

3 Model formulation

Formulating mathematical models by applying balance and conservation principles and constitutive relations for fluxes is the topic of this chapter. The aim is to give the reader tools and skills for:

- constructing models using balances on differential or macroscopic control volumes for momentum, heat, mass, and numbers (population balances);
- constructing models by simplifying general model equations.

3.1 Balances and conservation principles

Before formulating a model it is crucial to define the system boundary. The purpose of the boundary is to define the system in relation to its surroundings. In [Figure 3.1](#), a stirred tank is isolated from its surroundings by the dashed circle. All significant phenomena enclosed within this boundary need to be included in a successful model. The system boundary may be chosen in different ways, but for most systems the boundary to use is natural. Models derived from physicochemical principles are usually based on the general balance concept:

$$\left[\begin{array}{c} \text{accumulation} \\ \text{within system} \end{array} \right] = \left[\begin{array}{c} \text{net transport in} \\ \text{through system} \\ \text{boundaries} \end{array} \right] + \left[\begin{array}{c} \text{net generation} \\ \text{within system} \end{array} \right].$$

This relation is very general. The objective of model building is to transform the verbal concept into mathematical statements that are specific to the quantity of interest. We may balance mass, energy, and momentum as well as, for example, entropy and countable entities such as size and age distributions (population balances). Some of these entities are conserved, for example total mass, whilst some are not, for example the mass of a species in a mixture (due to chemical reactions).

By using the balance principle, we can derive model equations by balancing the quantities within the defined system boundary. A few examples of important balance equations are given in the following.

Overall (total) mass balance

The overall total mass balance describes the total mass in a system. Obviously there can be only one total mass balance equation, and the net generation term is zero, which means that mass is a conserved quantity.

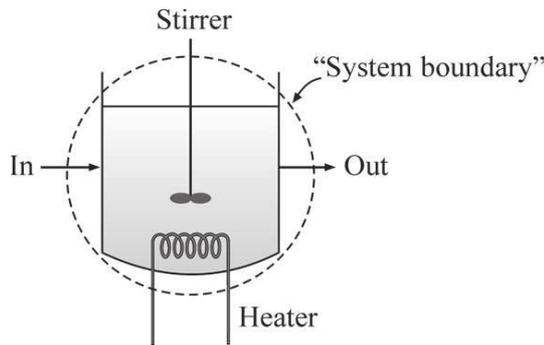


Figure 3.1. System boundary for a stirred tank.

Species (component, material) balance

Most chemical engineering systems contain more than one component. In contrast to the total mass, the components or species are not always conserved; they may be generated or consumed due to chemical reactions. In this case, the net generation rate within the system must be quantified by reaction rate equations.

An N -component system will have N balance equations. As the species balance equations and the total balance are related, the $N - 1$ species balances and the overall mass balance are sufficient to describe completely the mass flow in the system.

Energy balance

An energy balance equation for the total energy, TE , in the system, taking into consideration temperature-dependent thermal energy U , the potential energy PKE , pressure energy PE , and the kinetic energy KE , is given by

$$\left[\begin{array}{c} \text{accumulation} \\ \text{of } TE \\ \text{within system} \end{array} \right] = \left[\begin{array}{c} \text{net flow of } U, PKE, \\ PE, KE \text{ through} \\ \text{system boundaries} \end{array} \right] = \left[\begin{array}{c} \text{net generation} \\ \text{within} \\ \text{system} \end{array} \right].$$

In general, transformation between all these energies must be considered.

In some cases, the transformation of mechanical energy, i.e. between PKE , PE , and KE , is of primary interest, and isothermal conditions may be assumed.

In other cases, the potential and kinetic energies can be neglected, because the difference in elevation and low velocities contribute to small changes in total energy. Consequently, it is often possible to neglect the transformation of potential and kinetic energies to thermal energy, and the energy balance simplifies to a balance equation for the thermal energy.

As an example, consider a pipe flow where the fluid is being heated externally to 20°C and is simultaneously decelerated due to an increase in the pipe diameter. In this case, the kinetic energy will typically contribute little to temperature change in comparison to the heating. Let us assume that the velocity at the inlet equals 1 m/s . The limiting case with a maximum temperature increase occurs with infinite pipe expansion, where the velocity reduces to 0 m/s . The balance between enthalpy and kinetic energy is given by $\rho c_p \Delta T = \rho \Delta v^2 / 2$. For water, a fluid with a high heat capacity, approximately $4.2\text{ J g}^{-1}\text{ K}^{-1}$, the temperature increase will be $\Delta T \approx 0.1^\circ\text{C}$. Consequently, the kinetic

Table 3.1. Constitutive relations in transport phenomena models

Mechanism	Dimension	Flux	Name
Momentum	N m^{-2}	$\tau_{yx} = -\mu \frac{\partial v_x}{\partial y}$	Newton
Heat	$\text{J m}^{-2} \text{ s}^{-1}$	$q_x = -k \frac{\partial T}{\partial x}$	Fourier
Mass	$\text{mol m}^{-2} \text{ s}^{-1}$	$J_{A,x} = -C D_{AB} \frac{\partial y_A}{\partial x}$	Fick
Flow (porous)	$\text{m}^{-3} \text{ m}^{-2} \text{ s}^{-1}$	$q_x = -\frac{k}{\mu} \frac{\partial P}{\partial x}$	Darcy

energy leads to an almost negligible increase in temperature. In this heating application, the balance equation can be reduced safely to a thermal energy balance.

Because the thermal energy not only depends on temperature, but also on the composition, the energy balance equation is most often accompanied by species (material) balance equations.

Several phenomena may cause heat generation within a system, e.g. reaction heat (exothermic and endothermic reactions), heating and cooling due to convection, conduction, radiation, condensation, evaporation, work done by the system on the surroundings, and shaft work due to an impeller.

Momentum balance

Momentum and force are vector quantities, and the number of equations equals the number of spatial dimensions in the model, e.g. a 2D model must contain momentum balances for x - and y -momentum. Three kinds of forces are typically accounted for in chemical engineering: pressure force, shear force, and gravitational force. A force is associated with momentum production (Newton's second law) and thus enters via the last term in the general balance.

3.2 Transport phenomena models

The most common types of models in chemical engineering are those related to the transport of mass, heat, and momentum. In addition to the balance equation, a constitutive equation that relates the flux of interest to the dependent variable (e.g. mass flux to concentration) is needed. These relations (in simple 1D form) for the microscopic level and for flow at the porous media level are given in [Table 3.1](#). It should be noted that all these relations have the general form

$$\text{flux} = \text{transport coefficient} \times \text{gradient}.$$

A simple example of setting up a model at the microscopic level (1D transient heat conduction with a heat source) is given in Example 3.1.

