Fundamentals of chemical kinetics

ENV-200

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Learning objectives

You should be able to

1. explain the difference between rates and rate constants.
2. determine if a reaction follows zero-, (pseudo-)first-, or second-order kinetics and apply kinetic models to derive rate constants.
3. calculate half-lives for reactions of different order.
4. use kinetic models to predict contaminant concentrations in different systems.

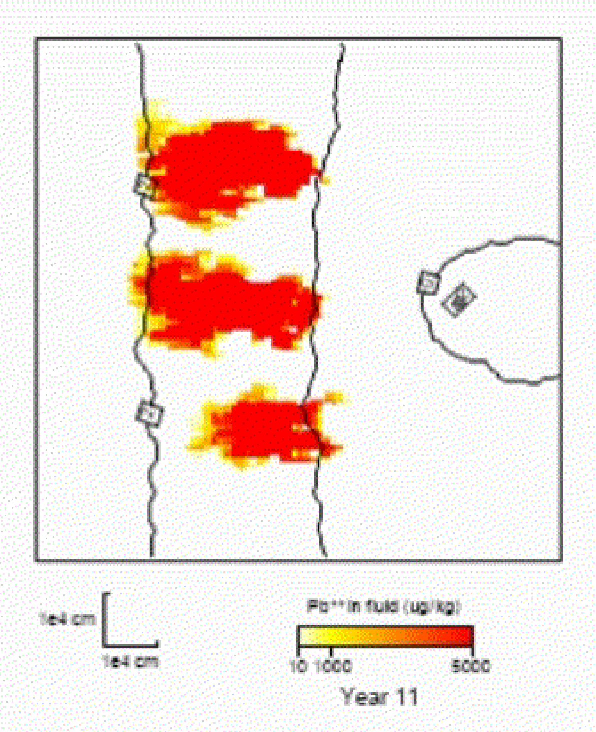
Resources

- Water Chemistry, by Brezonik and Arnold (Oxford University Press), Chapter 5: Fundamentals of chemical kinetics

Environmental engineering applications

A basic understanding of the kinetics and mechanisms of important reactions and processes (e.g., sorption/desorption, precipitation/dissolution, and redox) in natural systems such as soils and sediments is necessary to accurately determine the speciation, mobility, and bioavailability of contaminants in the environment. This is relevant, e.g., for

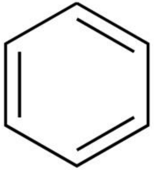
- Pollution control
- Groundwater transport
- Remediation processes



Environmental engineering challenge

An unknown quantity of benzene has entered a well-mixed reservoir that is used as a drinking storage. As an environmental engineer, you are asked to evaluate the water quality, and decide if the water is still fine for human consumption.

Benzene



Thermodynamics vs. kinetics

For natural systems in which the time scales of chemical reactions and phase transfers are fast relative to the time scales of mass and heat transport, we may approximate the system as being at chemical equilibrium.

In cases where the processes of interest are significantly far from chemical equilibrium, chemical kinetics may have to be considered. Kinetics describe the rate at which chemical reactions occur, thereby bringing a system at non-equilibrium state towards an equilibrium state.

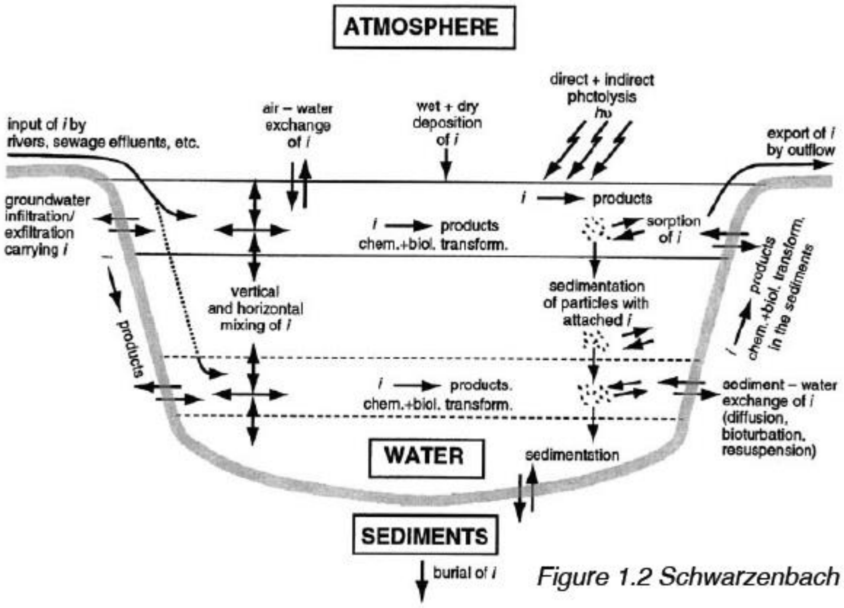


Figure 1.2 Schwarzenbach et al. 2003

Thermodynamics vs. kinetics

- Where do we need to consider kinetics?
  - Acid-base reactions: Acid-base reactions are rapid and usually reach equilibrium in times of sub-seconds to a few seconds. Consequently, we generally do not need to worry about their kinetics.
  - Complexation reactions: kinetics are important
  - Dissolution/precipitation reactions: kinetics are important
  - Redox reactions: kinetics are important and can be significantly affected by microorganisms

Terminology

- Link between thermodynamics and kinetics: The ratio of the forward and reverse reaction rate constants (k_f and k_r) is given by the thermodynamic equilibrium constant K

$$A \underset{k_r}{\overset{k_f}{\rightleftharpoons}} B \qquad K_{eq} = \frac{k_f}{k_r}$$

- **Reversible reactions**: Reactions for which the forward and reverse rates are both significant. The system is not far from equilibrium.

$$A \underset{k_r}{\overset{k_f}{\rightleftharpoons}} B$$

- **Irreversible reactions**: Reactions for which the reverse rate is negligible on a relevant time scale. The system is far from equilibrium.

$$A \xrightarrow{k_f} B$$

Terminology

Transformation: Chemical, biological and physical processes that cause the molecular structure to change (e.g., CO_2 going to H_2CO_3)

Persistence: Potential of contaminants to resist transformation (POPs = persistent organic pollutants). Compounds are considered persistent if their half life is greater than 100 days.

