4. Physical, Chemical, and Biological Transformations

In the previous chapters, concentrations change in response to transport processes, such as diffusion, advection, and dispersion, and we have considered these processes in mass conserving systems. Now, we would like to look at systems where the mass of a given species of interest is not conserving. Processes that remove mass can be physical, chemical or biological in nature. Since the total mass of the system must be conserved, these processes generally change the species of interest into another species; thus, we will call these processes transformation.

This chapter begins by describing the common types of transformation reactions. Since we are interested in concentration changes, we review reaction kinetics and derive rate laws for first- and second-order systems. The methods are then generalized to higher-order reactions. Transformation is then added to our transport equation for two types of reactions. In the first case, the reaction becomes a source or sink term in the governing differential equation; in the second case, the reaction occurs at the boundary and becomes a boundary constraint on the governing transport equation. The chapter closes with an engineering application to bacteria die-off downstream of a wastewater treatment plant.

4.1 Concepts and definitions

Transformation is defined as production (or loss) of a given species of interest through physical, chemical, or biological processes. When no transformation occurs, the system is said to be conservative, and we represent this characteristic mathematically with the conservation of mass equation

$$\frac{dM_i}{dt} = 0 \tag{4.1}$$

where M_i is the total mass of species i. When transformation does occur, the system is called reactive, and, for a given species of interest, the system is no longer conservative. We represent this characteristic mathematically as

$$\frac{dM_i}{dt} = S_i \tag{4.2}$$

where S_i is a source or sink term. For reactive systems, we must supply these reaction equations that describe the production or loss of the species of interest. Since the total system mass must be conserved, these reactions are often represented by a system of transformation equations.

Transformation reactions are broadly categorized as either homogeneous or heterogeneous. Homogeneous reactions occur everywhere within the fluid of interest. This means that they are distributed throughout the control volume; hence, they are represented as a source or sink term in the governing differential equation. By contrast, heterogeneous reactions occur only at fluid boundaries. They are not distributed throughout the control volume; hence, they are specified by source or sink boundary conditions constraining the governing differential equation.

Some reactions have properties of both homogeneous and heterogeneous reactions. As an example, consider a reaction that occurs on the surface of suspended sediment particles. Because the reaction occurs only at the sediment/water interface, the reaction is heterogeneous. But, because the sediment is suspended throughout the water column, the effect of the reaction is homogeneous in nature. Models that represent the reaction through boundary conditions (i.e. they treat the reaction as heterogeneous) are sometimes called two-phase, or multi-phase, models. Models that simplify the reaction to treat it as a homogeneous reaction are called single-phase, or mixture, models. To obtain analytical solutions, we often must use the single-phase approach.

4.1.1 Physical transformation

Physical transformations result from processes governed by the laws of physics. The classical example, which comes from the field of nuclear physics, is radioactive decay. Radioactive decay is the process by which an atomic nucleus emits particles or electromagnetic radiation to become either a different isotope of the same element or an atom of a different element. The three radioactive decay paths are alpha decay (the emission of a helium nucleus), beta decay (the emission of an electron or positron), and gamma decay (the emission of a photon). Gamma decay alone does not result in transformation, but it is generally accompanied by beta emission, which does.

A common radioactive element encountered in civil engineering is radon, a species in the uranium decay chain. Radon decays to polonium by alpha decay according to the equation

$$^{222}\text{Rn} \rightarrow {}^{218}\text{Po} + \alpha \tag{4.3}$$

where α represents the ejected helium nucleus, ${}^{4}_{2}\text{He}$. As we will see in the section on kinetics, this single-step reaction is first order, and the concentration of radon decreases exponentially with time. The time it takes for half the initial mass of radon to be transformed is called the half-life.

Another common example that we will treat as a physical transformation is the settling of suspended sediment particles. Although settling does not actually transform the sediment into something else, it does remove sediment from our control volume by depositing it on the river bed. This process can be expressed mathematically by heterogeneous transformation equations at the river bed; hence, we will discuss it as a transformation.

4.1.2 Chemical transformation

Chemical transformation refers to the broad range of physical and organic chemical reactions that do not involve transformations at the atomic level. Thus, the periodic table of the elements contains all the building blocks of chemical transformations.

