Chapter 6
Chemical Kinetics

Abstract Reaction kinetics deals with the question how fast a chemical reaction proceeds. From a mathematical point of view, problems in reaction kinetics are formulated as rate equations, i.e., differential equations in time. In the limit $t \to \infty$ the results of reaction kinetics and thermodynamics (chemical equilibrium) must coincide. We consider this in detail in Problem 6.4. At the end of the chapter we deal with the fascinating field of autocatalysis and oscillating chemical reactions.

6.1 Basic Concepts

In the following it is assumed that the reader is familiar with stoichiometry (Chap. 2), especially the concept of the extent of reaction.

6.1.1 Reaction Rate

There is an obvious phenomenological definition of the reaction rate r based on the *change of extent of reaction with time*,

$$\boxed{r = \frac{1}{V}\frac{d\xi}{dt} = \frac{1}{\nu_J}\frac{d[J]}{dt}} \tag{6.1}$$

where $[J] = \frac{n_J}{V}$ is the concentration of species J in a given volume V. Hence, a reaction rate can be measured, for example, by observing the *decay* of the concentration of an educt. But how does the reaction rate depend on the conditions under which a reaction proceeds?

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6.1.2 Reaction Rate Laws

Obviously, the reaction rate r depend on the educt concentrations. To classify chemical kinetics, it is common to consider a **rate law** and to introduce **reaction orders**[1]:

$$\boxed{r = k\,[J_1]^{\alpha_1}\,[J_2]^{\alpha_2}\ldots} \tag{6.2}$$

Here, k is the **rate constant**, and α_i is the order of the reaction with regard to educt J_i, the latter being present with the concentration $[J_i]$. The sum of the specific orders α_i is the **integral order** or simply the **order** of the reaction. It is important to realize that the coefficients α_i are *not* the stoichiometric numbers of the reaction. Only in the special case of an *elementary reaction* can the order be deduced by a simple inspection of the reaction. The determination of the reaction orders, either experimentally, or by deduction from a suitable *reaction mechanism*, is a frequent task of reaction kinetics.

If we combine the rate law Eq. (6.2) with Eq. (6.1) for one of the educts or products, we obtain a differential equation for the concentration of this species as a function of time, which may be solved by integration observing the initial conditions.

6.1.2.1 Elementary Reaction

In general, a chemical reaction has to be taken as a *net* reaction as the result of an underlying reaction mechanism. The latter can be further characterized by introducing the concept of elementary reaction. A reaction is called an elementary reaction if it occurs in a single step, i.e., it cannot be subdivided into further reaction steps.

6.1.2.2 Molecularity

What kinds of elementary reactions are possible? Fortunately, there are only three relevant types, differing in the number of educt molecules participating in the elementary reaction step. This number is called the molecularity of the reaction. Molecularity one is an **unimolecular reaction** $\mathrm{A} \longrightarrow$ Products, which is a **decay reaction**. Molecularity two is called a **bimolecular reaction**, either of type $2\mathrm{A} \longrightarrow$ Products, or the somewhat more complicated type $\mathrm{A} + \mathrm{B} \longrightarrow$ Products. Molecularity three is called a **termolecular reaction**, in its most general case

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[1] Note that there are cases where the most general form $r = kf([J_1], [J_2], \ldots)$ is more appropriate.

$A + B + C \longrightarrow$ Products. It is obvious that the probability of a simultaneous impact of three molecules is much smaller in comparison with a collision of only two molecules. However, depending on the number of product molecules, the laws of energy and momentum conservation sometimes require the presence of a third collision element. An elementary reaction of molecularity four, however, is so unlikely that we do not even have to consider it. Thus, a net chemical reaction may be mapped to only these few relevant types of elementary steps, and, of course, their variations.

6.1.2.3 Determination of the Reaction Order

Combining Eqs. (6.1) and (6.2), we obtain a differential equation, which can be integrated to determine the concentration of a certain educt or product as a function of time. By comparison with experimental data, a certain reaction order can be verified or falsified.

Another technique is the *analysis of initial reaction rate*, r_0, as a function of the initial concentrations, $[J]_0$. From Eq. (6.1) we obtain:

$$\boxed{\ln r_0 = \ln k + \alpha_1 \ \ln[J_1]_0 + \alpha_2 \ \ln[J_2]_0 + \cdots} \tag{6.3}$$

A plot of $\ln r_0$ against $\ln[J_1]_0$ should give a straight line with a slope α_1. Thus, by means of systematic variation of the initial concentration of all educts, all reaction orders can be determined.

6.1.2.4 Temperature Dependence of the Rate Constant

The reaction rate typically increases with temperature, although sometimes, the opposite is observed. Phenomenologically, this temperature dependence is described by means of the temperature-dependent **rate constant** k (see Eq. (6.2)). The simplest approach is described by the **Arrhenius** equation,

$$\boxed{k(T) = A \ \exp\left(-\frac{E_a}{RT}\right).} \tag{6.4}$$

E_a is called the **energy of activation**, A is the **pre-exponential factor**. A frequent task is to determine the activation energy and the pre-exponential factor from experimental data. The determination of an activation energy within a reaction mechanism provides information about the *energy barrier* that has to be overcome for a certain reaction to occur. In theoretical terms, the energy barrier depends on the reaction path on the *potential energy surface* characterizing a reaction (see Fig. 6.1).

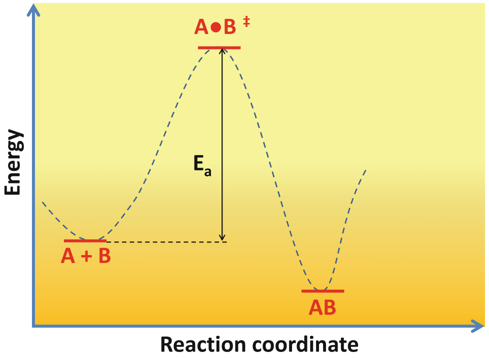

Fig. 6.1 Schematic illustration of a potential energy surface in one dimension for a hypothetical reaction A + B → AB. E_a is the activation energy as the height of the energy barrier relative to the educts A and B. The maximum energy characterizes the *transition state* $AB^{\ddagger}$ leading to bond formation

More general models consider an additional weak temperature dependence in the pre-exponential factor:

$$k(T) = AT^{\beta} \exp\left(-\frac{E_a}{RT}\right). \tag{6.5}$$

For example, a consideration of the number of collisions in a gas of two different species based on the kinetic theory of gases would predict[2] $\beta = \frac{1}{2}$ in Eq. (6.5).

6.2 Problems

Problem 6.1 (Reaction Order and Half Life)

a. Consider the reaction $A \xrightarrow{k} P$ with the rate constant k. The initial concentration of the educt A is $c_A(0)$. If $\alpha > 1$ is the order of the reaction, show that the half-life is

$$t_{\frac{1}{2}} = \frac{2^{\alpha-1} - 1}{\alpha - 1} \frac{1}{k\, c_A(0)^{\alpha-1}} \tag{6.6}$$

b. At an initial concentration of $1\,\mathrm{mol\,dm^{-3}}$ the half-life of the educt A was 200 s. When the initial concentration was doubled, the half-life reduced to 141 s. Determine the reaction order and the rate constant of the reaction.

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[2] According to kinetic theory (Eq. (7.3)), the collision rate between N_A particles of a species A and N_B particles of species B at temperature T is $N_A N_B \sigma_{AB} \left(\frac{8k_B T}{\mu}\right)^{\frac{1}{2}}$ where σ_{AB} is the collision cross section and μ is the effective mass.

