right). \tag{16.16}$$

When the reaction process has completely run its course, the concentration will be $c_D = 2c_{B,0}$ at time $t = \infty$.

Second-Order Reactions Single-step reactions

$$B + B' \rightarrow \text{products},$$

which result from random encounters of *two* particles, are called *bimolecular* reactions. They follow a rate law in which r is proportional to *both* concentrations c_B and $c_{B'}$:

$$r = k \cdot c_B \cdot c_{B'}. \tag{16.17}$$

This relation becomes clear when one considers that two particles of the types B and B′ will encounter each other more often, the more B there is and the more B′ is present. A rate law for the overall order of 2 is valid here. The rate coefficient k now has the unit $m^3\ mol^{-1}\ s^{-1}$.

Our analysis becomes simpler when the following conversion formula:

$$2\ B \rightarrow \text{products}$$

is taken as the basis. We then obtain

$$r = k \cdot c_B^2. \tag{16.18}$$

Taking the conversion number $\nu_B = -2$ into account, the following holds for the rate density:

$$r = -\frac{1}{2}\frac{dc_B}{dt}. \tag{16.19}$$

The differential equation to be considered is then

$$-\frac{dc_B}{dt} = 2k c_B^2. \tag{16.20}$$

The relation

$$\frac{1}{c_B} = \frac{1}{c_{B,0}} + 2kt \tag{16.21}$$

is a solution for this equation. Solving for c_B yields:

$$c_B = \frac{c_{B,0}}{1 + 2k t c_{B,0}}. \tag{16.22}$$

In order to find the integrated rate law, we proceed analogously to what we do with first-order reactions. Starting with the differential equation (16.20), we first separate the variables:

$$-\frac{dc_B}{c_B^2} = 2k dt.$$

In order to solve the equation, we will need the following standard integral (compare Sect. A.1.3 in the Appendix):

$$\int \frac{1}{x^2}\, dx = -\frac{1}{x} + \text{constant}.$$

The integration limits correspond to those of the first-order reaction, resulting in

$$-\int_{c_{B,0}}^{c_B} \frac{dc_B}{c_B^2} = 2k \int_0^t dt.$$

After integrating, we obtain

$$\frac{1}{c_B} - \frac{1}{c_{B,0}} = 2kt,$$

from which, after transformation, Eq. (16.21) results.

When c_B is plotted as a function of t (Fig. 16.8), we notice that for the same initial concentration $c_{B,0}$ and the same initial rate, the curve approaches zero much more slowly than it would in a first-order reaction.

In order to verify that we are really dealing with a second-order reaction, we plot $1/c_B$ as a function of t (Fig. 16.9). According to Eq. (16.21), this must result in a straight line from whose slope the rate coefficient can be determined.

We can obtain the half-life $t_{1/2}$ again by inserting the value $c_{B,0}/2$ for c_B:

$$t_{1/2} = \frac{1}{2kc_{B,0}}. \tag{16.23}$$

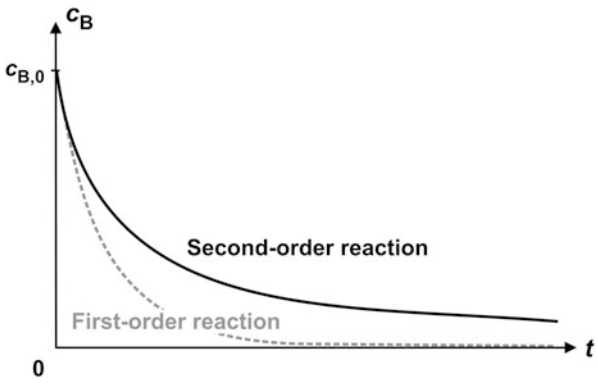


Fig. 16.8 Temporal progression of a second-order reaction (compared to a first-order reaction).

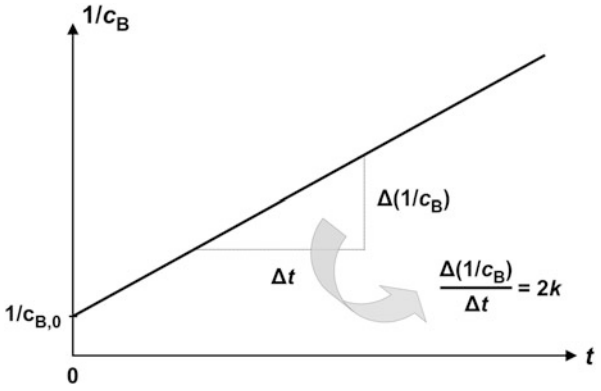


Fig. 16.9 Determining the rate coefficient k of a second-order reaction by representing $1/c_B$ as a function of t.