A classic example from aqueous phase chemistry is the dissolution of carbon dioxide (CO_2) in water (H_2O), given by the equilibrium equation

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+ \tag{4.4}$$

where HCO_3^- is called bicarbonate and H^+ is the hydrogen ion. The terms on the left-hand-side of the equation are called the reactants; the terms on the right-hand-side of the equation are called the products. Equilibrium refers to the state in which the formation of products occurs at the same rate as the reverse process that re-forms the reactants from the products. This give-and-take balance between reactants and products is indicated by the $\rightleftharpoons$ symbol.

4.1.3 Biological transformation

Biological transformation refers to that sub-set of chemical reactions mediated by living organisms through the processes of photosynthesis and respiration. These reactions involve the consumption of a nutritive substance to produce biomass, and are accompanied by an input or output of energy.

The classical photosynthesis equation shows the production of glucose, $C_6H_{12}O_6$, from CO_2 through the input of solar radiation, h_ν:

$$6CO_2 + 6H_2O \underset{h_\nu}{\rightarrow} C_6H_{12}O_6 + 6O_2. \tag{4.5}$$
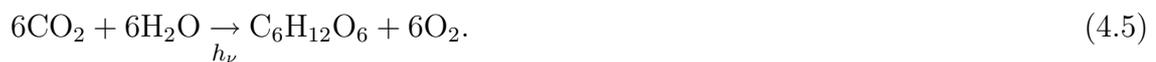
Photosynthesis and respiration (particularly in the form of biodegradation) are of particular interest in environmental engineering because they affect the concentration of oxygen, a component essential for most aquatic life.

4.2 Reaction kinetics

Reaction kinetics is the study of the rate of formation of products from reactants in a transformation reaction. All reactions occur at a characteristic rate $k = 1/\Delta t_k$. A common measure of this characteristic rate is the half-life, the time for half of the reactants to be converted into products. The other physical processes of interest in our problems (i.e. diffusion and advection) also occur with characteristic time scales, Δt_p. Comparing these characteristic time-scales, three cases can be identified:

- $\Delta t_k \ll \Delta t_p$: For these reactions we can assume the products are formed as soon as reactants become available, and we can neglect the reaction kinetics. Such reactions are called instantaneous and are reactant-limited; that is, the rate of formation of products

is controlled by the rate of formation of reactants and not by the reaction rate of the tranformation equation.

• $\Delta t_k \gg \Delta t_p$: For these reactions the reaction can be ignored altogether, and we have a conservative (non-reacting) system.

• $\Delta t_k \approx \Delta t_p$: For these reactions neither the reaction nor the reaction kinetics can be ignored. Assuming the products are readily available, such reactions are called rate-limited, and the rate of formation of products is controlled by the reaction kinetics of the chemical transformation.

This last case, where the reactions are rate-limited, is the case of interest in this chapter, and in this section we discuss the rate laws of chemical kinetics.

To formulate the rate laws for a generic reaction, consider the mixed chemical reaction

$$aA + bB \rightarrow cC + dD, \tag{4.6}$$

where the lower-case letters are the stoichiometric coefficients of the reaction and the upper-case letters are the reactants (A and B) and products (C and D). The general form of the rate law for species A can be written as

$$\frac{d[A]}{dt} = R_A, \tag{4.7}$$

where R_A is a function describing the rate law for species A. We use the $[A]$-notation to designate concentration of species A (we will also use the equivalent notation C_A). From the stoichiometry of the reaction, the following ratios can also be inferred:

$$\frac{d[A]/dt}{d[B]/dt} = \frac{a}{b}, \text{ and}$$

$$\frac{d[A]/dt}{-d[C]/dt} = \frac{a}{c}.$$

Substituting the rate laws gives the relationships

$$R_A = +\frac{a}{b} R_B, \text{ and} \tag{4.8}$$

$$R_A = -\frac{a}{c} R_C. \tag{4.9}$$

We still require a means of writing the rate law for species i, R_i.

The general form of the rate law for product i formed from j reactants is

$$R_i = k_i C_1^{n_1} C_2^{n_2} ... \, C_j^{n_j}, \tag{4.10}$$

where k is the rate constant of the reaction, n_j is the order of the reaction with respect to constituent j, and $K = \sum_{i=1}^{j} n_i$ is the overall reaction order (note that the units of k depend on K). In general, reaction order cannot be predicted (except for simple, single-step, elementary reactions, where reaction order is the stoichiometric coefficient). Hence, reaction rate laws are determined on an experimental basis.