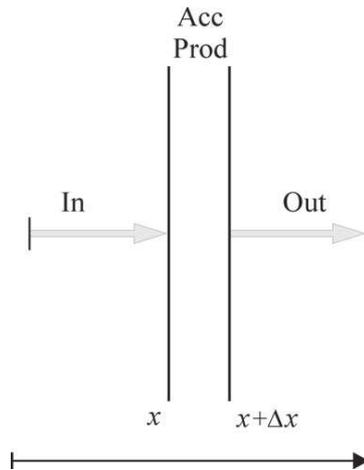


Figure 3.2. Simple shell balance.

Example 3.1 1D transient heat conduction with a source term

The variables and parameters used in this example are as follows: p = density, c_p = heat capacity, q = heat flux, k = thermal conductivity, A = cross-sectional area, S = source strength ($\text{J m}^{-3} \text{s}^{-1}$).

accumulation: $\rho c_p \Delta T (A \Delta x)$;
 in (conduction): $(qA)|_x \Delta t$;
 out (conduction): $(qA)|_{x+\Delta x} \Delta t$;
 production: $SA \Delta x \Delta t$.

Insertion of these terms into the balance equation yields

$$\rho c_p \frac{\Delta T}{\Delta t} = \frac{q|_x - q|_{x+\Delta x}}{\Delta x} + S.$$

By taking the limit as $\Delta x \rightarrow 0$ and $\Delta t \rightarrow 0$ we have

$$\rho c_p \frac{\partial T}{\partial t} = -\frac{\partial q}{\partial x} + S.$$

Finally, introducing Fourier's law, $q_x = -k(\partial T/\partial x)$, yields

$$\rho c_p \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial x^2} + S,$$

that is to be solved with proper boundary and initial conditions.

General microscopic transport equations can be found in standard text books on transport phenomena (see the bibliography). For example, the transient 3D binary mass transport equation in rectangular coordinates is obtained by using a differential control volume in three dimensions, as depicted in [Figure 3.3](#).

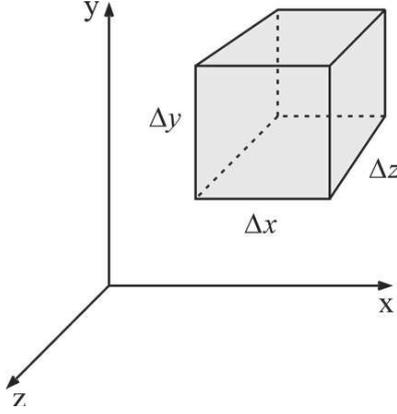


Figure 3.3. Differential control volume in three dimensions.

Example 3.2 Derivation of the transient 3D binary mass transport equation in rectangular coordinates

The variables and parameters used in this example are as follows: C_A = concentration, J_A = diffusion flux, v = velocity, R_A = source term ($\text{mol m}^{-3} \text{s}^{-1}$).

accumulation:	$\Delta C_A \Delta x \Delta y \Delta z;$
in (diffusion):	$x\text{-direction } J_{A,x} _x \Delta y \Delta z \Delta t,$ $y\text{-direction } J_{A,y} _y \Delta x \Delta z \Delta t,$ $z\text{-direction } J_{A,z} _z \Delta x \Delta y \Delta t;$
In(flow):	$x\text{-direction } (v_x C_A) _x \Delta y \Delta z \Delta t,$ $y\text{-direction } (v_y C_A) _y \Delta x \Delta z \Delta t,$ $z\text{-direction } (v_z C_A) _z \Delta x \Delta y \Delta t;$
Out (diffusion):	$x\text{-direction } J_{A,x} _{x+\Delta x} \Delta y \Delta z \Delta t,$ $y\text{-direction } J_{A,y} _{y+\Delta y} \Delta x \Delta z \Delta t,$ $z\text{-direction } J_{A,z} _{z+\Delta z} \Delta x \Delta y \Delta t;$
Out (flow):	$x\text{-direction } (v_x C_A) _{x+\Delta x} \Delta y \Delta z \Delta t,$ $y\text{-direction } (v_y C_A) _{y+\Delta y} \Delta x \Delta z \Delta t,$ $z\text{-direction } (v_z C_A) _{z+\Delta z} \Delta x \Delta y \Delta t;$
Production:	$R_A \Delta x \Delta y \Delta z \Delta t.$

Using the balance equation and taking the limit as $\Delta x, \Delta y, \Delta z, \Delta t \rightarrow 0$ yields

$$\frac{\partial C_A}{\partial t} = -\frac{\partial(v_x C_A)}{\partial x} - \frac{\partial(v_y C_A)}{\partial y} - \frac{\partial(v_z C_A)}{\partial z} - \frac{\partial J_{A,x}}{\partial x} - \frac{\partial J_{A,y}}{\partial y} - \frac{\partial J_{A,z}}{\partial z} + R_A. \quad (3.1)$$

Finally, using Fick's law, $J_{A,x} = -D_{AB}(\partial C_A/\partial x)$, we obtain

$$\begin{aligned} \frac{\partial C_A}{\partial t} = & -\frac{\partial(v_x C_A)}{\partial x} - \frac{\partial(v_y C_A)}{\partial y} - \frac{\partial(v_z C_A)}{\partial z} + D_{AB} \frac{\partial^2 C_A}{\partial x^2} + D_{AB} \frac{\partial^2 C_A}{\partial y^2} \\ & + D_{AB} \frac{\partial^2 C_A}{\partial z^2} + R_A, \end{aligned} \quad (3.2)$$

or, in vector notation,

$$\frac{\partial C_A}{\partial t} = -\nabla \cdot (vC_A) + D_{AB}\nabla^2 C_A + R_A. \quad (3.3)$$

For convenience, the general equations for mass, momentum, and heat transport, in rectangular, cylindrical, and spherical coordinates, are provided in Appendix A.

Given these general equations, one approach to mathematical modeling is to apply appropriately and simplify these equations for the particular problem. This involves a clear statement of assumptions and an estimation of the relative importance of various terms (e.g. using dimensional analysis; see [Chapter 4](#)). In Example 3.3, the energy balance equation has been simplified from its generic form to an equation describing the heat conduction in one dimension (Example 3.1).