Secondary or tertiary persistence: the parent compound degrades to a product that is persistent

The kinetics of transformation reactions tell us:

- Is the compound persistent?
- At what rate (how quickly) does a transformation reaction occur?
- How can the rate be influenced?
- What is the mechanism of the reaction?

Elementary reactions

Reaction mechanisms involving an individual reaction step are called elementary reactions.

Example: Decomposition of ozone (four sequential elementary reactions):

$O_3 + H_2O \rightarrow HO_3^+ + OH^-$

$HO_3^+ + OH^- \rightarrow 2\ HO_2$

$O_3 + HO_2 \rightarrow OH^{\cdot} + 2O_2$

$OH_{\cdot} + HO_2 \rightarrow H_2O + O_2$

Most overall reactions of interest are non-elementary, but proceed as a series of elementary reactions between molecules. The overall reaction is determined by summing the elementary reactions and canceling out the compounds that occur on both sides of the reaction:

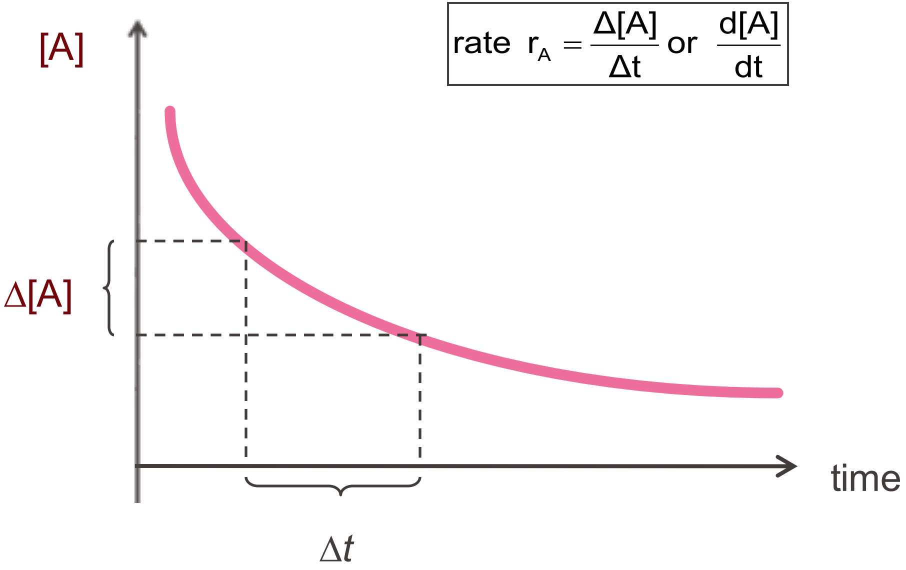
$2\ O_3 \rightarrow 3\ O_2$

From this overall reaction we cannot determine the reaction mechanisms or the intermediate products, and empirical expressions must be developed to determine the kinetics of the reaction.

Reaction rate r

The rate r of a non-elementary reaction indicates how the concentration of a substance changes over time (the change in concentration is determined empirically). The rate is negative if the concentration decreases over time, and positive if the concentration increases. **The rate has units of concentration/time or mass/time.**

$$\boxed{\text{rate } r_A = \frac{\Delta[A]}{\Delta t} \text{ or } \frac{d[A]}{dt}}$$



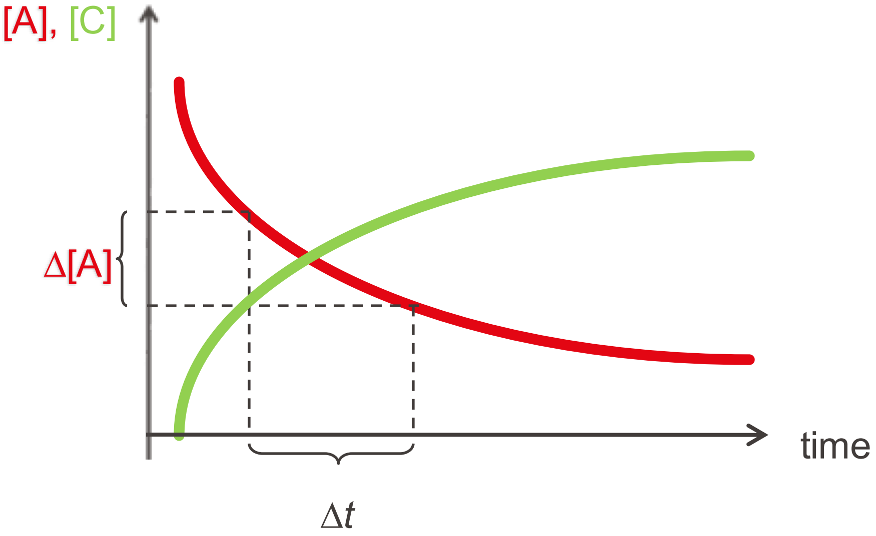
Factors affecting reaction rates:

- Concentration of the reactants (except for zero-order reactions)
- Temperature
- Presence of a catalyst

Reaction stoichiometry

The reaction stoichiometry indicates how the degradation/production rates of all substances are related. Consider the following reaction: $A \rightarrow C$

The rate of the disappearance of A is equal in magnitude but opposite in sign to the rate of the appearance of C



$$A \rightarrow C$$

$$r_A = \frac{d[A]}{dt} = -r_C = -\frac{d[C]}{dt}$$

Reaction rate constant k

The reaction rate is a function of the rate constant and the concentrations of the species involved in the transformation reaction. This function is expressed by the rate law, a differential equation, that describes the turnover rate of the compound of interest.

Consider the following reaction:

$A + B \rightarrow C + D$ → rate law: $r_A = \frac{d[A]}{dt} = -k[A]^x[B]^y$

(Note: C and D do not influence the degradation rate of A or B!)

x, y : orders of the reactants, i.e., the extent to which rate depends on concentration of A and B

x + y = overall reaction order n

k: the reaction rate constant. k does NOT depend on the concentration of the reactants.