As one might expect, the reaction rate k is temperature dependent. One way to find a relationship for $k(T)$ is to use Arrhenius equation for an ideal gas

$$k = A \exp(-E_a/(RT)), \tag{4.11}$$

where A is a constant, E_a is the activation energy, R is the ideal gas constant, and T is the absolute temperature. Defining $k_1 = k(T_1)$ we can rearrange this equation to obtain

$$k(T) = k_1 \exp\left(\frac{E_a(T - T_1)}{RTT_1}\right). \tag{4.12}$$

for small temperature changes, this equation can be linearized by defining the constant

$$\theta = \frac{E_a}{RT_2 T_1}. \tag{4.13}$$

Then, for $T_1 \leq T \leq T_2$,

$$k(T) = k_1 \exp(\theta(T - T_1)). \tag{4.14}$$

This form of the temperature dependence is often applied to non-gaseous systems as well.

4.2.1 First-order reactions

The general equation for a first-order reaction is

$$\frac{dC}{dt} = \pm kC, \tag{4.15}$$

where k has units $[1/T]$. Common examples are radioactive decay and the dye-off of bacteria in a river.

This is a standard initial-value problem, whose solution can be found subject to the initial condition

$$C(t = 0) = C_0. \tag{4.16}$$

First, rearrange the governing equation to obtain

$$\frac{dC}{C} = \pm k dt. \tag{4.17}$$

Next, integrate both sides, yielding

$$\int \frac{dC}{C} = \int \pm k dt$$
$$\ln(C) = \pm kt + C_1, \tag{4.18}$$

where C_1 is an integration constant. Solving for C we obtain

$$C = C_1' \exp(\pm kt), \tag{4.19}$$

where C_1' is another constant (given by $\exp(C_1)$). After applying the initial condition, we obtain

$$C(t) = C_0 \exp(\pm kt). \tag{4.20}$$

Figure 4.1 plots this solution for $C_0 = 1$ and $k = -1$.

As already discussed above, the characteristic reaction time is given by the time it takes for the ratio $C(t)/C_0$ to reach a specified value. For radioactive decay, k is negative,
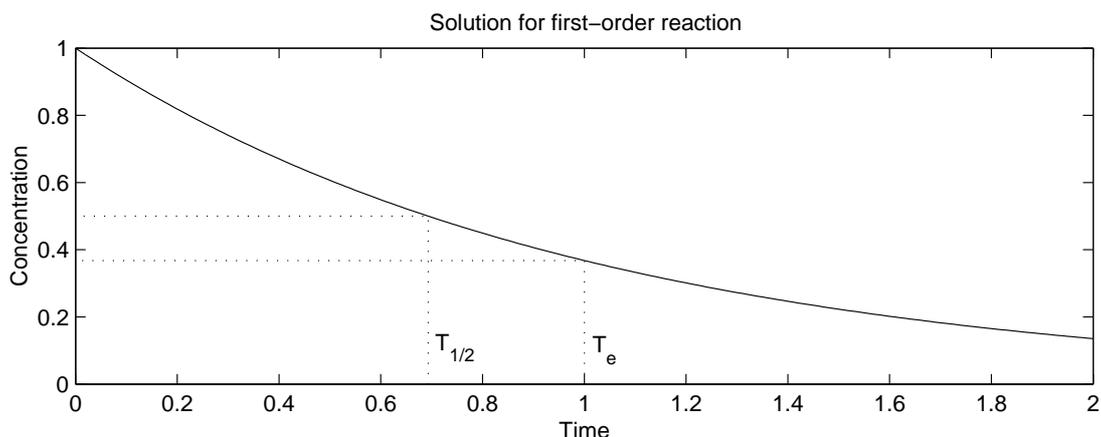
Fig. 4.1. Solution for a first-order transformation reaction. The reaction rate is $k = -1$.

and two common characteristic times are the half-life and the e-folding time. The half-life, $T_{1/2}$, is the time required for the concentration ratio to reach $1/2$. From (4.20), the half-life is

$$
\begin{aligned}
T_{1/2} &= \frac{\ln(1/2)}{k} \\
&\approx -\frac{0.69}{k}.
\end{aligned}
\tag{4.21}
$$

The e-folding time is the time required for the concentration ratio to reach $1/e$, given by

$$
T_e = -\frac{1}{k}.
\tag{4.22}
$$

Hence, the characteristic times for first-order reactions are independent of the initial concentration (or mass).