Example 3.3 Reduction of the general energy balance in Example 3.1

The energy balance equation for rectangular coordinates is given by (see Appendix A)

$$\rho c_p \left(\frac{\partial T}{\partial t} + v_x \frac{\partial T}{\partial x} + v_y \frac{\partial T}{\partial y} + v_z \frac{\partial T}{\partial z} \right) = k \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) + S.$$

In Example 3.1, there is no convective flow, consequently there is no heat convection, and the following terms are canceled:

$$v_x \frac{\partial T}{\partial x}, v_y \frac{\partial T}{\partial y}, v_z \frac{\partial T}{\partial z} \equiv 0.$$

Furthermore, it is a 1D problem, which means that conduction in the y - and z -directions can also be omitted, i.e.

$$k \frac{\partial^2 T}{\partial y^2}, \quad k \frac{\partial^2 T}{\partial z^2} \equiv 0.$$

The only terms that remain in the general balance equation are accumulation, conduction in the x -direction, and the source term. Thus, the balance equation simplifies to

$$\rho c_p \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial x^2} + S,$$

which is the same model equation as derived in Example 3.1.

In Example 3.1, the flow was set to zero by definition. In many situations the problem is more complex and involves estimating the various terms. For instance, in Example 3.3 there may be both flow and conduction of heat. To estimate if one mechanism dominates, a dimensionless number comparing the terms can be used.

The total flux of a quantity is the sum of its molecular flux and convective flux. The ratio of the convective flux to the molecular flux (the Péclet number) can be used to determine the relative importance of each flux. The dimensionless Péclet numbers are

defined by

$$\begin{aligned} \text{Pe}_{heat} &= uL/\alpha && \text{(heat transfer),} \\ \text{Pe}_{mass} &= uL/D_{AB} && \text{(mass transfer).} \end{aligned}$$

Here, u and L are the characteristic velocity and length scales, and α and D_{AB} are the diffusivities for heat and mass transport, respectively. They obviously both have the same unit (m^2/s). Heat diffusivity is defined as $\alpha = \lambda/(\rho c_p)$ where λ is the heat conductivity.

Depending on the magnitude of the Péclet number, we have

$$\begin{aligned} \text{Pe} \ll 1 & \quad \text{total flux} \approx \text{molecular flux,} \\ \text{Pe} \approx 1 & \quad \text{total flux} = \text{molecular flux} + \text{convective flux,} \\ \text{Pe} \gg 1 & \quad \text{total flux} \approx \text{convective flux.} \end{aligned}$$

3.3 Boundary conditions

Equally as important as formulating the differential equation(s) when developing a mathematical model is the selection of an appropriate set of boundary conditions and/or initial conditions. In order to calculate the values of arbitrary constants that evolve in the solution of a differential equation, we generally need a set of n boundary conditions for each n th-order derivative with respect to a space variable or with respect to time. For example, the differential equation

$$\rho c_p \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial x^2} + S \quad (3.4)$$

requires the value of T to be specified at two locations of x and one value of t .

Appropriate boundary conditions arise from the actual process or the problem statement. They essentially are given, or, more often, must be deduced from, physical principles associated with the problem. These physical principles are usually mathematical statements that show that the dependent variable at the boundary is at equilibrium, or, if some transport is taking place, that the flux is conserved at the boundary. Another type of boundary condition uses interfacial transport coefficients (e.g. heat transfer or mass transfer coefficients) that express the flux as the product of the interphase transport coefficient and some kind of driving force.

The common boundary conditions for use with momentum, energy, and mass transport are tabulated in [Tables 3.2–3.4](#). Note the similarities among the three modes of transport. These boundary conditions apply to all strata of description shown in [Tables 3.2](#), except for the molecular one.

Recall the mathematical classification of boundary conditions summarized in [Table 3.5](#). For example, in energy transport, the first type corresponds to the specified temperature at the boundary; the second type corresponds to the specified heat flux at the boundary; and the third type corresponds to the interfacial heat transport governed by a heat transfer coefficient.

Table 3.2. Common boundary conditions for use with the transport of mass.

Description	Math
Concentration at a boundary is specified	$C = C_0$
Mass flux across a boundary is continuous	$(n_i)_{x=0-} = (n_i)_{x=0+}$
Concentrations on both sides of a boundary are related functionally	$(C_i)_{x=0-} = f(C_i)_{x=0+}$
Convective mass (mole) flux at a boundary is specified	$(N_A)_{x=0} = k_c(C_{bulk} - C_{surface})$
Rate of reaction at a boundary is specified	$(N_A)_{x=0} = R_A$

Table 3.3. Common boundary conditions for use with the transport of momentum

Description	Math
Velocity at a boundary is specified	$v_{rel} = 0$ (no-slip condition at solid–fluid interface)
Momentum flux across a boundary is continuous	e.g. τ is continuous at a liquid–liquid interface
Velocity at a boundary is continuous	$(v)_{x=0-} = (v)_{x=0+}$
Momentum flux is specified	e.g. τ in liquid is approximately zero at gas–liquid interfaces (at low relative velocities)

Table 3.4. Common boundary conditions for use with the transport of energy

Description	Math
Temperature at a boundary is specified	$T = T_0$
Heat flux across a boundary is continuous	$(q_i)_{x=0-} = (q_i)_{x=0+}$
Temperature at a boundary is continuous	$(T)_{x=0-} = (T)_{x=0+}$
Convective heat flux at a boundary is specified	$(q)_{x=0} = h(T_{bulk} - T_{surface})$
Heat flux at a boundary is specified	$q = q_0$

Table 3.5. Classification of boundary conditions

Type	Description	Math
Dirichlet (first type)	specifies the value a solution must take at its boundary	$y(0) = \gamma_1$
Neumann (second type)	specifies the value the derivative of the solution must take at its boundary	$\left. \frac{\partial y}{\partial x} \right _{x=0} = \gamma_1$
Robin (third type)	specifies a linear combination of the value of the function and the value of its derivatives at the boundary	$a_1 y + b_1 \frac{\partial y}{\partial x} = \gamma_1$

In setting up the domain to be modeled, all symmetries in the problem should be used to reduce the computational domain. (As long as this does not compromise the physics of the system, i.e. we do not want to restrict the solution.)

3.4 Population balance models

The basis of a population balance model is that the number of entities with some property in a system is a balanceable quantity. Properties include, among others, size, mass, and age.

There are many examples in the process industries for which discrete entities are created, destroyed, or changed in some way as a result of processing. A classical example concerns crystallization, where the size distribution of crystals and its evolution is of the highest relevance. In this application, the evolution of the crystal size distribution is predicted using population balance models and closures describing mechanisms such as nucleation, growth, and breakage. Granulation is another example; in this process, fine particles are bound together into larger granules. Applications include manufacturing of pharmaceuticals, detergents, and fertilizers. Consequently, population balance models serve as a tool to predict, control, and optimize the complex dynamics of these systems. Many biochemical processes also have characteristics that lend themselves to analysis via the population balance model. Other examples include flocculation for purifying drinking water, gas–liquid dispersions, and liquid–liquid extraction and reaction. The residence time distribution (RTD) theory is a special case of the general population balance.

