

Chapter 1

Model Formulation

An engineering model is a symbolic object, usually one or more equations, which describe a given physical situation. The essence of engineering modeling is to capture the important aspects of the physical reality while discarding irrelevant detail. Engineering models are therefore not judged by whether they are “true” or “false”, but by how well they describe the situation in question. It may therefore often be possible to devise several different models of the same physical reality and one can pick and choose among these depending on the desired model accuracy and on their ease of analysis. One can argue that engineering models are nothing but curve fits, although the fitting functions are most often given implicitly via differential equations and are restricted to those functions that satisfy the relevant constitutive equations and laws of nature.

It is assumed that the reader of this book has already taken the traditional chemical engineering transport classes, i.e. fluid mechanics and heat and mass transfer as well as an introductory reaction kinetics class. So, although this chapter does briefly review much of this theory, it is not intended to cover these topics in depth but simply to refresh the reader’s memory concerning transport and kinetics, to establish a nomenclature and vocabulary and, primarily of course, to provide the reader with additional training in formulating mathematical models. This training will be accomplished through a large number of examples and comments regarding the salient points of the examples.

1.1 Classical models

Most mathematical modeling problems in chemical engineering at some point make use of a conservation or balance equation of the form

$$\text{rate in} - \text{rate out} = \text{rate of accumulation} - \text{rate of production} + \text{rate of consumption}$$

or shorter

in - out = accumulation - generation

in which formulation the generation term can be either positive or negative. A balance equation can be written for anything that satisfies some conservation law such as moles, thermal energy or numbers of some object. For extensive variables, in other words. Balance equations cannot be written for intensive variables such as concentration, temperature or pressure although these are the variables that usually end up as the unknowns in the model.

Balance equations are written over a well defined control volume (CV). The control volume can be a physical volume such as the volume of a vessel, an abstract volume such as a range of ages in age space or a volume of some defined amount of matter, matter which may even split into separate parts with time as it passes through a process. In the latter case, one usually refers to it as a basis rather than as a control volume. A control volume need not be fixed in space or have a fixed shape or physical volume, although this often is the case. Evidently the control volume must be clearly and unambiguously defined, usually done by specifying the surface of the control volume, and model errors occasionally occur because the modeler is confused about what exactly the control volume is. Picking the “best” control volume is an important step in model formulation. Any control volume is in principle correct, but some are more convenient than other in the sense that they give models that are easier to solve.

The “in” and “out” terms in the balance equation refer to the rates of transport, often called the fluxes, of the conserved variable across the control volume surface. Transport across the **entire** surface must be accounted for and modeling errors often occur when one or several fluxes are left out or forgotten.

The generation terms accounts for production or consumption via chemical reactions or other processes such as nuclear reactions.

1.1.1 Macroscopic balances

Macroscopic balances are balances on control volumes that are larger than differential volumes, usually process vessels and containers.

1.1.1.1 Mass and energy balances

In simple cases involving only process streams, the rates “in” and “out” of a variable are the flow rates of the process streams multiplied by their concentrations, energy density or some other intensive variable.

A simple steady state model of a recycle reactor is considered in the first example. The example serves to illustrate the use of control volumes for formulating model equations and introduces the concept of a complete model. A model is said to be complete or closed if it has enough equations to allow one to solve, in principle at least, for the unknowns. From a practical point, this means that a model must

have at least as many equations as unknowns. For complicated models, one may not be able to find an analytical solution but, from various mathematical theorems, a solution can be shown to exist and it can be found using numerical methods. The example illustrates the point that, in general, balance equations alone are insufficient for a complete model and that additional equations must be obtained from other sources.

Example 1.1: Steady State Balances on Recycle Reactor.

The reactor to be considered is sketched in Fig. 1.1. The reactor inlet stream is made by mixing the process feed stream and a recycle stream. The outlet stream from the reactor is separated into a product stream and a side stream, and the latter is split into a recycle stream and a purge. All flow rates are molar flow rates and are indicated by F 's. Composition is given in terms of mole fractions, indicated by ω 's.

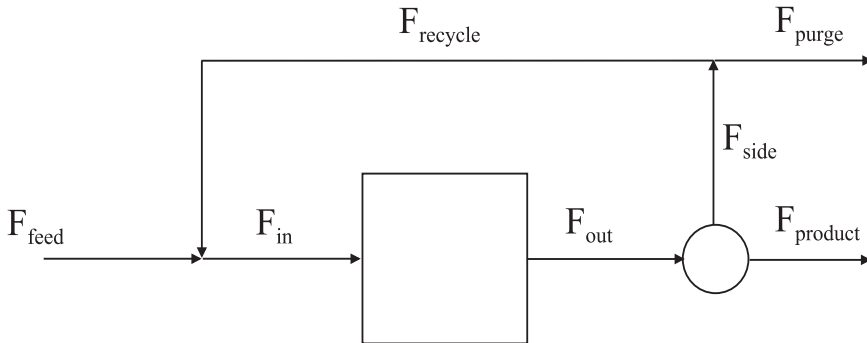
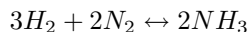


Fig. 1.1 Recycle Reactor.