Example Box 4.1:
Radioactive decay.

A radioactive disposal site receives a sample of high-grade plutonium containing 1 g of ^{239}Pu and a sample of low-grade plutonium containing 1 g of ^{242}Pu. The half-lives of the two samples are 24,100 yrs for ^{239}Pu and 379,000 yrs for ^{242}Pu. On average, how many atoms transform per sample of plutonium?

The instantaneous disintegration rate is given by

$$
\begin{aligned}
\frac{\partial C}{\partial t} &= -kC \\
&= \frac{\ln(0.5)}{t_{1/2}}C.
\end{aligned}
$$

The molar weight of plutonium is 244.0642 g/mol; hence, we have $N_0 = 2.467 \cdot 10^{21}$ atoms per sample. For ^{239}Pu, we have

$$
\begin{aligned}
\frac{\partial N}{\partial t} &= -2.876 \cdot 10^{-5} N_0 \\
&= -2.248 \cdot 10^9 \text{ atoms/s}
\end{aligned}
$$

and for ^{239}Pu, we have

$$
\begin{aligned}
\frac{\partial N}{\partial t} &= -1.829 \cdot 10^{-6} N_0 \\
&= -1.430 \cdot 10^8 \text{ atoms/s}.
\end{aligned}
$$

Hence, even though the half-lives are very long, we still have a tremendous number of transformations per second in these two samples of plutonium.

Example Box 4.2:
Radio-carbon dating.

Radio-carbon dating can be used to estimate the age of things that once lived. The principle of radio-carbon dating is to compare the ^{14}C ratio in something when it was alive to the ^{14}C ratio in the artifact now and use (4.20) to estimate how long the artifact has been dead. The main assumption is that all living things absorb the same ratio of radioactive carbon, ^{14}C, to stable carbon, ^{12}C, as has the atmosphere. For this method, scientists require an accurate estimate of the half-life of ^{14}C, which is 5730±40 yrs. Use the error-propogation equation (3.72) to estimate the accuracy of this method.

Currently, the radioactive carbon in the atmosphere is about $1 \cdot 10^{-10}$ % of the total carbon. Thus, per mole of C, there would be $6.022 \cdot 10^{11}$ atoms of ^{14}C. If we assume the atmosphere has historically had the same ^{14}C ratio, then we can use this number for C_0. A student carefully measures the ^{14}C content of a sample to have $C = 7.528 \cdot 10^{10}$ atoms of ^{14}C per mole. Thus, the age of the sample is

$$t = -\frac{1}{k} \ln\left(\frac{C}{C_0}\right)$$
$$= 17190 \text{ yrs old.}$$

We can estimate the accuracy as follows. First, re-write the estimate equation as

$$t = -\frac{1}{k}\left(\ln(C) - \ln(C_0)\right).$$

Second, we calculate the necessary derivatives

$$\frac{\partial t}{\partial k} = \frac{1}{k^2} \ln\left(\frac{C}{C_0}\right)$$
$$\frac{\partial t}{\partial C} = -\frac{1}{kC}$$
$$\frac{\partial t}{\partial C_0} = -\frac{1}{kC_0}.$$

Finally, we incorporate these derivatives into the error-propagation equation

$$\delta t = \left[\left(\frac{1}{k^2}\ln\left(\frac{C}{C_0}\right)\delta k\right)^2 + \left(\frac{1}{kC}\delta C\right)^2 + \left(\frac{1}{kC_0}\delta C_0\right)^2\right]^{1/2}.$$

Assuming an accuracy of ±0.1% for the ^{14}C concentrations, the accuracy of our estimate is

$$\delta t = \sqrt{119.4^2 + 8.2^2 + 8.3^2}$$
$$= \pm 120 \text{ yrs.}$$

Hence, the error in the half-life is the most important error, and leads of an error of ±120 yrs for this sample.

4.2.2 Second-order reactions

The general equation for a second-order reaction is

$$\frac{dC}{dt} = \pm kC^2, \tag{4.23}$$

where k has units $[L^3/M/T]$. An example is the reaction of iodine gas given by the reaction

$$2\text{I(g)} \rightarrow \text{I}_2\text{(g)}, \tag{4.24}$$

which has rate constant $k = 7 \cdot 10^9$ l/(mol·s).