Solution 6.1 The half-life of an educt is the time after which its concentration decays to half of its initial value:

$$c_{\mathrm{A}}(t_{\frac{1}{2}}) = \frac{1}{2} c_{\mathrm{A}}(0) \tag{6.7}$$

In **subproblem (a)**, we shall prove the relationship between $t_{\frac{1}{2}}$, the rate constant, and the initial concentration $c_{\mathrm{A}}(0)$ given by Eq. (6.6). This relation is valid if the order of the reaction α is greater than 1. The rate law (Eq. (6.2)) for this reaction is:

$$r = k\, c_{\mathrm{A}}(t)^{\alpha},$$

which, on the other hand, can be expressed by the change of c_{A} with time (Eq. (6.1)):

$$r = -\frac{dc_{\mathrm{A}}(t)}{dt}$$

Thus, the differential equation describing the change in c_{A} is

$$-\frac{dc_{\mathrm{A}}(t)}{dt} = k\, c_{\mathrm{A}}(t)^{\alpha} \tag{6.8}$$

The separation of variables

$$\frac{dc_{\mathrm{A}}}{c_{\mathrm{A}}^{\alpha}} = -k\, dt$$

is followed by an integration step:

$$\int_{c_{\mathrm{A}}(0)}^{c_{\mathrm{A}}(t)} \frac{dc_{\mathrm{A}}}{c_{\mathrm{A}}^{\alpha}} = -k \int_{0}^{t} dt.$$

Using the integral table (Eq. (A.35)), we obtain:

$$\frac{1}{1-\alpha} \left[c_{\mathrm{A}}^{1-\alpha} \right]_{c_{\mathrm{A}}(0)}^{c_{\mathrm{A}}(t)} = -k\, t$$

and thus

$$\frac{1}{\alpha - 1}\left(\frac{1}{c_{\mathrm{A}}(t)^{\alpha-1}} - \frac{1}{c_{\mathrm{A}}(0)^{\alpha-1}}\right) = k\,t.$$

Note that we could solve now for $c_{\mathrm{A}}(t)$ and obtain the explicit expression for the concentration of the educt as a function of time, always provided that $\alpha > 1$, as stated above. In the next step, we use the definition of the half-life (Eq. (6.7)): after the time $t_{\frac{1}{2}}$, the concentration c_{A} has decayed to half of its initial value. Inserting this in the last expression, we obtain:

$$t_{\frac{1}{2}} = \frac{1}{k(\alpha-1)}\left(\frac{1}{\frac{1}{2^{\alpha-1}}c_{\mathrm{A}}(0)^{\alpha-1}} - \frac{1}{c_{\mathrm{A}}(0)^{\alpha-1}}\right) = \frac{2^{\alpha-1}-1}{k(\alpha-1)c_{\mathrm{A}}(0)^{\alpha-1}}$$

which is simply the maintained equation.

In **subproblem (b)**, we apply this equation to determine the reaction order α and also to rate constant k from the measurements of the half-life at two different initial concentrations. For $c_{\mathrm{A}}(0) = 1\,\mathrm{mol\,dm^{-3}}$ we have $t_{\frac{1}{2}} = 200\,\mathrm{s}$. If the initial concentration is increased to $\tilde{c}_{\mathrm{A}}(0) = 2\,\mathrm{mol\,dm^{-3}}$, the reaction proceeds faster and $\tilde{t}_{\frac{1}{2}} = 141\,\mathrm{s}$. The data pairs given are sufficient to determine α and k. However, the structure of Eq. (6.6) does not allow us to solve for α. The trick is to form the ratio of half-lives, which eliminates the unknown k:

$$\frac{t_{\frac{1}{2}}}{\tilde{t}_{\frac{1}{2}}} \overset{\text{Eq. (6.6)}}{=} \left(\frac{\tilde{c}_{\mathrm{A}}(0)}{c_{\mathrm{A}}(0)}\right)^{\alpha-1} = 2^{\alpha-1}$$

By considering the natural logarithm and the rules for logarithms (see appendix Sect. A.3.3), we can solve for α:

$$\alpha = 1 + \frac{\ln\left(t_{\frac{1}{2}}/\tilde{t}_{\frac{1}{2}}\right)}{\ln 2} = 1 + \frac{\ln(200/141)}{\ln 2} = 1.504 \tag{6.9}$$

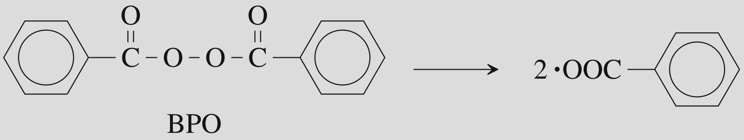
Hence, the sought reaction order is about $\frac{3}{2}$. Inserting this result into Eq. (6.7) together with one data pair enables us to solve for the rate constant k:

$$k = \frac{2^{\alpha-1}-1}{t_{\frac{1}{2}}(\alpha-1)c_{\mathrm{A}}(0)^{\alpha-1}} = \frac{2^{\frac{1}{2}}-1}{\frac{1}{2}}\,\frac{1}{200\,\mathrm{s}\times 1\,\left(\mathrm{mol\,dm^{-3}}\right)^{\frac{1}{2}}}$$

Thus, the rate constant is $k = 4.13 \times 10^{-3}\,\mathrm{dm}^{\frac{3}{2}}\,\mathrm{mol}^{-\frac{1}{2}}\,\mathrm{s}^{-1}$. It is worth mentioning that the physical dimension of k always depends on the reaction order.

Problem 6.2 (First Order Decay)

Benzoyl peroxide (BPO) is an active pharmaceutical agent against acne. Its medical efficacy is based on the decay and the formation of benzoyloxy radicals, which shall be assumed to follow first-order kinetics:



(6.10)

a. In microcalorimetric experiments the rate constant of the above reaction was determined as a function of temperature (F. Zaman et al., Int. J. Pharm. **277**, 133 (2001).):

T (°C)	20	25	30	35	40	45
k ($10^{-9}\,\mathrm{s}^{-1}$)	1.16	4.33	6.85	20.0	58.4	107.0

   Determine the energy of activation and the pre-exponential factor assuming an Arrhenius law for the temperature dependence of the rate constant.

b. A salve containing 10% by weight BPO was stored at a temperature of 25 °C. Determine the mass fraction after a storage period of 60 days.

c. A portion of 0.02 g of the salve is applied to the skin. If a temperature of the skin of 35 °C is assumed, how many benzyloxy radicals are formed within a residence time of 2 h?

Solution 6.2 As temperature has an enormous impact on reaction rates (and other degradation processes), the room-temperature storage of pharmaceuticals may be an important issue. Here, we consider the stability of a typical radical former assuming first-order kinetics.

In **subproblem (a)**, we determine the energy of activation and the pre-exponential factor from a suitable plot of rate constants measured at different temperatures. Starting from the Arrhenius law Eq. (6.4), we interpret

$$\ln k = -\frac{E_a}{R}\frac{1}{T} + \ln A$$

Table 6.1 Kinetic data qualified to determine the energy of activation and the pre-exponential factor using an Arrhenius-type plot (see Fig. 6.2)

T^{-1} (10^{-3} K^{-1})	3.411	3.354	3.299	3.245	3.193	3.143
$\ln k$	−20.57	−19.26	−18.80	−17.73	−16.66	−16.05

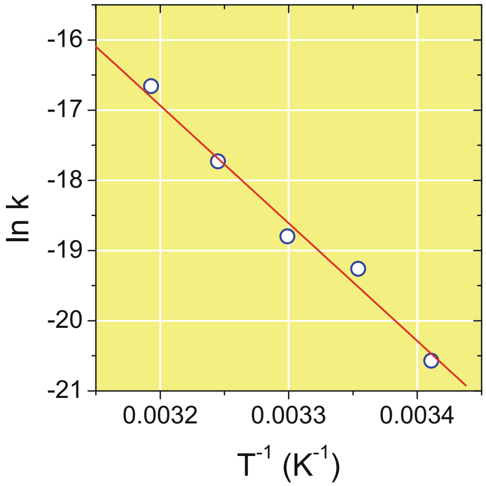


Fig. 6.2 Arrhenius type plot of the kinetic data given in Table 6.1. A linear regression of the data yields a slope of −16770 ± 860 K, and an axis intercept of 37 ± 3

as a linear equation. A plot of $\ln k$ against the reciprocal temperature should be a line with a slope $-\frac{E_a}{R}$, and the axis intercept $\ln A$. There is one point to consider, which often leads to errors: the latter expression requires an absolute temperature, whereas the original data in the above table are given in degrees Celsius. The kinetic data in the form qualified to determine the energy of activation E_a and the pre-exponential factor A are given in Table 6.1. The Arrhenius plot is shown in Fig. 6.2.

A linear regression of the data yields a slope of $s = -16{,}770\,\mathrm{K}$. Because of the scattering in the experimental raw data, there is an uncertainty of 860 K. Hence, the sought energy of activation is $E_a = -R\,s = 8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}} \times 16{,}770\,\mathrm{K} = 139.4\,\mathrm{kJ\,mol^{-1}}$. From the evaluated intercept of $c = 37 \pm 3$, the pre-exponential factor $A = \mathrm{e}^c = 1.2 \times 10^{16}\,\mathrm{s^{-1}}$ follows. This value is quite high. Typical values for A in a first-order reaction are within the range $10^{13}\,\mathrm{s^{-1}}$, which is the range of molecular vibrational frequencies.[3] From the statistical error, however, an uncertainty of one order of magnitude can be deduced from these data.