The units of k depend on the reaction order n and are (concentration^{1-n} / time) or (mass^{1-n} / time)

First-order kinetics

Consider the reaction: $A \rightarrow \text{Products}$

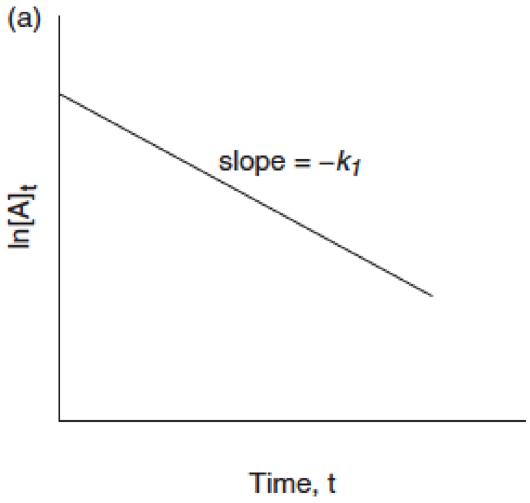
The rate is proportional to [A], the decay of [A] is exponential.

Rate law: $\frac{d[A]}{dt} = -k[A]$

Integrated rate law: $[A] = [A]_0 e^{-kt}$

[A] indicates the concentration of a compound A at time t

$[A]_0$ indicates the concentration of a compound A at time t=0

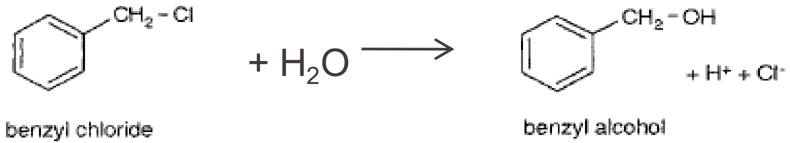


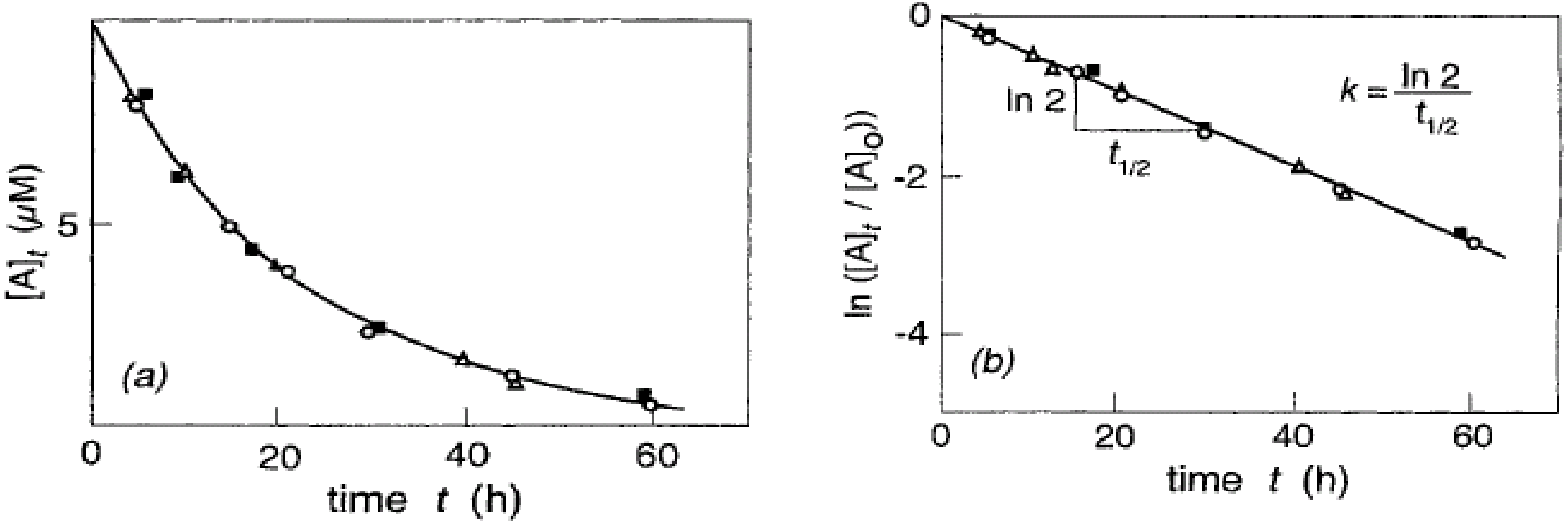
Graphical method to determine k:

- Transform the integrated rate law to $\ln[A]/[A]_0 = -kt$
- Plot $\ln[A]/[A]_0$ vs. t and determine k from the slope of the line (units of k: 1/time)

Graphical method to determine k

Example: Reaction of benzyl chloride in water to benzyl alcohol





Schwarzenbach, 2003

Exercise 1: Reaction of sucrose

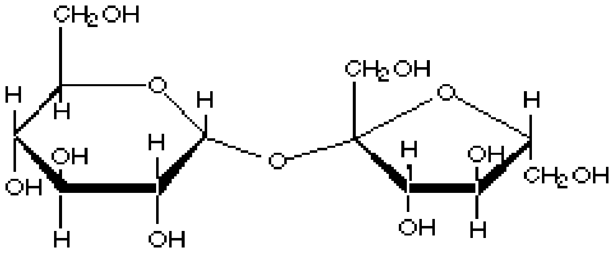
The rate equation for the reaction of sucrose in water is:

$$\text{rate} = -k[C_{12}H_{22}O_{11}].$$

After 2.57 h at 27°C, 5.00 g/L of sucrose has decreased to 4.50 g/L.

Find k.

$C_{12}H_{22}O_{11} + H_2O \Rightarrow 2\ C_6H_{12}O_6$



Sucrose

Second-order kinetics

Case I: The reaction involves the collision of two equal molecules

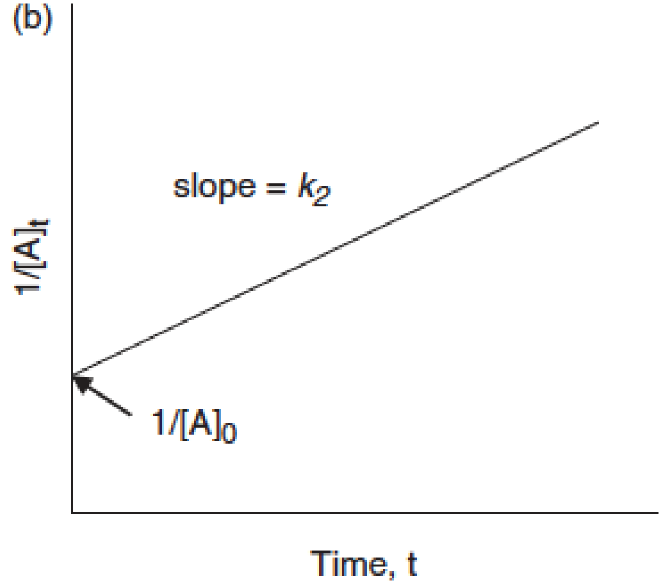
$$A + A \rightarrow \text{Products}$$

Rate law: $$\frac{d[A]}{dt} = -k[A]^2$$

Integrated rate law: $$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$$

Graphical method to determine k:

- plot $\frac{1}{[A]}$ vs. t; the slope of the line = k
- Units of k: 1/(concentration • time)



Exercise 2: Ammonium cyanate

Ammonium cyanate, NH_4NCO, rearranges in water to give urea, $(NH_2)_2CO$. If the original concentration of NH_4NCO is 0.458 mol/L and k = 0.0113 M^{-1} min^{-1}, how much time elapses before the concentration is reduced to 0.300 mol/L?

$NH_4NCO \rightarrow (NH_2)_2CO_{(aq)}$ rate = $-k[NH_4NCO]^2$

Second-order kinetics

Case II: The reaction involves the collision of two different molecules, and is proportional to both:

$$A + B \rightarrow \text{Products}$$

Rate law: $$\frac{d[A]}{dt} = -k[A][B]$$

Integrated rate law: $$\frac{[A]}{[B]} = \frac{[A]_0}{[B]_0} e^{([A]0-[B]0)kt}$$

Frequently, B>>A. Therefore, B remains almost constant during the reaction. We can rearrange the rate law:

$$\frac{d[A]}{dt} = -k'[A] \qquad \text{where } k' = k[B] \text{ (constant!)}$$

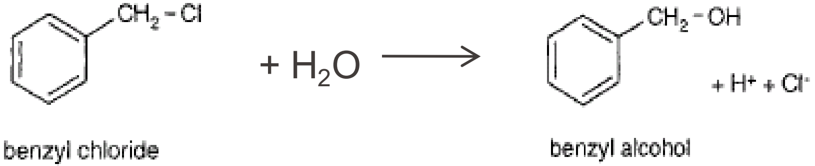
This is a ***pseudo-first-order reaction***. The same integrated rate law as for first-order reactions applies:

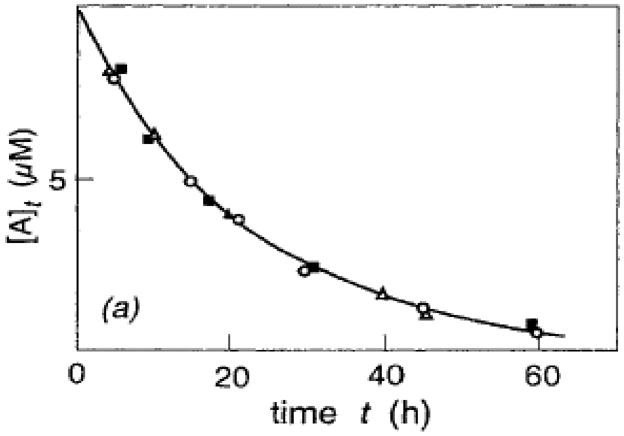
$$[A] = [A]_0 e^{-k't} \qquad \text{where } k' = k[B]$$

Pseudo-first-order reactions are very common in the degradation of contaminants.

Pseudo-first-order kinetics

Let’s revisit the previous example: Reaction of benzyl chloride with water to benzyl alcohol





In fact, reaction proceeds as A + B → Products

A = benzyl chloride, B = H_2O

$[H_2O]$= 55.4 M; [benzyl chloride] = 10^{-5} M

Therefore, B >> A

Reaction is pseudo-first-order!

$[A] = [A]_0 e^{-k't}$ with $k' = k[H_2O]$

Zeroth-order kinetics

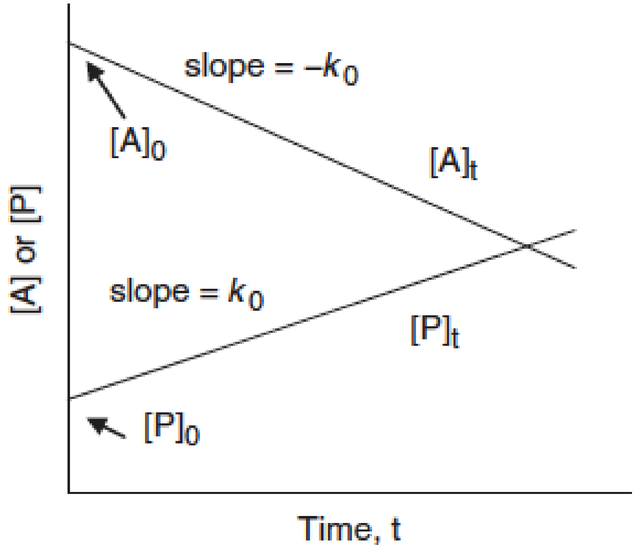
The reaction is independent of the concentrations of the reactants

Rate law: $\frac{d[A]}{dt} = -k$

Integrated rate law: $[A] = [A]_0 - kt$

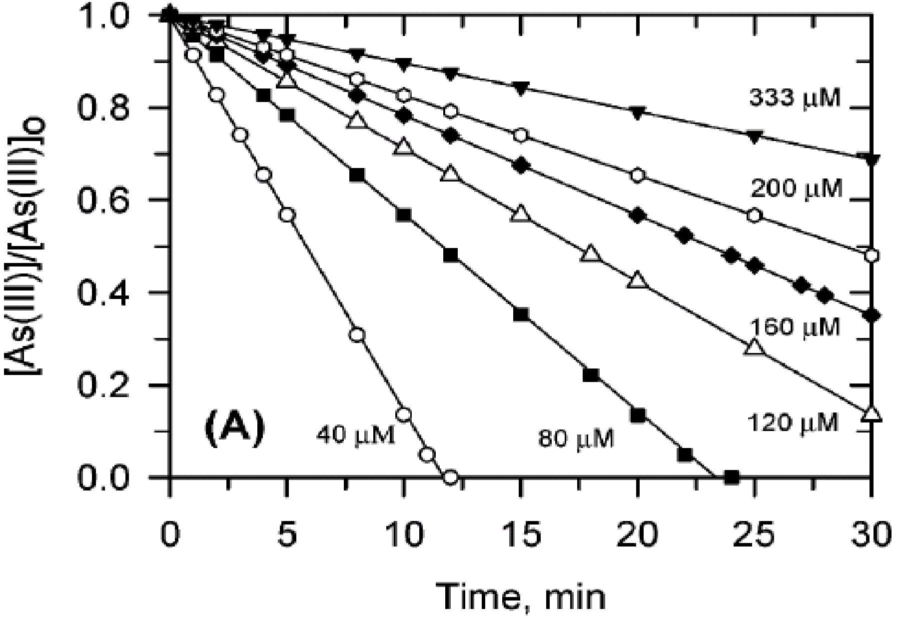
Graphical method to determine k:

- plot [A] vs. time; the slope of the line = k
- Units of k: concentration/time



Zeroth-order reactions

Example: Surface reaction limited by the number of available reaction sites (e.g., a catalyst), here: oxidation of As(III) by a TiO_2 catalyst



Dutta et al., Environ. Sci. Technol. 2005, 39, 1827-1834

Exercise 3: Reaction order

What is the reaction order in A and the overall reaction order of the following equations?

1. $-d[A]/dt = k[B]$
2. $-d[A]/dt = k[A]^2$
3. $-d[A]/dt = k[A]^{1.5}[B]$

Half lives

How long does it take for the concentration of a contaminant to decay to 50 % of its original valule? In other words: after how much time is $[A] = 0.5 * [A]_0$?

The necessary time is called the half life, $t_{½}$

(Pseudo-)first-order reaction:

$$[A] = [A]_0 e^{-kt} = 0.5 \cdot [A]_0 \quad \longrightarrow \quad e^{-kt} = 0.5 \quad \longrightarrow \quad t_{1/2} = \frac{\ln 2}{k}$$

Second-order reaction

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt = \frac{1}{0.5 \cdot [A]_0} \quad \longrightarrow \quad 1 + [A]_0 kt = 2 \quad \longrightarrow \quad t_{1/2} = \frac{1}{[A]_0 k}$$

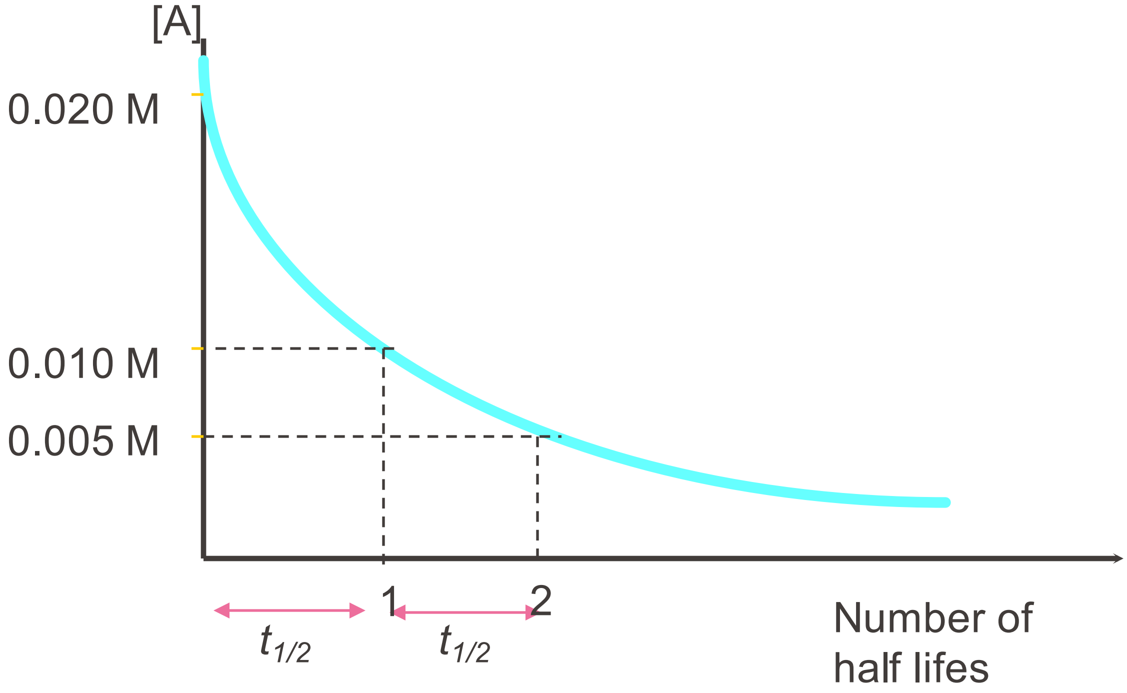
Zero-order reaction:

$$[A] = [A]_0 - kt = 0.5 \cdot [A]_0 \quad \longrightarrow \quad kt = 0.5 \cdot [A]_0 \quad \longrightarrow \quad t_{1/2} = \frac{[A]_0}{2k}$$

Half lives are useful to evaluate the persistance of a contaminant. They are a function of the contaminant and of the type of transformation reaction, as well as the environmental factors.

Half lives of a first order reaction

First order reactions are the only ones where the half-life is independent of concentration



Half lives of contaminants

Contaminant	$t_{1/2}$ in soil	$t_{1/2}$ in groundwater
Anthracene	50 d – 1.4 y	100 d – 2.5 y
Benzene	5 – 16 d	10 d – 2 y
Naphtalene	16 – 48 d	258 d
Phenol	1 – 10 d	5 – 7 d
Pyrene	210 d – 5.1 y	1.1 – 10.4 y
Toluene	0.1 – 1 d	0.5 – 1 y
Xylene	7 – 28 d	14 d – 1 y

Exercise 4: Half-life of SO_2Cl_2

The decomposition of SO_2Cl_2 is first order in SO_2Cl_2 and has a half-life of 4.1 h. If you begin with 1.6×10^{-3} mol of SO_2Cl_2 in a flask, how many hours elapse before the quantity of SO_2Cl_2 has decreased to 2.00×10^{-4} mol?