Let us first, as an introduction, discuss a commonly used population balance model for flocculation in stirred reactor tanks. The aim of flocculation is to agglomerate fine particles in water, using chemical additives, to large aggregates that are easy to separate in sedimentation processes. The agglomerates are formed due to binary collisions of particles. Not every collision is successful, however, so the collision efficiency has to be accounted for. As the agglomerates grow, there is an increasing risk that they fragment into smaller aggregates or even “primary” particles. This may be the result of shear forces or collisions with the impeller, walls, or other particles.

Figure 3.4 shows the experimental results, using laser techniques, to follow the evolution of floc sizes over time. The primary data has been evaluated, using image analysis techniques, and the result is also shown in the figure as the evolution of the number concentration of flocs of different sizes (“population”) over time. It can be seen that the number of small flocs decrease, and larger flocs form, over time.

The population balance, including these effects, can be written as follows:

$$\frac{dn_k}{dt} = \frac{1}{2} \sum_{i+j=k} \alpha(i, j)\beta(i, j)n_i n_j - \sum_{i=1}^{\infty} \alpha(i, k)\beta(i, k)n_i n_k - \chi(k)n_k + \sum_{i>k}^{\infty} \chi(i)n_i. \quad (3.5)$$

In this equation, the term on the left-hand side represents the rate of change of the number concentration of agglomerates of size k (valid for any size k). This is the result of the processes accounted for on the right-hand side of the equation. The first term accounts for the formation of agglomerates of size k due to collisions of two smaller

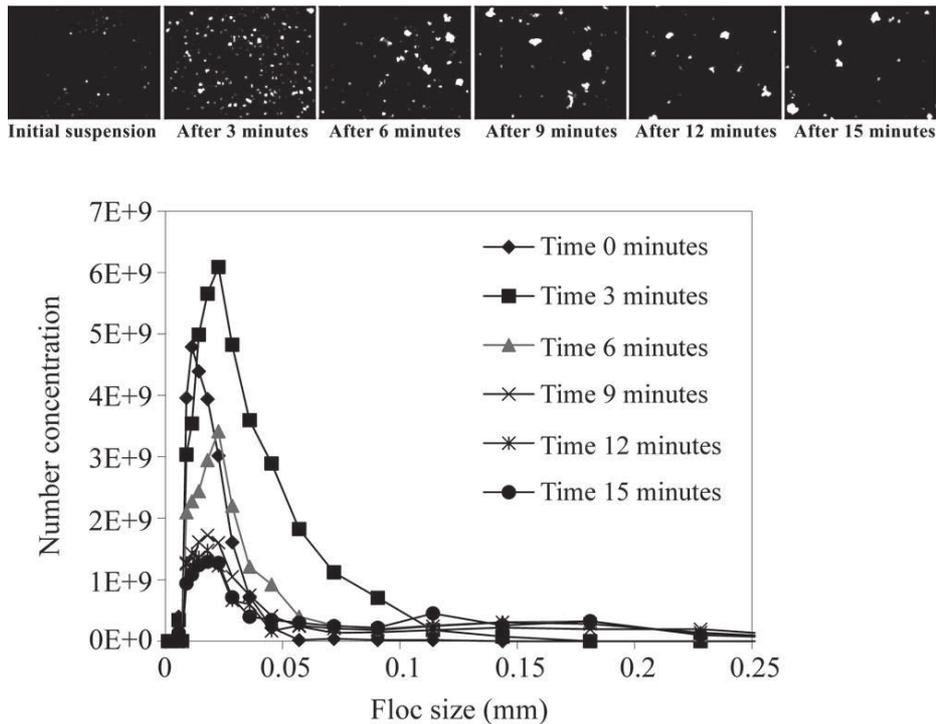


Figure 3.4. Change in floc size distribution during a flocculation process (Pelin, K., Licentiate thesis, Chalmers University of Technology 1999).

particles with sizes i and j (the factor of $\frac{1}{2}$ is to avoid counting the same collision twice). The second term gives a decrease in the number of k agglomerates, due to collisions with existing agglomerates of this size and other particles with arbitrary size i (note the negative sign). The third term, also negative, is a breakage function for particles of size k ; and the last term is a breakage function for agglomerates larger than k giving fragments of size k . Here

$\alpha(i, j)$ is the collision efficiency of binary collision between i and j (a number between 0 and 1);

$\beta(i, j)$ is the collision frequency between i and j (strongly dependent upon local flow conditions);

$\chi(i)$ is the breakage function.

This population balance model is able to reproduce the results in [Figure 3.4](#).

Flocculation is an example of a *discrete* growth of particles. In other processes, notably crystallization, the growth is *continuous*. As a second, introductory, example, we derive the population balance for batch crystallization (well mixed), only accounting for continuous growth given by the growth rate:

$$v = \frac{dm}{dt},$$

where m is the crystal mass. The number distribution is now given by $f(m, t)$, where

$f(m, t)\Delta m$ represents the number of crystals with mass within the range $m, m + \Delta m$ at time t .

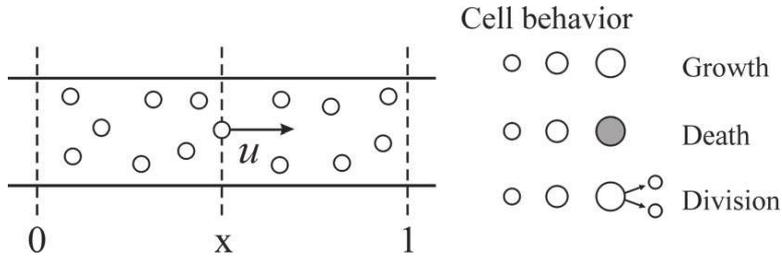


Figure 3.5. Cell behavior in a simple flow reactor.

The population balance for this case becomes

$$\Delta f \Delta m = [(fv)|_m - (fv)|_{m+\Delta m}] \Delta t.$$

The left-hand side of this relation represents the change in the number of crystals in the size range $m, m + \Delta m$ at time t . The right-hand side gives the number of smaller crystals that reach this size by continuous growth minus the number of crystals of the “right” size growing to a larger size.

Taking the limit as $\Delta m \Delta t \rightarrow 0$, we obtain

$$\frac{\partial f}{\partial t} = -\frac{\partial(fv)}{\partial m}, \quad (3.6)$$

which is to be solved with appropriate boundary conditions.