In **subproblem (b)**, we investigate how much of the BPO has reacted after a room-temperature storage period of 60 days. As we can assume first-order kinetics, the combination of Eqs. (6.1), (6.2), and (6.10) yields the following differential

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[3] See Problem 10.1.

equation for the concentration of BPO:

$$-\frac{d\,[\mathrm{BPO}]}{dt} = k\,[\mathrm{BPO}]$$

The integration in the manner demonstrated in Problem 6.1 is straightforward. The result is the well-known exponential decay of the concentration:

$$[\mathrm{BPO}]\,(t) = [\mathrm{BPO}]\,(0)\exp\left(-kt\right) = 0.978 \times [\mathrm{BPO}]\,(0) \tag{6.11}$$

Here we have taken the room-temperature value for the rate constant, $k = 4.33 \times 10^{-9}\,\mathrm{s}^{-1}$, and we have inserted $t = 60 \times 24 \times 3600\,\mathrm{s}$. We can assume a direct proportionality between the concentration of BPO and its mass fraction in the salve. Thus, starting with an initial mass fraction of 10% BPO in the salve, a 60-day period of storage reduces the mass fraction to 9.78%. Apparently, there is no significant loss of efficacy during this time.

In **subproblem (c)**, we finally assess the number of benzyloxy radicals freed within 2 h by a portion of 0.02 g salve at a skin temperature of 35 °C. At this temperature, the rate constant is $k = 20.0 \times 10^{-9}\,\mathrm{s}^{-1}$. Assuming a mass fraction of 10% BPO, the initial mass of the BPO molecules in 0.02 g salve is 0.002 g. From Eq. (6.10) we can extract information about the molar mass of BPO, M_{BPO}. Its sum formula is $C_{14}H_{10}O_4$. Therefore, $M_{\mathrm{BPO}} = 242\,\mathrm{g\,mol}^{-1}$. Hence, the sample initially contains $n_{\mathrm{BPO}}(0) = \frac{0.002\,\mathrm{g}}{242\,\mathrm{g\,mol}^{-1}} = 8.26 \times 10^{-6}\,\mathrm{mol}$ BPO molecules. After 2 h the number of BPO molecules is reduced by a factor $\exp\left(-kt\right) = \exp\left(-20.0 \times 10^{-9}\,\mathrm{s}^{-1} \times 7200\,\mathrm{s}\right) = 0.99986$. As a consequence, a fraction of 1.4×10^{-4} of the BPO molecules reacts, each molecule producing two benzyloxy radicals (see Eq. (6.10)). Thus, the number of radicals produced is:

$$Z = 2 \times 1.4 \times 10^{-4} \times 8.26 \times 10^{-6}\,\mathrm{mol} \times N_A = 1.4 \times 10^{15}.$$

Problem 6.3 (Methane Decay) An important decay channel of the atmospheric trace gas methane (CH_4) is via the reaction with hydroxyl radicals:

$$CH_4 + OH \xrightarrow{k} CH_3 + H_2O \tag{6.12}$$

a. Write down the rate law of this reaction assuming that reaction Eq. (6.12) is an elementary reaction.
b. If the initial concentrations of methane and hydroxyl radicals are $1 \times 10^{-9}\,\mathrm{mol\,m}^{-3}$ and $4 \times 10^{-12}\,\mathrm{mol\,m}^{-3}$, what is the half-life of OH? Assume a rate constant of $k = 4.75 \times 10^{3}\,\mathrm{m}^{3}\,\mathrm{mol}^{-1}\,\mathrm{s}^{-1}$.

Solution 6.3 This problem deals with the decay of methane and hydroxyl in a bimolecular reaction according to Eq. (6.12). The exercise is instructive as it demonstrates two different views of a classical problem in chemical kinetics.

In **subproblem (a)**, we write down the rate law for this elementary reaction of type A + P → Products, which is the first order for methane, and also first order for OH. Thus, the reaction rate is:

$$r = k[\mathrm{CH_4}]\,[\mathrm{OH}]. \tag{6.13}$$

In **subproblem (b)**, we shall determine the time t_{50}, after which the concentration of hydroxyl decays to 50% of its initial value $[\mathrm{OH}]^0 = 4 \times 10^{-12}\,\mathrm{mol\,m^{-3}}$. As mentioned above, there are two different ways to solve this problem. This is possible because there is an excess of the other reactant, methane: $[\mathrm{CH_4}]^0 = 1 \times 10^{-9}\,\mathrm{mol\,m^{-3}}$. Note that after a complete decay of OH, the concentration of methane is still $9.96 \times 10^{-10}\,\mathrm{mol\,m^{-3}} \approx [\mathrm{CH_4}]^0$. Under these conditions, we may treat the problem as a first-order decay of OH with an effective rate constant:

$$k_{\mathrm{eff}} = k\,[\mathrm{CH_4}]^0 = 4.75 \times 10^3 \times 1 \times 10^{-9}\,\mathrm{s^{-1}} = 4.75 \times 10^{-6}\,\mathrm{s^{-1}} \tag{6.14}$$

$$-\frac{d\,[\mathrm{OH}]}{dt} = k_{\mathrm{eff}}\,[\mathrm{OH}]. \tag{6.15}$$

The well-known textbook result for the half-life is

$$t_{50} = \frac{\ln 2}{k_{\mathrm{eff}}} = \frac{0.69315}{4.75 \times 10^{-6}\,\mathrm{s^{-1}}} = 145{,}926\,\mathrm{s} \approx 41\,\mathrm{h}. \tag{6.16}$$

The second view of the problem is the exact treatment of the second order reaction. Ready to use analytical expressions can be found in textbooks, but it is instructive to recapitulate the details. If more than one reactant is present, then the integration of the rate law is more complicated than in the cases we have already dealt with in Problem 6.1. Focusing on the extent of reaction ξ we can write

$$r = \frac{1}{V}\frac{d\xi}{dt} = k\frac{n_{\mathrm{CH_4}}}{V}\frac{n_{\mathrm{OH}}}{V}, \tag{6.17}$$

where V is the volume. The amounts of methane and hydroxyl are (see Eq. (2.6))

$$n_{\mathrm{CH_4}} = n^0_{\mathrm{CH_4}} - \xi \tag{6.18}$$

and

$$n_{\mathrm{OH}} = n^0_{\mathrm{OH}} - \xi. \tag{6.19}$$

Insertion of these two expressions into Eq. (6.17) yields after separation of the variables and integration

$$\int_0^{\xi(t)} \frac{d\xi'}{\left(n^0_{\mathrm{CH_4}} - \xi'\right)\left(n^0_{\mathrm{OH}} - \xi'\right)} = \frac{k}{V}\int_0^t d\tau. \tag{6.20}$$

Integration using Eq. (A.38) in the appendix yields

$$\frac{1}{n^0_{\mathrm{CH_4}} - n^0_{\mathrm{OH}}} \ln\left(\frac{n^0_{\mathrm{CH_4}} - \xi}{n^0_{\mathrm{OH}} - \xi}\right)\Bigg|_0^{\xi(t)} = \frac{k}{V}t. \tag{6.21}$$

Further evaluation by insertion of the integration limits under special consideration of Eqs. (6.18) and (6.19) yields

$$\frac{1}{n^0_{\mathrm{CH_4}} - n^0_{\mathrm{OH}}} \ln\left(\frac{\frac{n_{\mathrm{CH_4}}(t)}{n^0_{\mathrm{CH_4}}}}{\frac{n_{\mathrm{OH}}(t)}{n^0_{\mathrm{OH}}}}\right) = \frac{k}{V}t \tag{6.22}$$

or, again in terms of concentration,

$$\frac{1}{[\mathrm{CH_4}]^0 - [\mathrm{OH}]^0} \ln\left(\frac{\frac{[\mathrm{CH_4}](t)}{[\mathrm{CH_4}]^0}}{\frac{[\mathrm{OH}](t)}{[\mathrm{OH}]^0}}\right) = kt. \tag{6.23}$$

This equation is the basis for the determination of the half-life of the hydroxyl radicals. After the time t_{50}, the concentrations of the reactants are

$$[\mathrm{OH}](t_{50}) = \frac{1}{2}[\mathrm{OH}]^0 \tag{6.24}$$

and[4]

$$[\mathrm{CH_4}](t_{50}) = [\mathrm{CH_4}]^0 - \frac{1}{2}[\mathrm{OH}]^0. \tag{6.25}$$

Insertion of these expressions into Eq. (6.23) yields

$$\begin{aligned} t_{50} &= \frac{1}{k}\frac{1}{[\mathrm{CH_4}]^0 - [\mathrm{OH}]^0} \ln \frac{\frac{[\mathrm{CH_4}]^0 - \frac{1}{2}[\mathrm{OH}]^0}{[\mathrm{CH_4}]^0}}{\frac{1}{2}} \\ &= \frac{1}{k}\frac{1}{[\mathrm{CH_4}]^0 - [\mathrm{OH}]^0} \ln 2\left(1 - \frac{1}{2}\frac{[\mathrm{OH}]^0}{[\mathrm{CH_4}]^0}\right) \\ &= 146{,}089\,\mathrm{s} \end{aligned} \tag{6.26}$$

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[4] According to Eq. (6.19), the extent of reaction at time t_{50} is $\xi_{50} = \frac{1}{2}[\mathrm{OH}]^0$.

which is fairly close to the above approximate result. This is obvious because in the second line in Eq. (6.26) the neglect of $[OH]^0$ transforms this expression just into Eq. (6.16). The example teaches us that it may be quite useful to look at the initial conditions. If there is an excess of one reactant, its concentration is approximately constant, and this can mean a considerable simplification. Experiments for the determination of the kinetics of a reaction with several reactants are often designed in such a way that there is an excess of all but one of the educts. In this way, the reaction order with regard to a certain reactant can be determined.