$$SO_2Cl_{2(g)} \rightleftharpoons SO_{2(g)} \quad + \quad Cl_{2(g)}$$

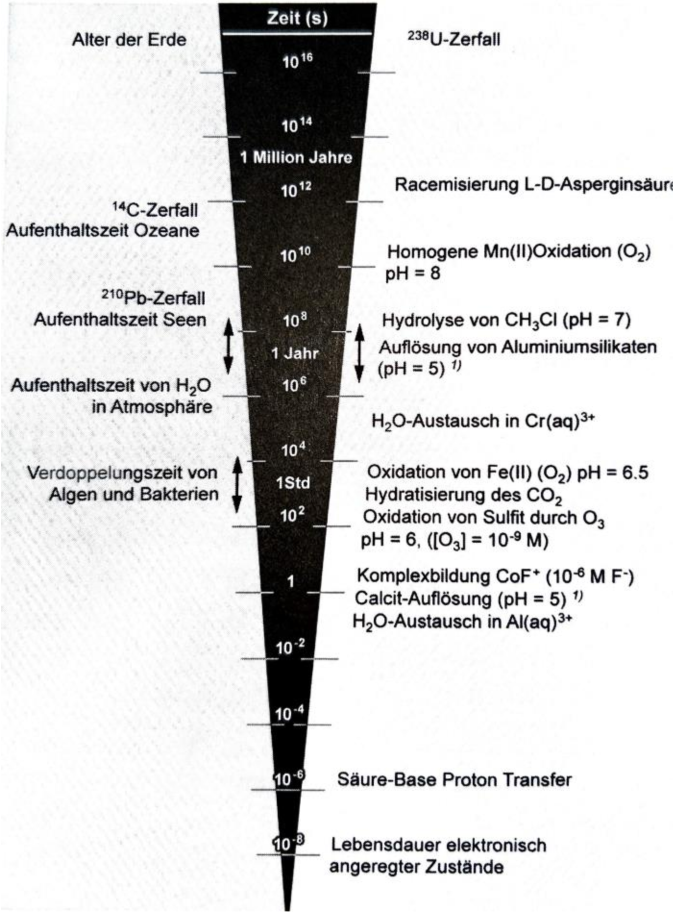
Characteristic reaction times

The characteristic reaction time is often used to indicate the time scale of a specific process.

$$\tau = \frac{1}{k_{\text{1st order}}}$$

Chemical reactions span a large range of relevant time scales, ranging from $\tau \sim$ ps to $\tau \sim 10^9$ years.

The shortest possible time scale is determined by the speed of molecular diffusion: at the ambient p, T conditions of the troposphere, the maximal $k_{\text{2nd order}} = 10^{11}$ $M^{-1}s^{-1}$



Summary of reaction kinetics (irreversible reactions)

	Zero order	First order	Second order
Rate law	$\frac{dC}{dt} = -k$	$\frac{dC}{dt} = -kC$	$\frac{dC}{dt} = -kC^2$
Integrated rate law	$C = C_0 - kt$	$C = C_0 e^{-kt}$	$\frac{1}{C} = \frac{1}{C_0} + kt$
Units of k	$\frac{conc.}{time}$	$\frac{1}{time}$	$\frac{1}{conc.*time}$
Half life	$t_{1/2} = \frac{C_0}{2k}$	$t_{1/2} = \frac{\ln 2}{k}$	$t_{1/2} = \frac{1}{C_0 k}$
Linear plot to determine k	C vs. t	$\ln C$ vs. t	$\frac{1}{C}$ vs. t

More complex reaction mechanisms

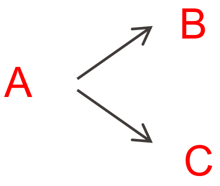
So far, we have considered rate laws for simple reaction mechanisms.

- Irreversible
- Single stage

$A \longrightarrow B$ or $A + B \longrightarrow C + D$

We will now consider some more complex cases:

- Reversible reactions $A \rightleftharpoons B$ or $A + B \rightleftharpoons C + D$
- Parallel (or concurrent/side) reactions



- Consecutive (or series) reactions $A \longrightarrow B \longrightarrow C$

Reversible reactions

If both reactants and products exist under equilibrium conditions, this indicates that the reaction is reversible:

$$A+B \underset{k_{reverse}}{\overset{k_{forward}}{\rightleftharpoons}} C+D$$

$$r_{forward} = \frac{d[A]}{dt} = \frac{d[B]}{dt} = -k_{forward}[A][B]$$

$$r_{reverse} = \frac{d[C]}{dt} = \frac{d[D]}{dt} = -k_{reverse}[C][D]$$

At equilibrium: $r_{forward} = r_{reverse}$

$$K_{eq} = \frac{[C][D]}{[A][B]} = \frac{k_{forward}}{k_{reverse}}$$

Kinetic expressions for reversible reactions are quite complicated. For a very simple reaction

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$$

where $C_T = A+B$

we can write: $-\frac{d[A]}{dt} = \frac{d[B]}{dt} = k_1[A] - k_2[B]$

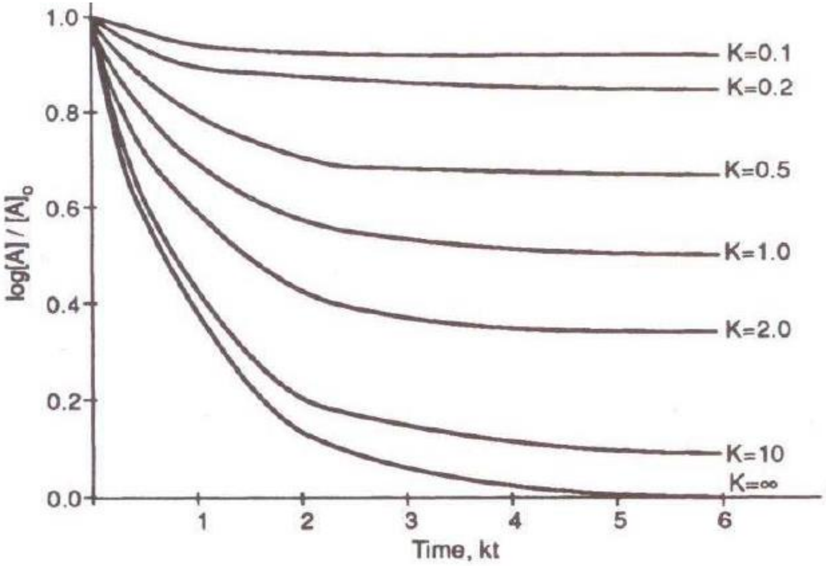
For the initial condition $[B]_0 = 0$, the solution is: $[B] = \frac{k_1[A]_0}{k_1+k_2}\left(1 - e^{-(k1+k2)t}\right)$