In contrast to a first-order reaction, the half-life depends upon the initial concentration of the reactant and is *not* characteristic for the reaction.

The general case

$$B + B' \rightarrow \text{products}$$

results in very similar relations when the initial concentrations $c_{B,0}$ and $c_{B',0}$ are identical, and both reaction partners participate equally in the reaction. The conversion number ν_B now equals -1, so the factor 2 drops out from all equations and we obtain

$$\frac{1}{c_B} = \frac{1}{c_{B,0}} + kt \tag{16.24}$$

for the integrated rate law. The half-life equals

$$t_{1/2} = \frac{1}{k c_{B,0}}. \tag{16.25}$$

If the initial concentrations of reactants B and B′ are not identical, integration will require a partial fraction decomposition. This is why only the final result will be shown (for the sake of completeness):

$$\ln \frac{c_B \cdot c_{B',0}}{c_{B'} \cdot c_{B,0}} = (c_{B,0} - c_{B',0})kt. \tag{16.26}$$

Second-order reactions are relatively common. We could mention the reaction between hydrogen and iodine to form hydrogen iodide or the decomposition of nitrogen dioxide according to

$$2\,NO_2 \rightarrow 2\,NO + O_2$$

as examples of reactions in the gas phase. In addition, numerous reactions in solution such as the alkaline ester saponification

$$CH_3COOC_2H_5 + OH^- \rightarrow CH_3COO^- + C_2H_5OH$$

obey this rate law as well.

There are rate laws corresponding to *tri-* or *higher molecular reactions*, in which *three* or *more* particles must encounter each other. However, these types of reactions are so rare that we do not really need to go into them separately.

Zero-Order Reactions Zero-order reactions have a rate that is independent of the concentration of the reactant(s), i.e., they are characterized by a constant rate density:

$$r = k. \tag{16.27}$$

The decrease of the reactant's concentration is then described by

$$-\frac{\mathrm{d}c_\mathrm{B}}{\mathrm{d}t} = k. \tag{16.28}$$

The solution to this differential equation is:

$$c_\mathrm{B} = c_{\mathrm{B},0} - kt. \tag{16.29}$$

Integration observing the known limits,

$$-\int_{c_{\mathrm{B},0}}^{c_\mathrm{B}} \mathrm{d}c_\mathrm{B} = k\int_0^t \mathrm{d}t,$$

yields the following integrated rate law:

$$c_\mathrm{B} - c_{\mathrm{B},0} = -kt.$$

Such behavior is not possible in single-step reactions alone, but only when a process that acts as a kind of "bottleneck" precedes or follows the actual reaction, a process which runs at a constant rate or serves to keep the concentration constant. These kinds of processes can be:

- Adsorption or desorption processes such as those playing a role in heterogeneous catalysis,
- Diffusion processes,
- Radiation with constant light intensity in photochemical reactions,
- Dissolution processes.

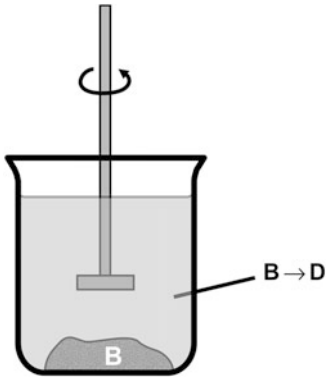


Fig. 16.10 Decomposition reaction of a reactant B in a saturated solution with excess solid solute as example of a (pseudo-) zero-order reaction.

Consider, for example, the decomposition of a reactant B in a saturated solution with excess solid solute (Fig. 16.10). The actual decomposition reaction is preceded by the solubility equilibrium

$$\mathrm{B}|\mathrm{s} \rightleftarrows \mathrm{B}|\mathrm{d}$$

[where the dissolved form is characterized by the abbreviation |d (lat. dissolutus)]. This always keeps the concentration c_B constant:

$$r = k \cdot c_\mathrm{B}(= \text{const.}) = k'. \tag{16.30}$$

This concentration can be combined with the actual rate coefficient k to produce a new rate coefficient k' so that the order is lowered. In this case, the term *pseudo-order* may be used.

A pseudo-order can occur when reactions take place in dilute solutions where the solvent (possibly water) simultaneously functions as the reaction partner. Because there is a great excess of it, the solvent concentration remains almost constant in comparison to the other substances and can, in turn, be included in the rate coefficient.