Problem 6.4 (Kinetic Look on Chemical Equilibrium) Consider the coupled reactions

$$\mathrm{A} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{B} \tag{6.27}$$

and assume that both forward and backward reactions follow a first-order kinetics with the rate constants k_1 and k_2 respectively.

a. Show that the equilibrium constant of this reaction is given by $K = \frac{k_1}{k_2}$.
b. If n_A^0 and n_B^0 are the initial amounts of A and B in a state far from chemical equilibrium, show that the extent of reaction is given by

$$\xi(t) = \frac{k_1 n_\mathrm{A}^0 - k_2 n_\mathrm{B}^0}{k_1 + k_2} \left(1 - e^{-(k_1+k_2)t}\right) \tag{6.28}$$

c. Two molecular conformers A and B are in chemical equilibrium with different amounts of A and B. At $t = 0\,\mathrm{s}$, a short heat pulse effects a momentary increase in temperature in the system, which cause the amounts of both conformers to change rapidly, as indicated in Fig. 6.3. Then, the system relaxes back into equilibrium. Extract the necessary information from Fig. 6.3 to estimate the equilibrium constant and the first-order rate constants of the forward and backward reactions.

Solution 6.4 In this problem, we investigate in detail how a chemical reaction comes to equilibrium. The problem sheds light on an important technique for determining rate constants: *relaxation methods*. The thermodynamic description of the equilibrium by means of the equilibrium constant $K(T)$ must be identical to the kinetic description in the limit $t \to \infty$. Hence, there must be a relationship between the rate constants and K, which we find in **subproblem (a)**. In the first step, we set up the differential equations for the concentrations of both species. We consider the forward and the backward reaction of Eq. (6.27), in addition to Eqs. (6.1) and (6.2):

$$\frac{d\,[\mathrm{A}]}{dt} = -k_1\,[\mathrm{A}] + k_2\,[\mathrm{B}] \tag{6.29}$$

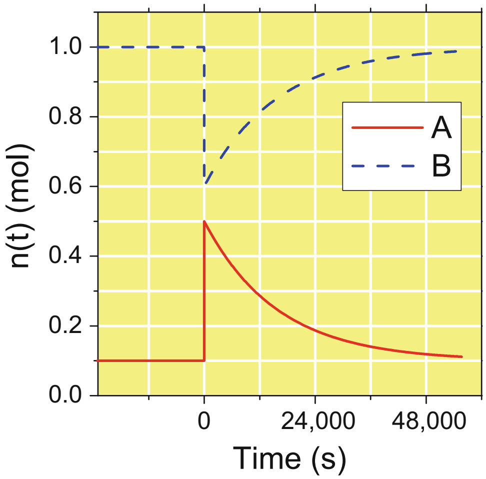

Fig. 6.3 Distortion and relaxation back into chemical equilibrium of two coexisting molecular conformers A and B

$$\frac{d\,[\mathrm{B}]}{dt} = k_1\,[\mathrm{A}] - k_2\,[\mathrm{B}] \tag{6.30}$$

These equations consider that A decays in a first-order kinetics with a rate constant k_1, and it builds up in a first-order kinetics with rate constant k_2. Conversely, B is formed in a first-order reaction with rate constant k_1, and it decays in a first-order reaction with rate constant k_2. In the second step, we assume additional conditions in the special case of chemical equilibrium. Under the stationary conditions of chemical equilibrium, the forward and backward reactions balance, so that the net changes in concentrations are exactly zero:

$$0 \overset{!}{=} -k_1\,[\mathrm{A}]_{\mathrm{eq}} + k_2\,[\mathrm{B}]_{\mathrm{eq}} \Leftrightarrow \frac{k_1}{k_2} = \frac{[\mathrm{B}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}} \tag{6.31}$$

Here, $[\mathrm{A}]_{\mathrm{eq}}$ and $[\mathrm{B}]_{\mathrm{eq}}$ are the equilibrium concentrations of A and B. On the other hand, the latter are related by the law of mass action to the equilibrium constant:

$$K = \frac{[\mathrm{B}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}} \tag{6.32}$$

Comparison of the last two equations thus establishes the important relation sought:

$$K = \frac{k_1}{k_2} \tag{6.33}$$

Similar relations between the rate constants of the forward and backward reactions and K could also be derived for the general case where the reaction orders differ from unity.

In **subproblem (b)**, we shall investigate in detail how the system comes to equilibrium. The goal is to integrate the coupled differential equations Eq. (6.29) and (6.30). We are advised to introduce the extent of reaction ξ and to prove Eq. (6.28). In doing so, we learn how to use the extent of reaction to solve more complicated examples of chemical kinetics problems. Using Eq. (2.6) we can express the amount of substances of A and B as a function of time:

$$n_\mathrm{A}(t) = n_\mathrm{A}^0 - \xi(t) \tag{6.34}$$

$$n_\mathrm{B}(t) = n_\mathrm{B}^0 + \xi(t) \tag{6.35}$$

Within a constant volume we can set up a differential equation for n_A based on Eq. (6.29),

$$\frac{d\,n_\mathrm{A}}{dt} = -k_1 n_\mathrm{A} + k_2 n_\mathrm{B}, \tag{6.36}$$

in which we insert the last two expressions. Because $\frac{d\,n_\mathrm{A}}{dt} = -\frac{d\xi}{dt}$, we obtain

$$-\frac{d\xi}{dt} = -k_1\left(n_\mathrm{A}^0 - \xi\right) + k_2\left(n_\mathrm{B}^0 + \xi\right) = (k_1 + k_2)\,\xi - k_1 n_\mathrm{A}^0 + k_2 n_\mathrm{B}^0 \tag{6.37}$$

We separate the variables and integrate with the proper boundaries $t = 0$, $\xi(0) = 0$, and $\xi(t)$ at an arbitrary time t:

$$\int_0^{\xi(t)} \frac{d\xi}{(k_1 + k_2)\,\xi - k_1 n_\mathrm{A}^0 + k_2 n_\mathrm{B}^0} = -\int_0^t d\tau \tag{6.38}$$

Using the integral Table in the appendix (Eq. (A.37)) we can solve the left integral. After insertion of the integration boundaries and application of Eq. (A.6) we obtain:

$$\ln \frac{(k_1 + k_2)\,\xi(t) + k_2 n_\mathrm{B}^0 - k_1 n_\mathrm{A}^0}{k_2 n_\mathrm{B}^0 - k_1 n_\mathrm{A}^0} = -(k_1 + k_2)\,t \tag{6.39}$$

If this equation is solved for the extent of reaction $\xi(t)$,

$$\xi(t) = \frac{k_1 n_\mathrm{A}^0 - k_2 n_\mathrm{B}^0}{k_1 + k_2}\left(1 - e^{-(k_1+k_2)t}\right) \tag{6.40}$$

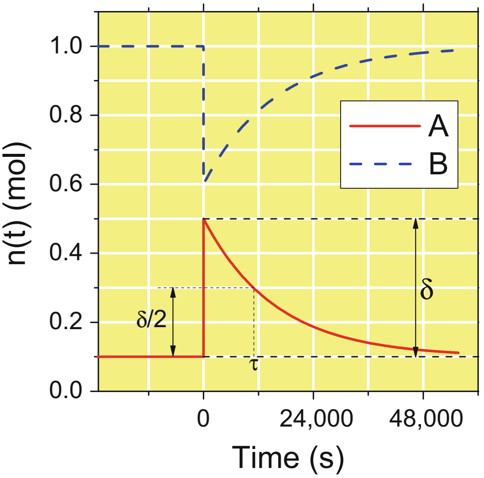

Fig. 6.4 Determination of the rate constants k_1 and k_2 for the forward and reverse reactions from the relaxation dynamics back to chemical equilibrium. The excess amount of conformer A due to perturbation is δ; the characteristic relaxation time is τ

is obtained, which was demonstrated. Together with Eqs. (6.34) and (6.35), this equation is the basis for calculating the amounts of both species A and B at an arbitrary time starting from $t = 0$, and the respective initial values n_A^0 and n_B^0.

It is worth inspecting this expression in more detail. It is striking that chemical equilibrium is established with an *effective rate constant* $k_1 + k_2$. In those cases, however, where equilibrium largely favors either A or B, one of the two rate constants can be ignored. Moreover, we briefly consider the special case where n_A^0 and n_B^0 are already the equilibrium amounts of A and B respectively. Because of $n_B^0 = Kn_A^0$ and $k_2 = \frac{k_1}{K}$, the prefactor in Eq. (6.28) is zero in this case and therefore $\xi = 0$.