And at long times (t→∞), i.e., when equilibrium is reached: $[B]_{equilibrium} = \frac{k_1[A]_0}{k_1+k_2}$ $\quad [A]_{equilibrium} = C_T - \frac{k_1[A]_0}{k_1+k_2}$

Reversible reactions

Find a curve where $k_{forward} << k_{reverse}$

Find a curve where $k_{forward} >> k_{reverse}$

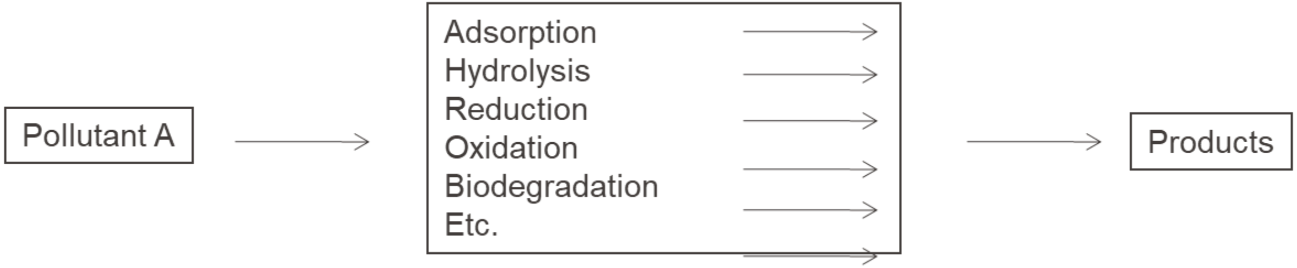


Effect of equilibrium constant K (= k_f/k_r) on shape of reactant disappearance curves for reversible first-order reactions. Dimensionless time in units of kt; k = $k_f + k_r$; k_f fixed at 10 t^{-1}; k_r varied to give K values shown by curves. Graph computed from Equation 2-43a reformulated to $[A]/[A]_o = 1/(1 + K) + \{K/(K + 1)\}\exp(-kt)$.

From: P.L. Brezonik, Chemical kinetics ina process dynamics in aquatic systems

Parallel reactions

A pollutant can undergo several simultaneous transformation reactions in the environment:



The total degradation rate r_{tot} corresponds to the sum of the individual rates r_i of each process.

Strongly simplified, we can write:

$$r_{tot} = \sum r_i = \frac{d[A]}{dt} = -\sum k_i [A]$$

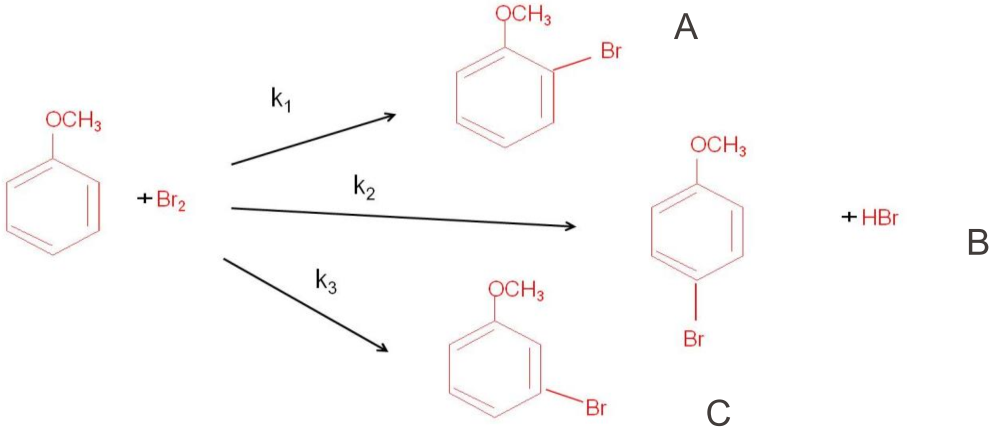
k_i is the reaction rate constant for transformation process i

[A] is the pollutant concentration

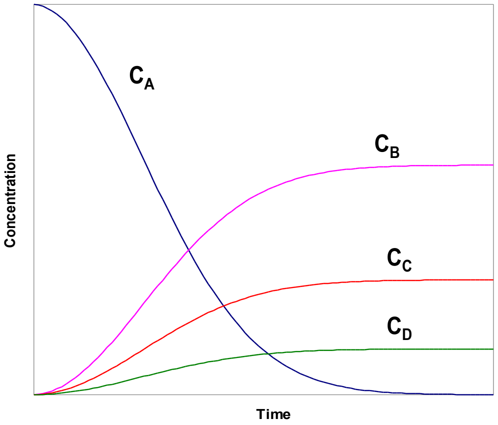
If the parallel reactions have different rate laws (i.e., not first- or pseudo-first order) then treatment is more complex! Usually, one or two processes dominate overall degradation.

Parallel reactions

Example:
bromination of anisole forms 3 products (A, B and C).
Assume $k_2 > k_3 > k_1$



The ratio of products of parallel reactions equals the ratio of the corresponding rate constants.

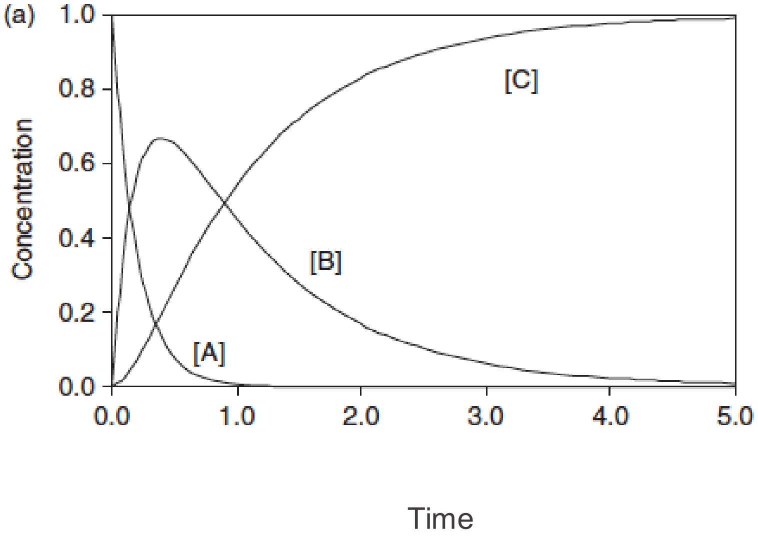


Consecutive reactions

Many reactions involve a sequence of steps with intermediate products that build up to measurable concentrations and then decline as they undergo further reaction.