The feed to the process consists of H_2 , N_2 and an inert called I . The mole fractions in the feed are $\omega_{H_2, \text{feed}} = 0.69$, $\omega_{N_2, \text{feed}} = 0.23$ and $\omega_{I, \text{feed}} = 0.08$. In the reactor the hydrogen and nitrogen are converted to ammonia by



and we seek a model which will allow us to determine the composition and magnitude of the product stream as a function of the recycle ratio $\alpha = F_{\text{recycle}}/F_{\text{feed}}$.

The first problem one is faced with when writing a model is to make sure that there is enough information available to even make this possible. Clearly, this is not yet the case for this reactor. Obviously, one must specify something about how much ammonia is formed in the reactor and something about how the components are partitioned between the product and side stream in the separator. We will eschew complicated reactor models at this time and assume that 90% of the hydrogen that enters the reactor is converted to ammonia. Thus, the hydrogen balance over the reactor is

$$0.1F_{\text{in}}\omega_{H_2, \text{in}} = F_{\text{out}}\omega_{H_2, \text{out}}$$

For the separator, we will assume that it separates the ammonia completely from the remaining compounds so that the product stream is pure ammonia, $\omega_{NH_3\text{productst}} = 1$, and the side stream contains no ammonia.

There are a large number of control volumes that can now be used. Some of these are depicted by the ovals in Fig. 1.2. Number 1 is a CV around the mixing point of the feed stream and the recycle stream. These two streams represent the “in” terms in the balances over this CV, and the reactor inlet stream, represents the “out” term in the balance. Number 2 is the reactor, number 3 the separator, number 4 the splitter and number 5 the entire process. Other control volumes are possible such as the reactor plus the separator, the separator plus the splitter etc.

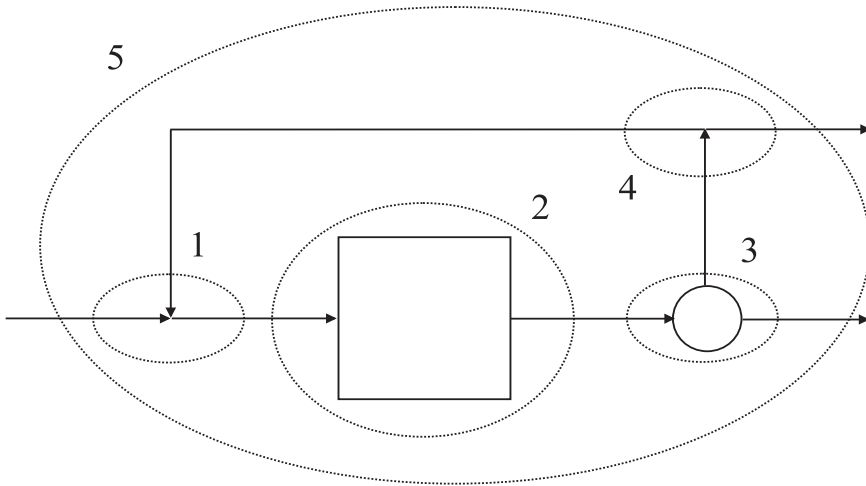


Fig. 1.2 Some of the possible control volumes that can be used to write balance equations on the recycle reactor.

Three types of balances can be written over these control volumes: elemental balances, compound balances and, when there is no reaction inside the control volume, total mole balances. The elemental balances and the total mole balances are the easiest to write since they are independent of the reactions that take place but they can never suffice for a model precisely because they do not capture any information about the chemical reactions and at least 1 component balance over a CV enclosing the reactor is required. Similarly, at least one of the model equation must capture information about the performance of the separator, one equation must capture information about the feed stream and its composition and one equation must capture information about the stoichiometry of the reaction.

One can mindlessly start writing all possible balances over all possible control volumes but this wastes a lot of effort because many of the balances will be dependent upon one another. For instance, the total mole balances on the separator

and the splitter are

$$F_{\text{out}} = F_{\text{side}} + F_{\text{products}}$$

$$F_{\text{side}} = F_{\text{purge}} + F_{\text{recycle}}$$

and summing these gives the total mole balance over the control volume which encloses the separator and the splitter

$$F_{\text{out}} = F_{\text{purge}} + F_{\text{recycle}} + F_{\text{products}}$$

this balance is therefore not independent of the balances over the separator and splitter and one of the three balances is therefore of no use.

It is better to start with the simplest balances and work backwards until one has a complete model. The challenge is to recognize how to get to that point the easiest way possible.