In **subproblem (c)**, we consider a simple example that demonstrates how the observation of chemical relaxation is used to determine rate constants of the forward and backward reactions. Figure 6.3 is reproduced in Fig. 6.4 with additional annotations. As can be deduced from the constant levels at $t < 0$, the two conformers A and B are in chemical equilibrium with $n_A^{eq} = 0.1\,\text{mol}$ and $n_B^{eq} = 1.0\,\text{mol}$. Hence, the equilibrium constant at this temperature is:

$$K = \frac{n_B^{eq}}{n_A^{eq}} = 10$$

Because of the heat pulse at $t = 0$, the system is temporarily perturbed, causing a momentary increase in the amount of conformer A to $n_A^{eq} + \delta$, i.e., to 0.5 mol. After the heat pulse, the system reaches its original temperature, and n_A and n_B change toward their initial values, n_A^{eq}, and n_B^{eq} respectively. We expect this relaxation to be described by Eqs. (6.34), (6.35), and (6.28). Therefore, for $t > 0$ the amount of conformer A is given by:

$$n_A(t) = \left(n_A^{eq} + \delta\right) - \delta\left(1 - e^{-(k_1+k_2)t}\right) = n_A^{eq} + \delta e^{-\frac{t}{\tau}}$$

where τ is the relaxation time defined as the time after which half of the excess amount δ is decayed. From the figure, we estimate a relaxation time of 11,000 s. This is consistent with an effective rate constant

$$k_1 + k_2 = \frac{\ln 2}{\tau} = \frac{\ln 2}{11{,}000\,\mathrm{s}} = 6.3 \times 10^{-5}\,\mathrm{s}^{-1}$$

Using Eq. (6.33), we can substitute k_2 and obtain $k_1 = 5.7 \times 10^{-5}\,\mathrm{s}^{-1}$ for the forward reaction. The rate constant of the backward reaction is thus:

$$k_2 = \frac{k_1}{K} = 5.7 \times 10^{-6}\,\mathrm{s}^{-1}.$$

Problem 6.5 (Competing Reactions) Consider the following scheme of elementary chemical reactions:

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \tag{6.41}$$

$$\mathrm{A} + \mathrm{A} \xrightarrow{k_2} \mathrm{C} \tag{6.42}$$

a. Set up the differential equation describing the decay of substance A.
b. If $[\mathrm{A}]_0$ is the initial concentration of A, show that the following relation holds:

$$\frac{1}{[\mathrm{A}](t)} = \left(\frac{2k_2}{k_1} + \frac{1}{[\mathrm{A}]_0}\right) e^{k_1 t} - \frac{2k_2}{k_1}. \tag{6.43}$$

c. Based on Eq. (6.43), derive a relation for the reaction half-life. Test your relation by considering the limits $k_1 \gg 2k_2[\mathrm{A}]_0$ and $2k_2[\mathrm{A}]_0 \gg k_1$ for which the half-life should take the forms of first-order and second-order reactions respectively.
d. Given $k_1 = 6 \times 10^{-4}\,\mathrm{s}^{-1}$, $k_2 = 10\,\mathrm{dm}^3\,\mathrm{mol}^{-1}\,\mathrm{s}^{-1}$, and $[\mathrm{A}]_0 = 1.2 \times 10^{-4}\,\mathrm{mol\,dm}^{-3}$, calculate the reaction half-life.

Solution 6.5 Sometimes, there are different possible reaction channels for a substance to decay. For example, the triphenylimidazolyl radical (TPI, see Fig. 6.5) can react with the solvent chloroform in a pseudo first-order reaction via hydrogen

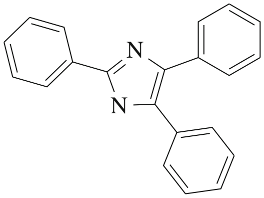

Fig. 6.5 The triphenylimidazolyl (TPI) radical

capture [1]

$$\mathrm{TPI} + \mathrm{CHCl_3} \xrightarrow{k_1} \mathrm{TPIH} + \mathrm{CCl_3} \tag{6.44}$$

However, TPI can also undergo a dimerization in a second-order reaction:

$$\mathrm{TPI} + \mathrm{TPI} \xrightarrow{k_2} \mathrm{TPID} \tag{6.45}$$

We thus have the reaction scheme outlined in Eqs. (6.41) and (6.42). The objective is of course to find an analytic solution for the concentration of the reactants as a function of time. The first step is to set up the rate equations, which we do in **subproblem (a)**. If we add up the reaction rates for the first-order decay according to Eq. (6.41) on the one hand, and the second-order reaction (6.42) on the other hand, we obtain

$$\frac{d\,[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] - 2k_2[\mathrm{A}]^2. \tag{6.46}$$

The rate equation has a nonlinear term. At first sight, an analytic solution seems to be tedious. In **subproblem (b)**, we simply prove that such an expression exists. Equation (6.43) contains the *reciprocal* concentration. Intuitively, it may thus be a good starting point to check whether the introduction of the reciprocal concentration might simplify the problem:

$$\frac{d\frac{1}{[\mathrm{A}]}}{dt} \overset{\text{Eq. (A.17)}}{=} -\frac{1}{[\mathrm{A}]^2}\frac{d\,[\mathrm{A}]}{dt} \overset{\text{Eq. (6.46)}}{=} k_1\frac{1}{[\mathrm{A}]} + 2k_2$$

Indeed, it does! The problem is reduced to a first-order linear heterogeneous differential equation, for which an analytic solution exists. If we define $f = \frac{1}{[\mathrm{A}]}$, we obtain

$$\frac{df(t)}{dt} - k_1 f(t) = 2k_2. \tag{6.47}$$

In mathematical terms, our problem is a special case of the *Bernoulli differential equation* (see Sect. A.3.20). For $t = 0, f(t) = \frac{1}{[\mathrm{A}]_0}$. Expressions for the solution of this differential equation are given in the appendix Sect. A.3.18. If we introduce the *integrating factor*

$$M(\tau) = e^{-\int k_1\, d\tau} = e^{-k_1 \tau}$$

the solution of Eq. (6.47) is:

$$f(t) = e^{k_1 t}\left[-\frac{2k_2}{k_1}e^{-k_1\tau}\Big|_0^t + C\right] = -\frac{2k_2}{k_1} + e^{k_1 t}\frac{2k_2}{k_1} + Ce^{k_1 t}$$

where C is an integration constant that is determined by the initial condition, $[\mathrm{A}](t = 0) = [\mathrm{A}]_0$. As a consequence, $C = \frac{1}{[\mathrm{A}]_0}$, and therefore

$$f(t) = \left(\frac{2k_2}{k_1} + \frac{1}{[\mathrm{A}]_0}\right)e^{k_1 t} - \frac{2k_2}{k_1}. \tag{6.48}$$

This result is simply Eq. (6.43). If the rate constants and $[\mathrm{A}]_0$ had been given, we would be able to calculate the concentration.

In **subproblem (c)**, however, we deal with the reaction half-life $t_{\frac{1}{2}}$ resulting from Eq. (6.43). We proceed in the same way as in Problem 6.1. Following the definition for the half-life given there (Eq. (6.7)), we can write

$$[\mathrm{A}](t_{\frac{1}{2}}) \overset{!}{=} \frac{1}{2}[\mathrm{A}]_0.$$

Hence,

$$\left(\frac{2k_2}{k_1} + \frac{1}{[\mathrm{A}]_0}\right)e^{k_1 t_{\frac{1}{2}}} - \frac{2k_2}{k_1} = \frac{2}{[\mathrm{A}]_0}$$

$$\frac{\frac{2}{[\mathrm{A}]_0} + \frac{2k_2}{k_1}}{\frac{2k_2}{k_1} + \frac{1}{[\mathrm{A}]_0}} = e^{k_1 t_{\frac{1}{2}}}$$

We solve for the half-life by taking the logarithm:

$$t_{\frac{1}{2}} = \frac{1}{k_1}\ln\frac{\frac{2}{[\mathrm{A}]_0} + \frac{2k_2}{k_1}}{\frac{2k_2}{k_1} + \frac{1}{[\mathrm{A}]_0}}$$

This can be written in a nicer way:

$$t_{\frac{1}{2}} = \frac{1}{k_1}\ln\left(1 + \frac{1}{1 + \frac{2k_2[\mathrm{A}]_0}{k_1}}\right) \tag{6.49}$$

We check whether this expression is correct by testing the limiting cases of $k_1 \gg 2k_2[\mathrm{A}]_0$ and $2k_2[\mathrm{A}]_0 \gg k_1$. In the first case, the fraction $\frac{2k_2[\mathrm{A}]_0}{k_1}$ becomes a very small number and thus:

$$t_{\frac{1}{2}} \approx \frac{1}{k_1} \ln\left(1 + \frac{1}{1+0}\right) = \frac{\ln 2}{k_1}.$$