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

The slowest reaction (= rate-determining step) determines the rate of the overall process. If $k_1 > k_2$, the conversion of B to C determines the rate of final product formation. If $k_1 < k_2$, the conversion of A to B determines the rate of final product formation. If $k_1 \approx k_2$, both rates have to be considered. In this case, one must consider the time-dependence of the intermediate products (B) and the final products (C).



Consecutive reactions

The differential rate laws are (assuming first-order reactions):

$$\frac{d[A]}{dt} = -k_1[A] \qquad \frac{d[B]}{dt} = k_1[A] - k_2[B] \qquad \frac{d[C]}{dt} = k_2[B]$$

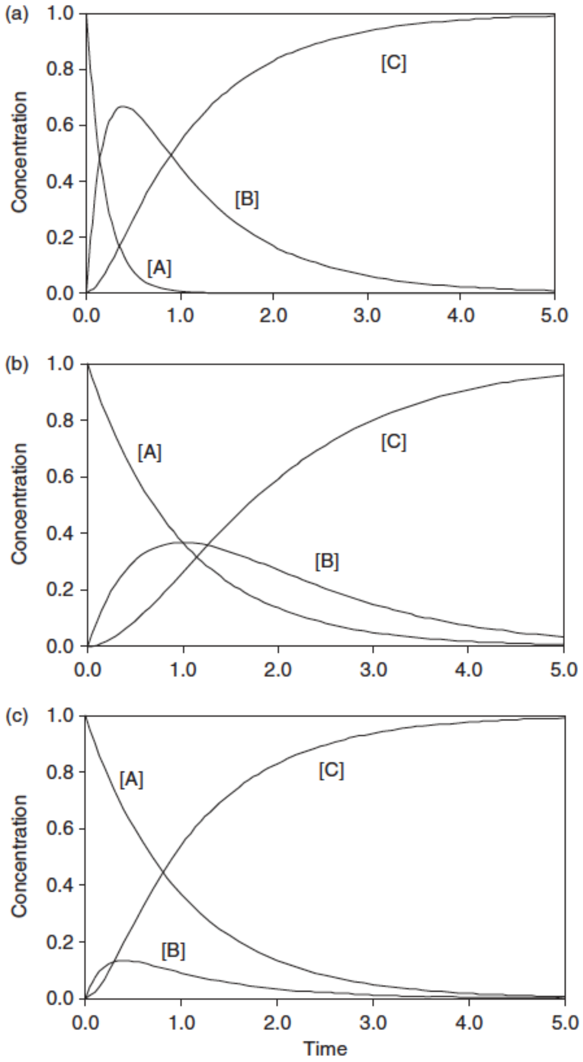
In the case where $[B]_0 = 0$ and $[C]_0 = 0$, the mass balance requires that at all times: $[A]+[B]+[C]=[A]_0$

Since both reactions are first-order, the solution is:

$$[A] = [A]_0 e^{-k1*t} \qquad [B] = [A]_0\left(\frac{k_1}{k_2 - k_1}\right)\left(e^{-k1*t} - e^{-k2*t}\right) \qquad [C] = [A]_0 - [A] - [B]$$

Consecutive reactions

- Where is $k_2 > k_1$?
- Where is $k_2 < k_1$?

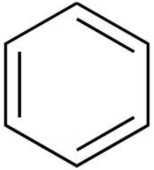


Water Chemistry, by Brezonik and Arnold (Oxford University Press).

Environmental engineering challenge

An unknown quantity of benzene has entered a well-mixed reservoir that is used as a drinking storage. As an environmental engineer, you are asked to evaluate the water quality and decide if the water is still ok for human consumption. It takes you 5 days until you can take the first water sample from the reservoir, and you measure a benzene concentration of 50 µM. Five days later, the concentration is 23.6 µM. Assume that the only transformation mechanism is biodegradation and that it follows first-order kinetics.

Benzene



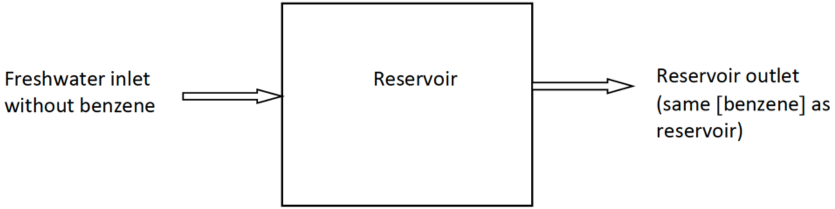
Environmental engineering challenge

a) What was the initial concentration of benzene in the reservoir?

b) What is the biodegradation rate after 5 days?

c) How long will it take until the water is potable again (benzene concentration < 0.1 µM)?

d) Based on exercise c), you decide that the time for the reservoir to reach drinking water quality is too long. Therefore, you suggest that the reservoir is flushed (i.e., a continuous input of fresh water and a continuous outlet of mixed pond water are installed, see picture), to dilute the benzene concentration in addition to biodegradation. The flushing can be considered a first-order reaction with a reaction rate constant of 0.2 day^{-1}. How long will it take now until the water is potable?



Freshwater inlet without benzene

Reservoir

Reservoir outlet (same [benzene] as reservoir)

Summary

- Chemical kinetics has to be considered under conditions where the processes of interest are significantly far from equilibrium.
- The reaction rate indicates how the concentration of a substance changes over time. The reaction rate constant is a constant that is independent of the concentrations of the reactants.
- The dependence of the reaction on the concentration of reactant(s) determines the reaction order.
- Reaction rate constants can be derived from experimental data using graphical methods. The method depends on the reaction order.