Before deriving the general population balances, we will give another example with one spatial dimension and one distributed property (mass of cell): continuous cell growth in a plug flow reactor.

Example 3.4 Population balance for cell behavior in a simple flow system

Let us consider a population of cells flowing through a plug flow reactor (Figure 3.5). The cells are characterized at time t by their position, x , and their mass, m . They are supposed to grow, to die, and to divide into two daughter cells (with mass conservation).

Figures 3.6(a) and (c) illustrate the “trajectories” of the cells in the physical space domain and in the mass–time domain, respectively. These two curves may be summarized in a single one, Figure 3.5(b), illustrating the mass–abscissa relationship. Figure 3.5(d) considers a small control surface Δx over Δm .

Let

$f(x, m, t) \Delta m \Delta x$ represent the number of cells within the range $m, m + \Delta m$ and $x, x + \Delta x$ at time t ;

$G(x, m, t) = G^+ - G^-$ be the net generation of cells (where G^+ represents birth and G^- represents death);

$v (= dm/dt)$ be the growth rate of an individual cell in a uniform medium of constant composition.

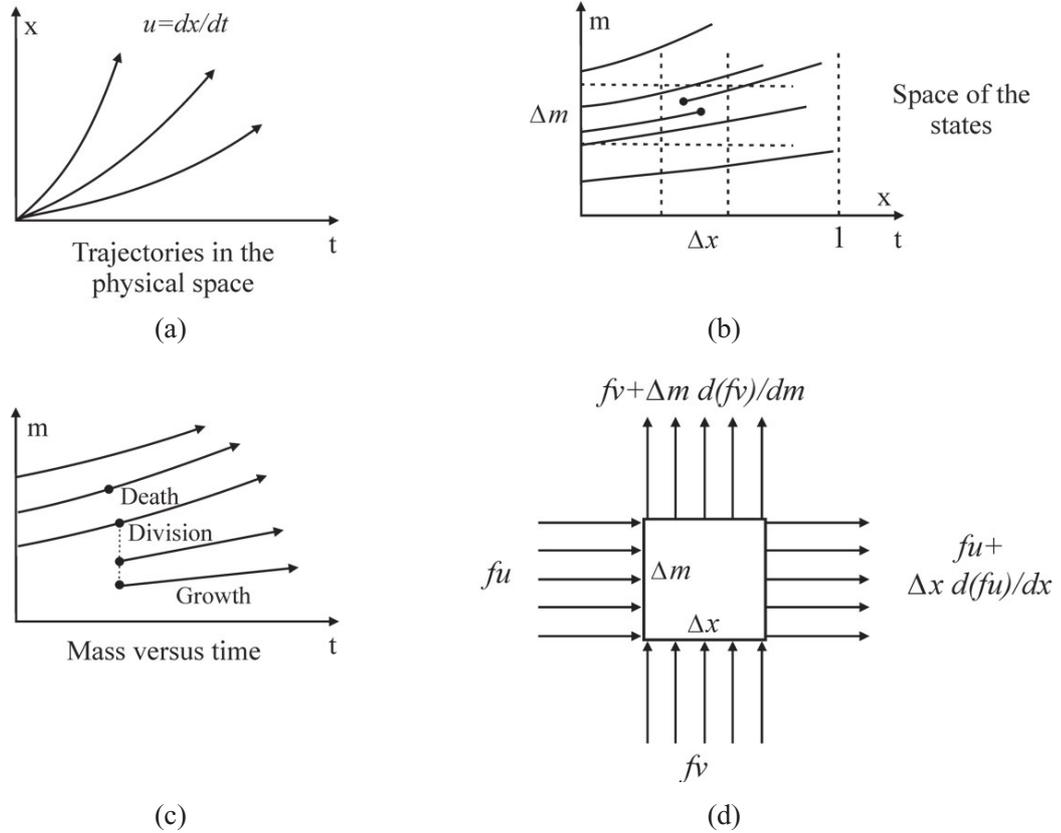


Figure 3.6. Illustration of the basis for establishing a population balance.

The mass balance for the cells in the (x, m, t) space is thus given by

$$\begin{aligned}
 \Delta f \Delta m \Delta x = & [(fv)|_m - (fv)|_{m+\Delta m}] \Delta x \Delta t + [(fu)|_x - (fu)|_{x+\Delta x}] \\
 \text{acc} & \qquad \qquad \text{net "growth"} & \qquad \qquad \text{net "inflow"} \\
 & \times \Delta m \Delta t + G \Delta x \Delta m \Delta t. \\
 & \qquad \qquad \qquad \text{generation}
 \end{aligned}$$

Taking the limit as $\Delta m \Delta x \Delta t \rightarrow 0$, we obtain

$$\frac{\partial f}{\partial t} = -\frac{\partial(fv)}{\partial m} - \frac{\partial(fu)}{\partial x} + G. \tag{3.7}$$

This equation is readily generalized to three spatial dimensions by replacing the term $\partial(fu)/\partial x$ by $\nabla \cdot (fu)$.

There is a growing interest in what is, somewhat misleadingly, called “multidimensional” population balance models. One example of a “2D” PB model is the description of a granulation process where not only the particle size distribution with time, but also the fractional binder content is predicted by the model. The binder (liquid) content of the granules governs the agglomeration process.

General 3D microscopic population balance equations, including several distributed properties, e.g. size and moisture content, can be derived using the same balance method.

Let us denote the distributed properties by p_i , where v_i is their respective rate of change ($v_i = dp_i/dt$). The local population balance equation then becomes

$$\frac{\partial f}{\partial t} = - \sum_{i=1}^n \frac{\partial(f v_i)}{\partial p_i} - \nabla \cdot (f u) + G. \quad (3.8)$$

In the case of granulation, there will now be two terms in the sum on the right-hand side of the equation: one associated with granule growth, and one associated with change in liquid content.

Note that particle velocity may differ from the fluid velocity due to slip or external forces.

In cases where diffusion cannot be neglected, the additional term $\nabla \cdot [D_p \nabla f]$ must be included in [Equation 3.8](#):

$$\frac{\partial f}{\partial t} = - \sum_{i=1}^n \frac{\partial(f v_i)}{\partial p_i} - \nabla \cdot (f u) + \nabla \cdot [D_p \nabla f] + G. \quad (3.9)$$

Sometimes it is convenient to define a *macroscopic population balance* by averaging over the physical space and over the inlet and outlet streams. Let us define

$$\begin{aligned} \langle f \rangle &= \frac{1}{V} \iiint_v f dV, \\ Q_{in} f_{in} &= \iint_{in} u f dS, \\ Q_{out} f_{out} &= \iint_{out} u f dS. \end{aligned}$$

Integrating [Equation \(3.8\)](#) over space and dividing by V (note that V is not necessarily constant with time) yields

$$\frac{1}{V} \frac{\partial(V \langle f \rangle)}{\partial t} = - \sum_{i=1}^n \frac{\partial(\langle f v_i \rangle)}{\partial p_i} - \frac{1}{V} (Q_{out} f_{out} - Q_{in} f_{in}) + \langle G \rangle. \quad (3.10)$$

Equation (3.10) can, of course, be derived directly using a macroscopic control volume.