This is simply the expression for the half-life of a first-order reaction. In the second case, $2k_2[\mathrm{A}]_0 \gg k_1$, the fraction $\frac{2k_2[\mathrm{A}]_0}{k_1}$ becomes a very large number, much greater than 1. Therefore, we can write:

$$t_{\frac{1}{2}} = \frac{1}{k_1} \ln\left(1 + \frac{1}{1 + \frac{2k_2[\mathrm{A}]_0}{k_1}}\right) \approx \frac{1}{k_1} \ln\left(1 + \frac{k_1}{2k_2[\mathrm{A}]_0}\right).$$

As $\frac{k_1}{2k_2[\mathrm{A}]_0}$ is a very small number in this case, we can use a power series expansion (see Eq. (A.56) in the appendix). If we ignore the higher terms, $\ln(1+x) \approx x + \cdots$, thus we obtain

$$t_{\frac{1}{2}} = \frac{1}{k_1} \ln\left(1 + \frac{k_1}{2k_2[\mathrm{A}]_0}\right) \approx \frac{1}{k_1} \frac{k_1}{2k_2[\mathrm{A}]_0} = \frac{1}{2k_2[\mathrm{A}]_0}.$$

This is simply the expression for a pure second-order reaction, as can be seen from Eq. (6.6) for $\alpha = 2$.

In **subproblem (d)**, finally, we calculate the reaction half-life in a concrete case. It is the example of the above-mentioned TPI radical. In Fig. 6.6 the concentration of TPI, based on Eq. (6.43) and the parameters k_1, k_2, and $[\mathrm{A}]_0$, is shown. The dashed lines indicate the moment when the concentration has decayed to 50% of its initial value $[\mathrm{A}]_0$. If we insert these parameters into Eq. (6.49), we obtain a reaction half-

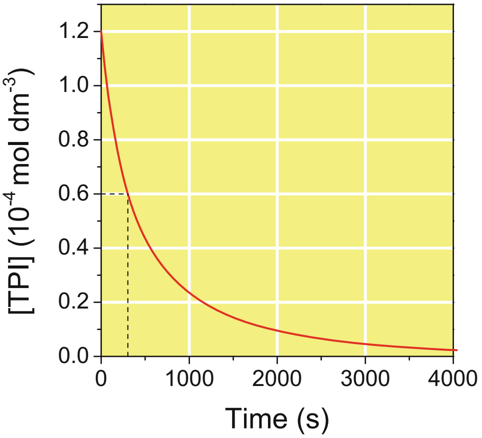

Fig. 6.6 Mixed first- and second-order decay of TPI radical according to Eq. (6.43)

life of $t_{\frac{1}{2}} = 304\,\text{s}$. For comparison, a first-order decay with $k_1 = 6 \times 10^{-4}\,\text{s}^{-1}$ would have a considerably longer reaction half-life of 1,155 s. In the initial stages of the reaction, when the reactant concentration is comparatively large, the second-order dimerization (Eq. (6.45)) is more effective, as the rate is proportional to $[\text{TPI}]^2$. Therefore, the reaction proceeds much faster in the initial stages than a first-order reaction. Then, as [TPI] becomes smaller, the pseudo first-order reaction (Eq. (6.44)) becomes more effective. As a consequence, the evolution of the TPI concentration resembles the prediction of neither first-order nor second-order kinetics. There are certainly situations in which experimental data can be fitted to first-order kinetics and second-order kinetics with only moderate agreement. In this case, the assumption of two different reaction channels, as discussed in this problem, might be reasonable. However, one should always take into account the fact that a model with three parameters generally always fits better than one with only two parameters.

Problem 6.6 (Oscillating Chemical Reactions I) Consider the following scheme of chemical reactions:

$$\text{A} + \text{B} \xrightarrow{k_1} 2\text{B} \tag{6.50}$$

$$\text{B} + \text{C} \xrightarrow{k_2} 2\text{C} \tag{6.51}$$

$$\text{C} \xrightarrow{k_3} \text{D} \tag{6.52}$$

The reactant A is either continuously supplied to the system, or is in excess; thus, a constant concentration $[\text{A}]_0$ can be assumed: $[\text{A}]_0 = 1\,\text{mol}\,\text{dm}^{-3}$, $k_1 = 2.8\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$, $k_2 = 142\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$, and $k_3 = 3.9 \times 10^{-3}\,\text{s}^{-1}$.

a. Reactions of the type Eqs. (6.50) and (6.51) are called *autocatalytic* reactions. Can you comment on this?
b. Write down the rate equations for the reactants B and C. Assuming a stationary state for the concentrations of reactants B and C, calculate the stationary concentrations $[\text{B}]_s$ and $[\text{C}]_s$ of the latter as a function of the rate constants and $[\text{A}]_0$.
c. Assume small variations of concentrations of B and C around the respective stationary state concentrations, i.e., $[\text{B}](t) = [\text{B}]_s + \beta(t)$ and $[\text{C}](t) = [\text{C}]_s + \gamma(t)$. Based on the rate equations from subproblem (b), show that the differential equations for β and γ are:

$$\frac{d\beta}{dt} = -k_3\gamma \tag{6.53}$$

$$\frac{d\gamma}{dt} = k_1\,[\text{A}]_0\,\beta \tag{6.54}$$

(continued)

Problem 6.6 (continued)

d. Show that $\beta(t) = \beta_0 \cos(\omega t)$ is a solution of this linearized problem with an amplitude β_0. Derive an expression for the oscillation frequency and calculate it. Furthermore, write down the associated expression for $\gamma(t)$ and discuss the phase shift between $\beta(t)$ and $\gamma(t)$.
e. At $t = 0$, the concentration of species B is $3.75 \times 10^{-5}\,\mathrm{mol\,dm^{-3}}$. Based on the preceding results, plot the intermediate concentrations [B] and [C] as a function of time. Also, plot [C] against [B]. What would happen if the concentration of one intermediate became zero?

Solution 6.6 Chemical reactions during which the concentration of some reactants oscillate with time are a fascinating phenomenon. Under special conditions, such a reaction, in principle, does not reach chemical equilibrium. Instead, the concentrations oscillate around their steady-state value. In this exercise, we investigate these oscillations in detail. The reaction mechanism defined by Eqs. (6.50)–(6.52) is the well-known *Lotka-Volterra* kinetic model.

In **subproblem (a)**, we comment on the term *autocatalytic* reaction used, e.g., for Eq. (6.50). A reaction is called autocatalytic if at least one reactant is also a product. This is the case for Eq. (6.50), where species B in a bimolecular reaction with reactant A is *reproduced*. As a consequence, the number of B molecules would increase continuously if species A were held constant. Moreover, Eq. (6.51) falls under the category autocatalytic reaction, in which species C is reproduced.

The formulation of the rate equations is our first task in **subproblem (b)**. We have to consider that the concentration of B increases with rate constant k_1 in reaction Eq. (6.50), and decreases with rate constant k_2 in reaction Eq. (6.51). Application of Eqs. (6.1) and (6.2) for the special case of a bimolecular reaction gives us:

$$\frac{d\,[\mathrm{B}]}{dt} = k_1\,[\mathrm{A}]_0\,[\mathrm{B}] - k_2\,[\mathrm{B}]\,[\mathrm{C}] \tag{6.55}$$

In a similar way, we obtain:

$$\frac{d\,[\mathrm{C}]}{dt} = k_2\,[\mathrm{B}]\,[\mathrm{C}] - k_3\,[\mathrm{C}] \tag{6.56}$$

where we consider the first-order decay of species C with rate constant k_3 and its production in reaction Eq. (6.51) with rate constant k_2. We note that the concentration of product D continuously increases if the system is fed with A. In that sense, a steady state, which we consider, is a *dynamic equilibrium* characterized by constant concentrations of the intermediates, $[\mathrm{B}]_s$ and $[\mathrm{C}]_s$ respectively. We find these steady-state concentrations assuming zero reaction rates for B and C in Eqs. (6.55) and (6.56). Thus,

$$0 = k_1\,[\mathrm{A}]_0\,[\mathrm{B}]_s - k_2\,[\mathrm{B}]_s[\mathrm{C}]_s$$

and

$$0 = k_2\,[\mathrm{B}]_s\,[\mathrm{C}]_s - k_3\,[\mathrm{C}]_s$$

Therefore, the nonzero steady-state concentrations of the intermediates are

$$[\mathrm{B}]_s = \frac{k_3}{k_2} \tag{6.57}$$

and

$$[\mathrm{C}]_s = \frac{k_1}{k_2}\,[\mathrm{A}]_0 \tag{6.58}$$

Inserting the given values for the rate constants and $[\mathrm{A}]_0$, we obtain $[\mathrm{B}]_s = 2.75 \times 10^{-5}\,\mathrm{mol\,dm^{-3}}$ and $[\mathrm{C}]_s = 0.02\,\mathrm{mol\,dm^{-3}}$ as the stationary concentrations of the reaction intermediates. It is worth mentioning that a second steady state exists: $[\mathrm{B}]_s = [\mathrm{C}]_s = 0$. As soon as $[\mathrm{B}](t)$ becomes zero, there is no further production of species C and the latter decays to zero according to Eq. (6.52).