This is another initial-value problem, which can be solved subject to the initial condition

$$C(t = 0) = C_0. \tag{4.25}$$

We begin by rearranging the governing equation to obtain

$$\frac{dC}{C^2} = \pm kt. \tag{4.26}$$

This time we integrate using definite integrals and our initial condition, giving

$$\int_{C_0}^{C} \frac{dC'}{C'^2} = \int_0^t \pm k dt$$
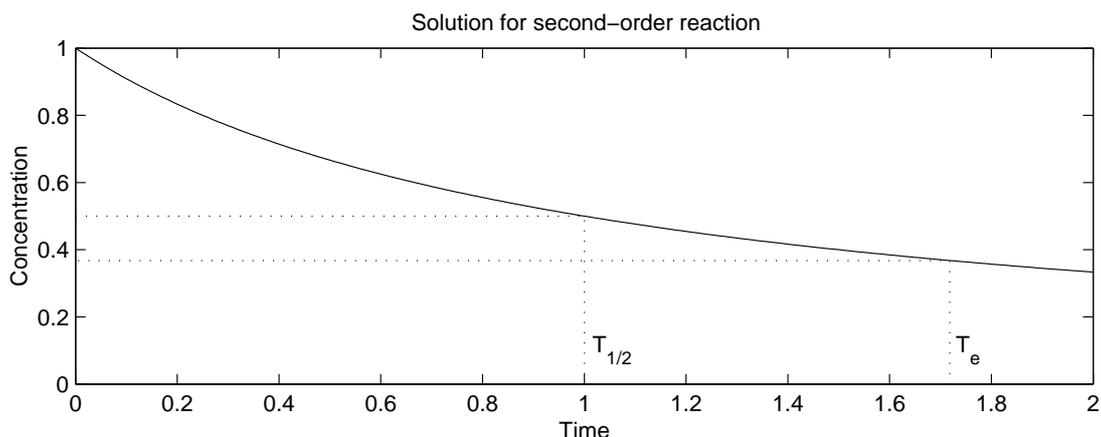$$-\left(\frac{1}{C} - \frac{1}{C_0}\right) = \pm kt. \tag{4.27}$$

Fig. 4.2. Solution for a second-order transformation reaction. The reaction rate is $k = -1$.

Solving for $C(t)$ gives

$$C(t) = \frac{1}{\mp kt + 1/C_0}. \tag{4.28}$$

Figure 4.2 plots this solution for $C_0 = 1$ and $k = -1$.

The characteristic times for a second-order reaction are given by

$$T_{1/2} = -\frac{1}{kC_0}, \text{ and} \tag{4.29}$$

$$T_e = -\frac{(e-1)}{kC_0}. \tag{4.30}$$

Hence, for second- and higher-order reactions, the characteristic times depend on the initial concentration!

4.2.3 Higher-order reactions

The general equation for an nth-order reaction is

$$\frac{dC}{dt} = \pm kC^n, \tag{4.31}$$

where k has units $[L^{3(n-1)}/M^{(n-1)}/T]$. The general solution subject to the initial condition $C(t = 0) = C_0$ is

$$\left(\frac{1}{(n-1)}\right)\left[\frac{1}{C^{n-1}} - \frac{1}{C_0^{(n-1)}}\right] = kt \tag{4.32}$$

for $n \geq 2$. Such reactions are rare, and one generally tries different values of n to find the best fit to experimental data.

A common means of dealing with higher-order reaction rates is to linearize the reaction in the vicinity of the concentration of interest, C_I. The linearized reaction rate equation is