3.4.1 Application to RTDs

The concept of residence time distributions (RTDs) is central to classical chemical engineering. In this concept, the outlet response of a system to a known input disturbance (i.e. tracer concentration) is analyzed. Relations are derived for the outlet age distribution using material balances. In the following, we will demonstrate that identical relations are obtained via a completely different route using population balances.

Let us consider the age of fluid “particles” in an arbitrary flow system (no generation). If we denote age by α , the growth rate of age is given by

$$v = \frac{d\alpha}{dt} = 1. \quad (3.11)$$

Let f be the number of fluid particles of age α . Equation (3.10) for this case becomes

$$\frac{1}{V} \frac{\partial(V\langle f \rangle)}{\partial t} = -\frac{\partial\langle f \rangle}{\partial\alpha} - \frac{1}{V}(Q_{out}f_{out} - Q_{in}f_{in}). \quad (3.12)$$

Define the normalized distributions:

$$\begin{aligned} \langle f_n \rangle &= \langle f \rangle / \langle C \rangle, \\ f_{in,n} &= f_{in} / C_{in}, \\ f_{out,n} &= f_{out} / C_{out}, \end{aligned}$$

where $\langle C \rangle$, C_{in} , and C_{out} are the mean concentration, and the inlet and outlet concentrations, respectively.

Insertion of these definitions into Equation (3.12) and using the mass balance,

$$\frac{\partial(V\langle C \rangle)}{\partial t} = Q_{in}C_{in} - Q_{out}C_{out}, \quad (3.13)$$

yields

$$\frac{\partial\langle f_n \rangle}{\partial t} = -\frac{\partial\langle f_n \rangle}{\partial\alpha} - \langle f_n \rangle \left(\frac{1}{\tau_{in}^1} - \frac{1}{\tau_{out}^1} \right) - \left(\frac{f_{out,n}}{\tau_{out}^1} - \frac{f_{in,n}}{\tau_{in}^1} \right), \quad (3.14)$$

where τ^1 are characteristic hydrodynamic times defined on a molar (or mass) basis, and

$$\begin{aligned} \tau_{in}^1 &= (V\langle C \rangle) / Q_{in}C_{in}, \\ \tau_{out}^1 &= (V\langle C \rangle) / Q_{out}C_{out}. \end{aligned}$$

Using standard RTD nomenclature:

$\langle f_n \rangle$ is the normalized internal age distribution, $I(\alpha, t)$,
 $f_{out,n}$ is the distribution of age in the outlet stream, $E(\alpha, t)$,
 $f_{in,n}$ is the normalized distribution of age in the inlet stream, i.e. $\delta(\alpha)$ (Dirac's delta function).

Consequently, Equation (3.14) may be written as follows:

$$\frac{\partial I}{\partial t} = -\frac{\partial I}{\partial\alpha} - I \left(\frac{1}{\tau_{in}^1} - \frac{1}{\tau_{out}^1} \right) - \left(\frac{E}{\tau_{out}^1} - \frac{\delta(\alpha)}{\tau_{in}^1} \right). \quad (3.15)$$

Equation (3.15) is the generalized relationship between the residence time distribution, E , and the internal age distribution, I , in the transient state for an arbitrary flow system.

For an incompressible fluid (given a constant volume),

$$Q_{in} = Q_{out}.$$

Assuming further steady state:

$$C_{in} = C_{out}$$

and

$$\tau_{in}^1 = \tau_{out}^1 = \tau^1.$$

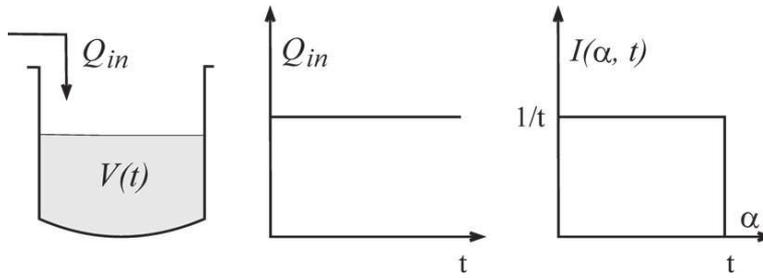


Figure 3.7. Internal age distribution in a semi-batch reactor.

Equation (3.15) simplifies to

$$\tau^1 \frac{dI}{d\alpha} + E = \delta(\alpha). \quad (3.16)$$

Example 3.5 Semi-batch reactor (incompressible)

Let us consider a single incompressible fluid that is poured into the reactor at a constant flow rate Q_{in} (see Figure 3.7). Since there is no outlet stream, $E = 1/\tau_{out}^1 = 0$. The inlet hydrodynamic time is given by

$$\tau_{in}^1 = V/Q_{in} = t Q_{in}/Q_{in} = t,$$

and Equation (3.12) reduces to

$$\frac{\partial I}{\partial t} = -\frac{\partial I}{\partial \alpha} - \frac{I}{t} + \frac{\delta(\alpha)}{t}.$$

The solution of this equation is

$$I(\alpha, t) = \frac{1}{t}(H(\alpha) - H(t - \alpha)),$$

where H is the Heaviside step function.

From this result, we can deduce the following:

- the ages are less than t (luckily!);
- the fraction of fluid particles of age between α and $\alpha + d\alpha$ is the volume $dV = Q_{in} d\alpha$ poured at $t - \alpha$ divided by the volume $V = Q_{in}t$ of fluid at time t .

Consequently,

$$I d\alpha = dV/V = d\alpha/t.$$

3.5 Questions

- (1) What are the key steps in deriving a transport phenomena model?
- (2) What does a generic balance equation describe?
- (3) Explain what is meant by a boundary condition, and how they can be classified.

- (4) What is the difference between a balance and a conservation principle?
- (5) What is a population balance?
- (6) What is the balanceable property in residence time distributions?