We continue with **subproblem (c)**, where we seek to find nonstationary solutions for our system. Analytic solutions, however, are difficult, because the coupled equations contain nonlinear terms. Therefore, we restrict our analysis to small perturbations $\beta(t)$ and $\gamma(t)$ of the nonzero stationary state values. In this case, terms containing the product $\beta\,\gamma$ can be ignored and the differential equations become linearized. To derive these equations we insert $[\mathrm{B}](t) = [\mathrm{B}]_s + \beta$ and $[\mathrm{C}](t) = [\mathrm{C}]_s + \gamma$ in Eq. (6.55) and obtain:

$$\begin{aligned}\frac{d\beta}{dt} &= k_1\,[\mathrm{A}]_0\,([\mathrm{B}]_s + \beta) - k_2\,([\mathrm{B}]_s + \beta)\,([\mathrm{C}]_s + \gamma)\\ &\approx k_1\,[\mathrm{A}]_0\,[\mathrm{B}_s] - k_2[\mathrm{B}]_s[\mathrm{C}]_s + k_1[\mathrm{A}]_0\beta - k_2[\mathrm{C}]_s\beta - k_2[\mathrm{B}]_s\gamma\end{aligned}$$

Insertion of Eqs. (6.57) and (6.58) proves that all but the last term on the right-hand side cancel each other out. This proves Eq. (6.53). In a similar manner, we proceed with Eq. (6.53), where we obtain:

$$\begin{aligned}\frac{d\gamma}{dt} &= k_2\,([\mathrm{B}]_s + \beta)\,([\mathrm{C}]_s + \gamma) - k_3\,([\mathrm{C}]_s + \gamma)\\ &\approx k_2[\mathrm{B}]_s[\mathrm{C}]_s - k_3[\mathrm{C}]_s + k_2[\mathrm{B}]_s\gamma - k_3\gamma + k_2[\mathrm{C}]_s\beta\end{aligned}$$

Where, again, all but the last term cancel each other out, which proves Eq. (6.54).

In **subproblem (d)** we deal with nonzero solutions of Eqs. (6.53) and (6.54), which constitute a coupled linear system with constant coefficients. The rigorous mathematical treatment of such a system is sketched in the appendix or described in mathematics textbooks. Here, we take a more direct way and take the derivative of Eq. (6.53)

$$\frac{d^2\beta}{dt} = -k_3\frac{d\gamma}{dt} \overset{\text{Eq. (6.54)}}{=} -k_3k_1[\mathrm{A}]_0\beta$$

and obtain the harmonic oscillator equation

$$\frac{d^2\beta}{dt} + \omega^2\beta = 0 \tag{6.59}$$

with the angular frequency

$$\omega = \sqrt{k_3k_1[\mathrm{A}]_0} = 0.104\,\mathrm{s}^{-1} \tag{6.60}$$

Equation (6.59) has harmonic solutions of the form $\beta(t) = \beta_0\cos(\omega t)$, which is easily shown by insertion. Because the derivative of $\cos(\omega t)$ is $-\omega\sin(\omega t)$, we obtain the related harmonic expression for γ from Eq. (6.53):

$$\gamma(t) = \frac{\omega}{k_3}\beta_0\sin(\omega t) \tag{6.61}$$

Hence, the concentrations of the reaction intermediates oscillate harmonically around their nonzero steady-state values. One period takes $\frac{2\pi}{\omega} \approx 60\,\mathrm{s}$. There is a phase shift of 90° between the perturbations β and γ. The oscillations and the phase shift are consequences of the coupling between the concentrations of the two intermediates. According to Eq. (6.54) γ grows if the concentration of species B is above its steady-state value. However, as the concentration of species C exceeds its average value and thus γ reaches a positive level, β starts to decay again and the concentration of species B thus diminishes.

In **subproblem (e)**, we plot the oscillating concentrations of the reaction intermediates. At $t = 0$, $[\mathrm{B}] = 3.75 \times 10^{-5}\,\mathrm{mol\,dm^{-3}}$, i.e., the amplitude β_0 of the oscillation around the stationary state value $[\mathrm{B}]_s$ is $10^{-5}\,\mathrm{mol\,dm^{-3}}$. A plot of the intermediate concentrations can be found in the left-hand diagram of Fig. 6.7. In the right-hand diagram [C] is plotted against [B]. The shape of the closed trajectory is elliptic, and its center is the stationary point. Let us discuss what would happen if the amplitude β_0 became larger so that the trajectory would cross the line $[\mathrm{B}] = 0$. In this case, there would be no further production of species C according to the autocatalytic reaction Eq. (6.51) and [C], from that time on, would decay exponentially with the rate constant k_3. On the other hand, [C] would reach a value of zero, and [B] would grow from that time on.

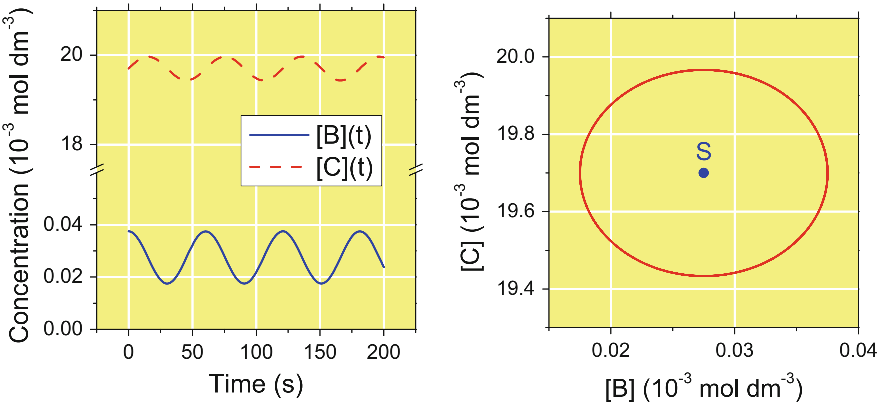

Fig. 6.7 Concentration of the reaction intermediates B and C oscillating around their stationary state values in harmonic approximation. Note the break and the different scaling of the ordinate axis. *Left*: Concentrations as a function of time. *Right*: Elliptic trajectory around the stationary state point *S*

Problem 6.7 (Oscillating Chemical Reactions II) *Hint: It is assumed that you have dealt before with Problem 6.6.* Consider the following scheme of chemical reactions:

$$\mathrm{A} + \mathrm{B} \xrightarrow{k_1} 2\mathrm{B} \quad (6.62)$$

$$\mathrm{B} + \mathrm{C} \xrightarrow{k_2} 2\mathrm{C} \quad (6.63)$$

$$\mathrm{C} \xrightarrow{k_3} \mathrm{D} \quad (6.64)$$

The reactant A is either continuously supplied to the system, or is in excess; thus, a constant concentration $[\mathrm{A}]_0$ can be assumed: $[\mathrm{A}]_0 = 1\,\mathrm{mol\,dm^{-3}}$, $k_1 = 2.8\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$, $k_2 = 142\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$, and $k_3 = 3.9 \times 10^{-3}\,\mathrm{s^{-1}}$.

a. The rate equations and the stationary state of the given reaction mechanism have been discussed already in Problem 6.6 (Eqs. (6.55)–(6.58)). Show that the dynamics of the system conserves the quantity

$$V = k_2\,([\mathrm{B}] + [\mathrm{C}]) - k_3 \ln[\mathrm{B}] - k_1 [\mathrm{A}]_0 \ln[\mathrm{C}] \quad (6.65)$$

b. Use numeric methods to solve the rate Eqs. (6.55) and (6.56). Assume $[\mathrm{B}](t = 0) = 3.75 \times 10^{-5}\,\mathrm{mol\,dm^{-3}}$ and for [C] the steady-state concentration. Plot the resulting concentrations of the reaction intermediates

(continued)

Problem 6.7 (continued)

[B] and [C] as a function of time. Also, make a plot [C] against [B] and compare these results with the curves obtained in Problem 6.6d. Determine the quantity $V(t)$ defined in subproblem (a) to test the numerical stability of your calculation.

c. Repeat your calculation for $[\mathrm{B}](t=0) = 4 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}$ and interpret the variation of the intermediate concentrations with time.