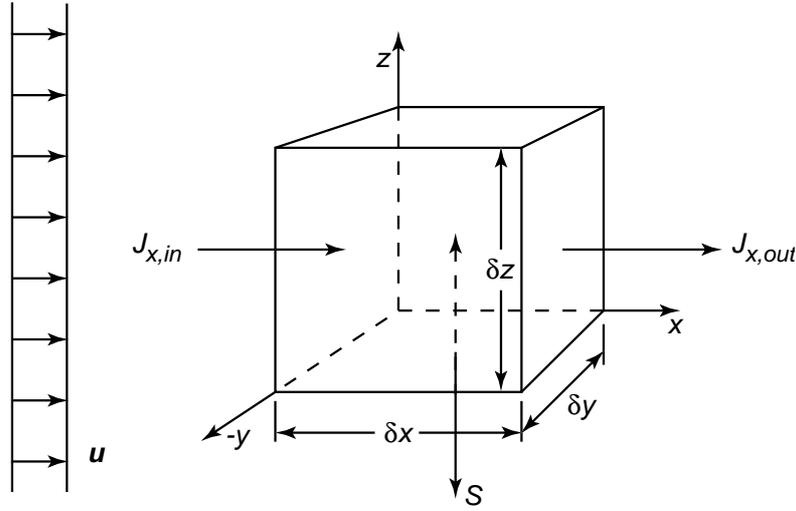$$R = k^*C - kC_I^2, \tag{4.33}$$

Fig. 4.3. Schematic of a control volume with crossflow and reaction.

where k is the real rate constant and k^* is the linearized rate constant; note that kC_I^2 is also a constant. Thus, higher-order reactions can be treated as first-order reactions in the vicinity of a known concentration C_I.

4.3 Incorporating transformation with the advective-diffusion equation

Having a thorough understanding of transformations and reaction kinetics, we are ready to incorporate transformations into our transport equation, the advective diffusion equation. As we pointed out earlier, reactions are treated differently, depending on whether they are homogeneous or heterogeneous. Homogeneous reactions add a term to the governing differential equation; whereas, heterogeneous reactions are enforced with special boundary conditions.

4.3.1 Homogeneous reactions: The advective-reacting diffusion equation

Homogeneous reactions add a new term to the governing transport equation because they occur everywhere within our system; hence, they provide another flux to our law of conservation of mass. Referring to the control volume in Figure 4.3, the mass conservation equation is

$$\frac{\partial M}{\partial t} = \sum J_{in} - \sum J_{out} \pm S, \tag{4.34}$$

where S is a source or sink reaction term. We have already seen in the derivation of the advective diffusion equation that

$$\sum J_{in} - \sum J_{out} = \left(D\frac{\partial^2 C}{\partial x_i^2} - u_i\frac{\partial C}{\partial x_i} \right) \delta x \delta y \delta z. \tag{4.35}$$

The reaction term is just the kinetic rate law integrated over the volume, giving

$$S = \pm R \delta x \delta y \delta z. \tag{4.36}$$

Combining these results in an equation for the concentration, we obtain

$$\frac{\partial C}{\partial t} + \frac{\partial u_i C}{\partial x_i} = D \frac{\partial^2 C}{\partial x_i^2} \pm R, \tag{4.37}$$

where R has the same form as in the sections discussed above. Appendix B presents solutions for a wide range of cases.

As an example, consider the solution for an instantaneous point source of a first-order reacting substance in one dimension. The solution for $C(t)$ can be found using Fourier transformation to be

$$C(x,t) = \frac{M}{A\sqrt{4\pi Dt}} \exp\left(-\frac{(x-ut)^2}{4Dt}\right) \exp(\pm kt), \tag{4.38}$$

where M is the total mass of substance injected, A is the cross-sectional area, D is the diffusion coefficient, u is the flow velocity, and k is the reaction rate constant. If we compare this solution to the solution for a first-order reaction given in (4.20), we see that the initial concentration C_0 is replaced by the time-varying solution in the absence of transformation. This observation is helpful for deriving solutions to cases not presented in Appendix B.

4.3.2 Heterogeneous reactions: Reaction boundary conditions

Heterogeneous reactions occur only at the boundaries; hence, they provide new flux boundary conditions as constraints on the governing transport equation. Examples include corrosion, where there is an oxygen sink at the boundary, and also catalyst reactions, where the presence of other-phase boundaries is needed to facilitate or speed up the reaction. Figure 4.4 shows a macroscopic and microscopic view of the solid boundary. To define the
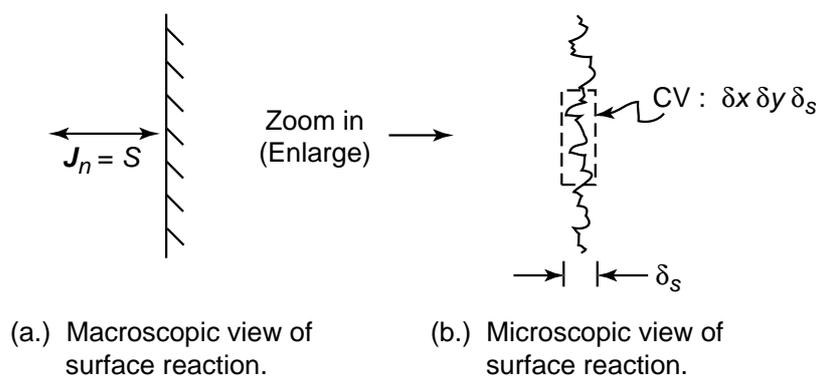

(a.) Macroscopic view of surface reaction.   (b.) Microscopic view of surface reaction.