3.6 Practice problems

- 3.1** A spherical nuclear fuel element consists of a sphere of fissionable material with radius R_F , surrounded by a spherical shell of aluminum cladding with outer radius R_C . Fission fragments with very high kinetic energies are produced inside the fuel element. Collision between these fragments and the atoms of the fissionable material provide the major source of thermal energy in the reactor. The volume source of thermal energy, in the fissionable material, is assumed to be

$$S_n = S_{n0} \left(1 + b \left(\frac{r}{R_F} \right)^2 \right) \text{ (J/m}^3, \text{ s)},$$

where b is a constant between 0 and 1, and $S_n = 0$ for $r > R_F$

Derive a model for heat flux and temperature profile at steady conditions. Assume constant temperature T_0 at the outer surface.

- 3.2** It is possible to increase the energy transfer between a surface and an adjacent fluid by increasing the surface area in contact with the fluid. This may be accomplished by attaching metal fins to the surface (See Figure P3.1) Derive, using a shell balance, a stationary model for the heat transfer in a single fin. The wall temperature is T_0 and the surrounding fluid is at temperature T_∞ . Radial temperature variations in the fin can be neglected, and the convective heat transfer coefficient, h , is given.

The cross-sectional area A and circumference P vary with distance from the wall according to $A = A(x)$ and $P = P(x)$.

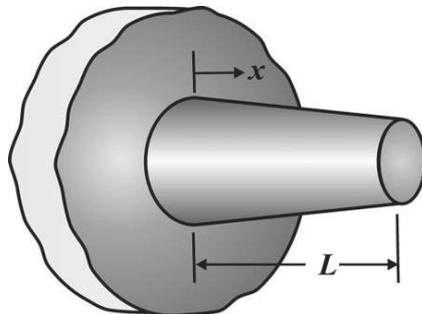


Figure P3.1

- 3.3** In the Liseberg Amusement Park in Gothenburg, there is a “fountain” where a water film flows along the outside of a vertical pipe. Derive a model for the velocity profile in the film:
- (a) by using a shell balance approach;
- (b) by simplifying the general momentum transport equation.

- 3.4** In making tunnels in the ground (porous material), water infiltration is a complicating factor. Assume a cylindrical tunnel (see Figure P3.2) with $P_1 > P_0$. Formulate a model that can be used to calculate the flow into the tunnel. Assume that Darcy's law is valid.

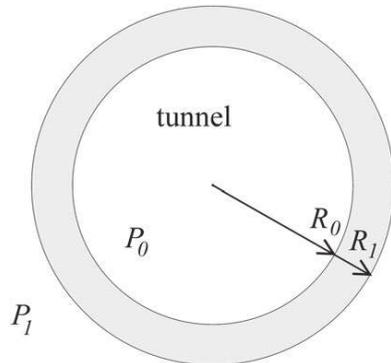


Figure P3.2

- 3.5** Around 1850, Fick conducted experiments that convinced him of the correctness of the diffusion equation. He dissolved salt crystals at the bottom of the experimental setups shown in Figure P3.3. The water in the top section was continually renewed to fix the concentration at zero. What concentration profiles did Fick obtain in the lower section at steady conditions?

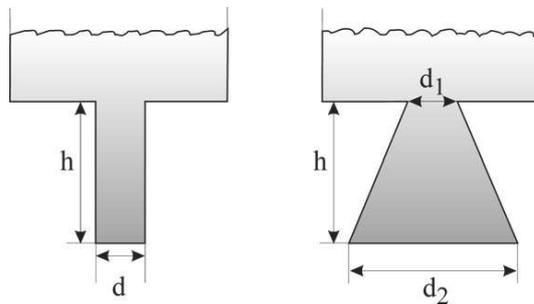


Figure P3.3

- 3.6** A fluid flows in the positive x -direction through a long flat duct of length L , width W , and thickness B , where $L \gg W \gg B$ (see Figure P3.4). The duct has porous walls at $y = 0$ and $y = B$, so that a constant cross flow can be maintained, with $v_y = v_0$. Derive, by simplifying the general transport equation, a steady-state model for the velocity distribution $v_x(y)$.

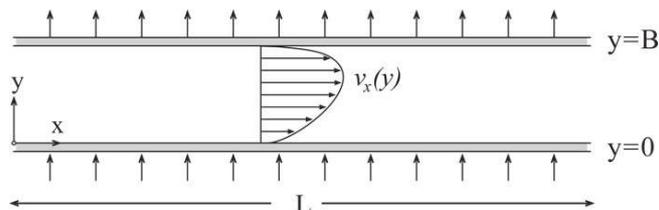


Figure P3.4

- 3.7** Consider two concentric porous spherical shells of radii κR and R (see Figure P3.5). The inner surface of the outer shell is kept at temperature T_1 and the outer surface of the inner shell is to be maintained at a lower temperature T_κ . Dry air

(mass flow w_r kg/s) at temperature T_κ is blown radially from the inner shell into the intervening space and out through the outer shell.

Develop, using a shell balance, an expression for the temperature at steady conditions. In addition, give an expression for the rate of heat removal from the inner sphere. Assume steady laminar flow.

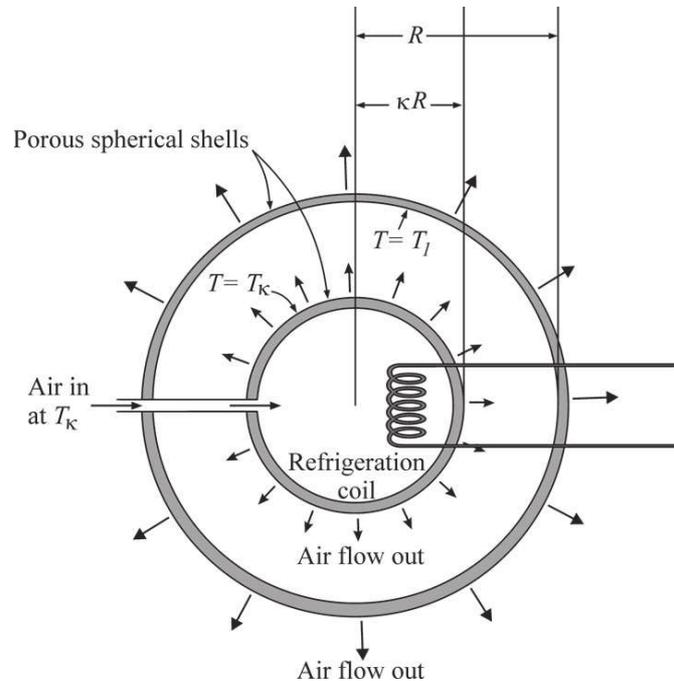


Figure P3.5

- 3.8** A liquid (B) is flowing at laminar conditions down a vertical wall (see Figure P3.6). For $z < 0$ the wall does not dissolve in the fluid, but for $0 < z < L$ the wall contains a species A that is slightly soluble in B. Develop a mathematical model for the dissolution process.