Solution 6.7 This problem assumes that you have already dealt with the Problem 6.6, where the reaction mechanism of the *Lotka-Volterra* reaction has been treated in a linearized approximation. This is valid if the variations of the concentrations of the reaction intermediates from the corresponding steady-state values are small. Now, we further investigate this model system of autocatalysis.

In **subproblem (a)**, we pick up the rate Eqs. (6.55) and (6.56) and consider the quantity V defined in Eq. (6.65). The task is to prove that V is conserved by the model, i.e., we must show that:

$$\frac{dV}{dt} = 0$$

Using Eqs. (6.65), (6.55)–(6.56), and the basic differentiation rule Eq. (A.23), we obtain

$$\begin{aligned}\frac{dV}{dt} &= k_2\frac{d\,[\mathrm{B}]}{dt} + k_2\frac{d\,[\mathrm{C}]}{dt} - \frac{k_3}{[\mathrm{B}]}\frac{d\,[\mathrm{B}]}{dt} - \frac{k_1\,[\mathrm{A}]_0}{[\mathrm{C}]}\frac{d\,[\mathrm{C}]}{dt}\\ &= k_2k_1\,[\mathrm{A}]_0[\mathrm{B}] - k_2^2[\mathrm{C}][\mathrm{B}] + k_2^2[\mathrm{C}][\mathrm{B}] - k_2k_3[\mathrm{C}] - k_3k_1[\mathrm{A}]_0 + k_3k_2[\mathrm{C}]\\ &\quad - k_1\,[\mathrm{A}]_0k_2[\mathrm{B}] + k_1[\mathrm{A}]_0k_3\\ &= 0\end{aligned}$$

All terms on the right-hand side cancel each other out. Thus, V is constant over time.

In **subproblem (b)**, we seek numerical solutions for the rate equations

$$\frac{d\,[\mathrm{B}]}{dt} = k_1\,[\mathrm{A}]_0\,[\mathrm{B}] - k_2\,[\mathrm{B}]\,[\mathrm{C}] \tag{6.66}$$

$$\frac{d\,[\mathrm{C}]}{dt} = k_2\,[\mathrm{B}]\,[\mathrm{C}] - k_3\,[\mathrm{C}], \tag{6.67}$$

starting with the same initial concentrations as in Problem 6.6d. This gives us the possibility of checking the validity of the harmonic approximation assumed in that exercise. In mathematical terms, this is an *initial value problem*. Nowadays, there are a number of mathematical software packages available to students that tackle

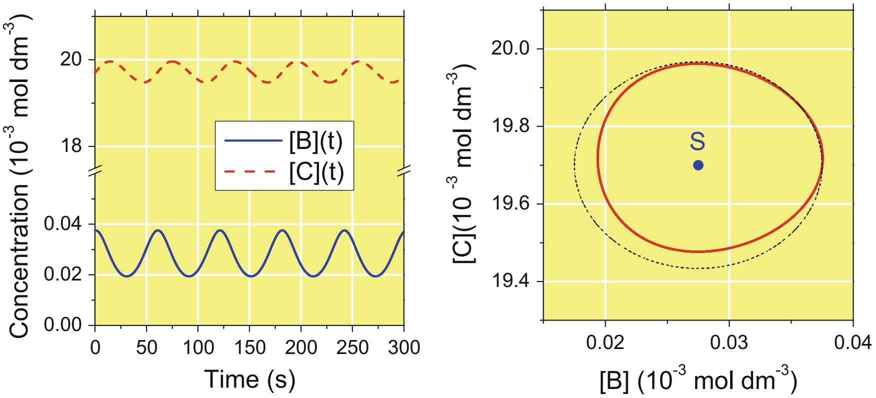

Fig. 6.8 Concentration of the reaction intermediates B and C oscillating around their stationary state values. Note the break and the different scaling of the ordinate axis. *Left*: Concentrations as a function of time. *Right*: Egg-shaped trajectory around the stationary state point *S*. The *dashed line* indicates the approximative trajectory from Problem 6.6d

the numerical solution of initial value problems. A minimum amount of coding is necessary to obtain numerical solutions. Other students who are eager to gain a deeper insight in the technical details of numerics use a programming language and code the problem on their own. Following the latter case, we have to choose a suitable numerical scheme and an adequate step length $h = t_{n+1} - t_n$ $(n = 1, 2, \dots)$ to calculate the concentrations $[\mathrm{B}](t_{n+1})$ and $[\mathrm{C}](t_{n+1})$ from $[\mathrm{B}](t_n)$ and $[\mathrm{C}](t_n)$, starting from the initial concentrations, $[\mathrm{B}](t_0 = 0)$ and $[\mathrm{C}](t_0 = 0)$. Some popular methods with different accuracies can be found in the appendix (Sect. A.3.21). The fourth order Runge-Kutta method, with a time interval $h = 10^{-3}$ s, yields the results shown in Fig. 6.8.

The oscillations of the intermediate concentrations around their stationary state values shown in the diagram on the left appear to be quite similar to those in Fig. 6.7. In the diagram on the right of Fig. 6.8, the nature of the resulting egg-shaped trajectory is directly compared with the elliptic trajectory predicted by the harmonic approximation (dashed line), which we have taken from the diagram on the right of Fig. 6.7. A closer inspection of the maxima and minima gives a time-period of 60.4 s for the oscillations, which is quite close to the harmonic value of 60 s obtained in Problem 6.6. Looking at the right-hand diagram, we notice that the numerical solution yields slightly smaller deviations from the stationary state point S, and the trajectory is egg-shaped, indicating a certain degree of anharmonicity. To check the integrity of our trajectory, we calculate the quantity V according to Eq. (6.65). Within a simulation time of 300 s, the numerically determined value of V is constantly 13.838545. From this, we deduce that the simulation provides meaningful results and we are able to investigate solutions to the problem for other initial conditions, which are beyond the limits of validity of harmonic approximation.

In **subproblem (c)**, we repeat the simulation with a much larger initial concentration $[\mathrm{B}](t = 0) = 4 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}$, whereas $[\mathrm{C}](t)$ starts again with

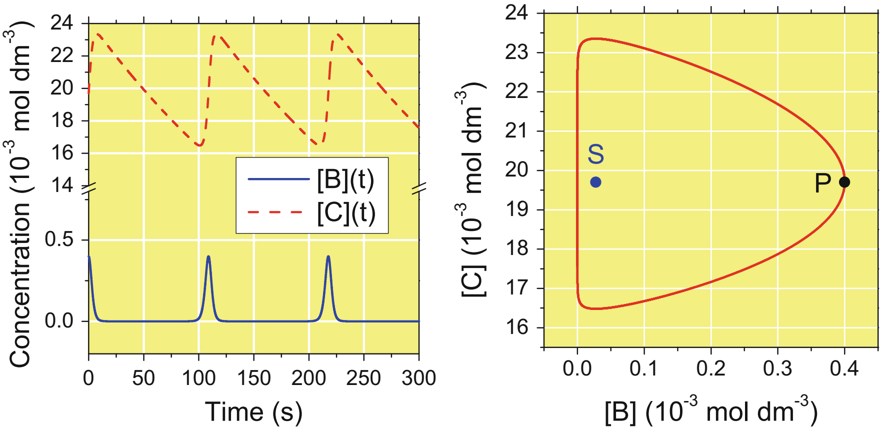

Fig. 6.9 Concentration of the reaction intermediates B and C oscillating around their stationary state values. Note the break and the different scaling of the ordinate axis. *Left*: Concentrations as a function of time. *Right*: Trajectory around the stationary state point *S*. Point *P* indicates the starting point of the simulation

its stationary state value. The results are shown in Fig. 6.9. The concentrations still show oscillatory behavior, but the curves are now largely anharmonic: [C](t) has the shape of a saw tooth, whereas [B](t) can be characterized by short pulses repeated periodically within about 110 s. The anharmonic behavior is apparent in the right diagram showing the trajectory. The point *P* marks the starting point of the trajectory, which is run anti-clockwise. Due to the high initial value of intermediate B, there is rapid production of C according to reaction Eq. (6.63), and also a rapid decay of B. The lack of B drastically reduces the production of C, which then decays exponentially with the rate constant k_3. This decay of C is continued until its concentration goes below the stationary state concentration. Intermediate B is then rapidly recovered according to Eq. (6.63) and again reaches the starting point *P*.

Looking back on our solution, we have used numerical methods to solve the rate equations for a reaction mechanism featuring oscillatory behavior. It is worth mentioning that in Chap. 10 we deal with the LASER[5] in Problems 10.10 and 10.11 in a similar manner. As it turns out, the mathematical description of a *lasing* system, consisting of an electromagnetic field within a resonator and an active medium in a dynamic equilibrium, is similar to the description of the kinetic model of the Lotka-Volterra type.

Reference

1. Lavabre D, Pemienta V, Levy G, Micheau JC (1993) J Phys Chem 97:5321

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[5] LASER is the abbreviation for light amplification by stimulated emission of radiation.