Fig. 4.4. Schematic representation of the reaction boundary condition. S represents the source or sink term, δ_s is the reaction sublayer, and $\delta x \delta y$ is the surface area into the page of the boundary control volume.

boundary condition, we require an expression for the source/sink flux, $\boldsymbol{J}_n$.

Writing the conservation of mass for the control volume in the microscopic view, we have

$$\frac{dM}{dt} = \pm S, \tag{4.39}$$

where S is the source or sink mass flux over the control volume. We can expand this expression to obtain

$$\delta x \delta y \delta_s \frac{dC_s}{dt} = \delta x \delta y \delta_s R, \tag{4.40}$$

where δ_s is the reaction sublayer depth and C_s is the mean surface concentration within the reaction sublayer. Since we are looking for a flux, $\boldsymbol{J}_n$, with units $[\mathrm{M}/(\mathrm{L}^2\mathrm{T})]$, we must write the above equation on a per unit area basis, that is

$$\delta_s \frac{dC_s}{dt} = \delta_s R = \boldsymbol{J}_n. \tag{4.41}$$

Thus, the general form of a reaction boundary condition is

$$\boldsymbol{J}_n = \delta_s R. \tag{4.42}$$

As an example, consider the one-dimensional case for a first-order reacting boundary condition. For first order reactions, $R = kC_s$, and for the one-dimensional case, $\boldsymbol{J}_n = D(dC/dx)|_s$. Substituting into the general case, we obtain

$$D\frac{dC}{dx}\bigg|_s = \delta_s k C_s. \tag{4.43}$$

The reaction constant, k, is controlled by the boundary geometry, the possible presence of a catalyst, and by the kinetics for the species of interest; hence, k is a property of both the species and the boundary surface. The reaction rate is often given as a reaction velocity, $k_s = k\delta_s$. These types of boundary conditions will be handled in greater detail in the chapter on sediment- and air/water interfaces.

4.4 Application: Wastewater treatment plant

A wastewater treatment plant (WWTP) discharges a constant flux of bacteria, $\dot{m}$ into a stream. How does the concentration of bacteria change downstream of the WWTP due to the die-off of bacteria? The river is $h = 20$ cm deep, $L = 20$ m wide and has a flow rate of $Q = 1$ m^3/s. The bacterial discharge is $\dot{m} = 5 \cdot 10^{10}$ bacteria/s, and the bacteria can be modeled with a first-order transformation equation with a rate constant of 0.8 day^{-1}. The bacteria are discharged through a line-source diffuser so that the discharge can be considered well-mixed both vertically and horizontally at the discharge location. Refer to Figure 4.5 for a schematic of the situation.

The solution for a first-order reaction was derived above and is given by

$$C(t) = C_0 \exp(-kt). \tag{4.44}$$
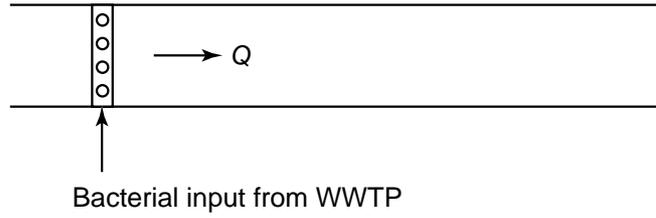
Fig. 4.5. Schematic of bacterial discharge at WWTP.
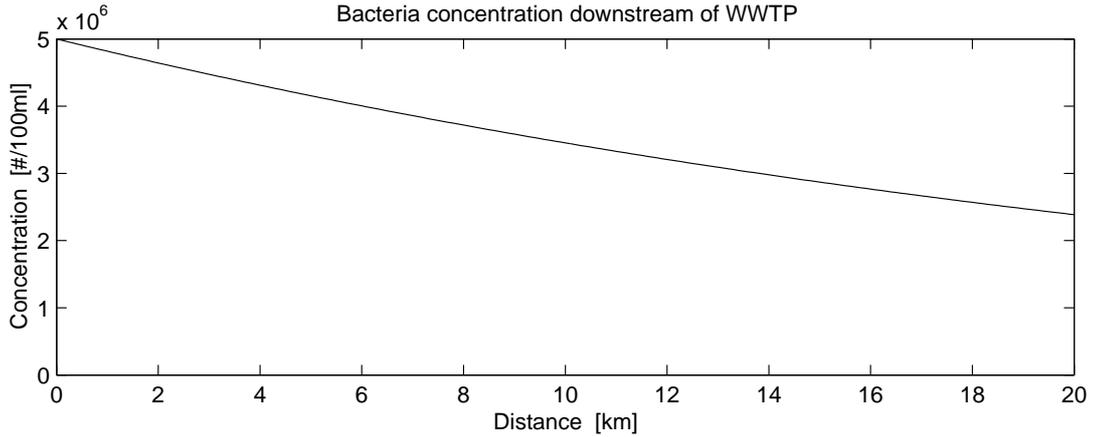