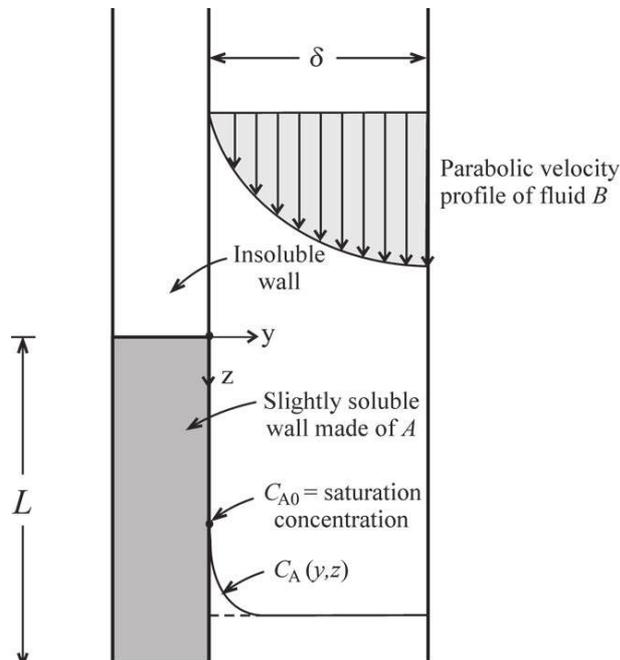


Figure P3.6

- 3.9** In a cookbook, a “gentle” way of preparing fish is suggested (a fish is ready when the temperature is around 60 °C).

A pan is filled with water that is boiled. The pan is then taken from the stove and put upon a heat-insulating material. Thereafter the piece of fish is placed into the pan and the lid is put on.

State a model for the process, assuming the following:

the piece of fish is “spherical” and initially at room temperature;
the water in the pan is well mixed.

- 3.10** Develop a model for the freezing of a spherical falling water drop (see Figure P3.7). The drop is surrounded by cool air at temperature T_∞ and its initial temperature is T_i ($>$ freezing temperature T_0). Assume no volume change in the freezing process.

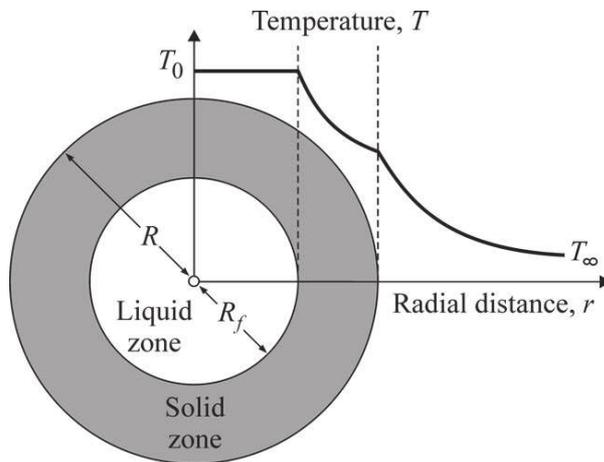


Figure P3.7

- 3.11** Chlorine dioxide (ClO_2) is a common chemical for bleaching aqueous suspensions of wood pulp. The ClO_2 reacts rapidly and irreversibly with lignin, which constitutes about 5% of the pulp; the remainder of the pulp (predominantly cellulose) is inert with respect to ClO_2 . In addition to its reaction with lignin, ClO_2 also undergoes a slow spontaneous decomposition. The bleaching process may be studied under simplified conditions by assuming a water-filled mat of pulp fibers exposed to a dilute aqueous solution of ClO_2 (see Figure P3.8). The solution–mat interface is at $x = 0$ and the thickness of the mat is taken to be infinite. As ClO_2 diffuses in and reacts, the boundary between brown (unbleached) and white (bleached) pulp moves away from the interface, the location of that boundary being denoted by $x = \delta(t)$. Assuming the reaction between ClO_2 and lignin to be “infinitely” fast, a sharp moving boundary is formed separating bleached and unbleached pulp. The concentration of ClO_2 at $x = 0$ is constant, C_{A0} , and the unbleached lignin concentration is C_{B0} . Lignin is a component of the pulp fibres and may be regarded as immobile. The decomposition of ClO_2 is assumed to be as a first-order chemical reaction.

Develop a model of the process.

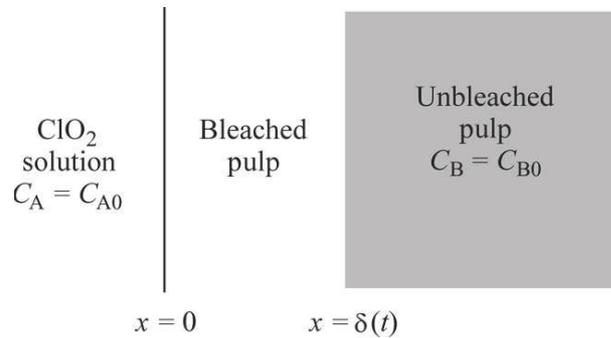


Figure P3.8

- 3.12** Erik released two newly born rabbits on the island of Tistlarna in the archipelago of Gothenburg during the summer. Now it is autumn, and he wonders how many rabbits there will be in five years.

Help Erik to solve this problem, assuming that rabbits are born pair-wise (one female and one male) and that the number of pairs follows the Fibonacci sequence: 1, 1, 2, 3, 5, 8, ... (every number in the series is the sum of its two predecessors). Assume further that the death frequency is given by

$$\text{deathfrequency}(\text{age}) = a \cdot \text{age}^2 - b \cdot \text{age} + c[\text{yr}^{-1}].$$

Develop a model, giving how many rabbits there are as a function of time, as well as the age distribution of the rabbits. Calculate the number of rabbits after five years by solving the discretized problem with time step 1 yr, $a = 0.015$, $b = 0.1$, and $c = 0.3$.

- 3.13** Formulate a population balance for the number of crystals with “characteristic” dimension (size), assuming:
- the crystallizer is operating at steady conditions and is well mixed (tank volume = V);
 - the flow-rate through the reactor is constant ($= Q$) and the inflow contains no crystals;
 - the growth rate is v (m/s);
 - agglomeration and breakage of crystals can be neglected.
- 3.14** Use the method of population balances to develop expressions for the RTDs in the following reactor systems:
- (a) ideal tank reactor with volume V , constant flow rate q , and no chemical reaction;
 - (b) as in (a) but in series with an ideal tube reactor with volume V_1 ;
 - (c) two ideal tank reactors in series (both with volume V).