Fig. 4.6. Bacteria concentration downstream of WWTP.

The initial concentration C_0 is the concentration at the discharge, which we can derive through the relationship

$$\dot{m}_0 = QC_0. \tag{4.45}$$

Substituting the values given above, $C_0 = 5 \cdot 10^6$ #/100ml. The next step is to covert the time t in our general solution to space x through the relationship

$$x = ut. \tag{4.46}$$

Substituting, we have

$$
\begin{aligned}
C(x) &= C_0 \exp\left(-k\frac{x}{u}\right) \\
&= 5 \cdot 10^6 \exp(-3.7 \cdot 10^{-5} x) \text{ \#/100ml.}
\end{aligned} \tag{4.47}
$$

The half-life for this case can be given in terms of downstream distance. From (4.21), we have

$$
\begin{aligned}
x_{1/2} &= -\frac{0.69}{k} \\
&= -\frac{0.69}{-3.7 \cdot 10^{-5}} \\
&= 18.6 \text{ km.}
\end{aligned} \tag{4.48}
$$

Figure 4.6 plots the solution for the first 20 km of downstream distance.

Summary

This chapter introduced the treatment of transformation processes. Three classes of transformations were considered: physical, chemical and biological. The rate laws governing the transformations were derived from chemical reaction kinetics. Solutions for first and second order reactions were derived, and methods for dealing with higher-order reactions and temperature dependence of rate constants were presented. These rate laws were then combined with the transport equation for two types of reactions: for homogeneous reactions, the rate law becomes a source or sink term in the governing differential transport equation; for heterogeneous reactions, a modified rate law becomes a boundary condition constraining the governing differential equation. An example of bacterial die-off downstream of a WWTP closed the chapter.

Exercises

4.1 Reaction order. A chemical reaction is of order 1.5. What are the units of the rate constant? What is the solution to the rate equation (i.e. what is $C(t)$)? Write an expression for the half-life.

4.2 Clean disposal. A chemical tanker runs aground near the shore of a wide river. The company declares the load on the tanker a complete loss, due to contamination by river water, and decides to slowly discharge the hazardous material into the river to dispose of it. The material (an industrial acid) reacts with the river water (the material is buffered by the river alkalinity) and is converted to harmless products with a rate constant of $k = 5{\cdot}10^{-5}\,\text{s}^{-1}$. Calculate the maximum discharge rate such that a concentration standard of 0.01 mg/l is not exceeded at a distance of 1.5 km downstream. The river flow rate is $Q = 15\,\text{m}^3/\text{s}$, the depth is $h = 2$ m, the width is $B = 75$ m, and the concentration of acid in the grounded tanker is 1200 mg/l. If the tanker contains 10000 m^3, how long will it take to safely empty the tanker?

4.3 Water treatment. In part of a water treatment plant, a mixing tank is used to remove heavy metals. Untreated water flows into the tank where is it rigorously mixed (instantaneously mixed) and brought into contact with other chemicals that remove the metals. A single outlet is installed in the tank. Assume the inflow and outflow rates are identical, and assume metals are removed in a first-order reaction with a rate constant of $k = 0.06\,\text{s}^{-1}$. The tank volume is 15 m^3. What is the allowable flow rate such that the exit stream contains 10% of the metals in the input stream? How high can the flow rate be if the reaction rate constant is doubled?