Two equations of the model are essentially given already. That is the specified recycle ratio α , from which

$$F_{\text{recycle}} = \alpha F_{\text{feed}} \quad (1.1)$$

and the equation for conversion of hydrogen over the reactor

$$0.1F_{\text{in}}\omega_{H_2,\text{in}} = F_{\text{out}}\omega_{H_2,\text{out}} \quad (1.2)$$

According to the stoichiometry of the reaction, 3 moles of hydrogen are consumed for each mole of nitrogen consumed. Since the feed contains hydrogen and nitrogen in this ratio, this ratio will remain 3-to-1 at all points in the system and it follows that 90% of the nitrogen in the reactor inlet must also be converted in the reactor. Thus, a nitrogen balance over the reactor is

$$0.1F_{\text{in}}\omega_{N_2,\text{in}} = F_{\text{out}}\omega_{N_2,\text{out}} \quad (1.3)$$

Notice that the mole fractions appear in identical ways in the hydrogen and nitrogen balances. This is only possible because the feed to the process contains hydrogen and nitrogen in the proper stoichiometric ratio for formation of ammonia. A different feed composition would have made these two balances very different in appearance.

Since the unknown we want to find is the magnitude of the product stream (its composition has been specified as pure ammonia) it makes sense to let the next equation in the model be an equation for this variable. The simplest equation is a total mole balance over the separator.

$$F_{\text{out}} = F_{\text{side}} + F_{\text{product}} \quad (1.4)$$

Two more easy equations are obtained from the total mole balances over the CVs that do not enclose chemical reactions, the splitter and the mixing point.

$$F_{\text{side}} = F_{\text{purge}} + F_{\text{recycle}} \quad (1.5)$$

$$F_{\text{feed}} + F_{\text{recycle}} = F_{\text{in}} \quad (1.6)$$

which gives 6 equations with 10 unknowns, F_{recycle} , F_{side} , F_{purge} , F_{out} , F_{in} , F_{product} , $\omega_{H_2,\text{in}}$, $\omega_{H_2,\text{out}}$, $\omega_{N_2,\text{in}}$ and $\omega_{N_2,\text{out}}$. The inert balance over the reactor provides another equation

$$F_{\text{in}}\omega_{I,\text{in}} = F_{\text{out}}\omega_{I,\text{out}} \quad (1.7)$$

as does the ammonia balance, which states that the moles of ammonia leaving the reactor is the amount entering plus the amount formed.

$$F_{\text{in}}\omega_{NH_3,\text{in}} + 2 \cdot 0.9 \cdot F_{\text{in}}\omega_{N_2,\text{in}} = F_{\text{out}}\omega_{NH_3,\text{out}}$$

However, as all the ammonia formed is removed in the separator, the recycle stream is ammonia free and thus $\omega_{NH_3,\text{in}} = 0$. The ammonia balance therefore simplifies to

$$2 \cdot 0.9 \cdot F_{\text{in}}\omega_{N_2,\text{in}} = F_{\text{out}}\omega_{NH_3,\text{out}} \quad (1.8)$$

The model now has 8 equations and 13 unknowns. We have still not made use of the information about the composition of the feed stream. This information can be included by writing a balance over the mixing point. The inert balance is the simplest.

$$0.08F_{\text{feed}} + F_{\text{recycle}}\omega_{I,\text{recycle}} = F_{\text{in}}\omega_{I,\text{in}} \quad (1.9)$$

which add another unknown, $\omega_{I,\text{recycle}}$ for a total of 9 equations with 14 unknowns.

To keep the model as simple as possible, one should look for additional equations that do not introduce new unknowns. An obvious source, but for some reason often overlooked, comes from the fact that the mole fractions in a stream sum to 1. This gives three additional equations, one for the reactor inlet, one for the reactor outlet and one for the recycle stream (which has the same composition as the purge stream). Only the first two do not introduce new unknowns, while the equation for the recycle stream introduces two additional unknowns $\omega_{H_2,\text{recycle}}$ and $\omega_{N_2,\text{recycle}}$.

$$\omega_{H_2,\text{in}} + \omega_{N_2,\text{in}} + \omega_{I,\text{in}} = 1 \quad (1.10)$$

$$\omega_{H_2,\text{out}} + \omega_{N_2,\text{out}} + \omega_{NH_3,\text{out}} + \omega_{I,\text{out}} = 1 \quad (1.11)$$

$$\omega_{I,\text{recycle}} + \omega_{H_2,\text{recycle}} + \omega_{N_2,\text{recycle}} = 1 \quad (1.12)$$

These three equations must always be satisfied and must be included in the model to make it complete. They could have been stated at the very beginning. The two new unknowns $\omega_{H_2,\text{recycle}}$ and $\omega_{N_2,\text{recycle}}$ are related by the fact that the hydrogen-to-nitrogen ratio equals 3 in all streams.

$$\omega_{H_2,\text{recycle}} = 3\omega_{N_2,\text{recycle}} \quad (1.13)$$

Three possible additional equations that do not introduce new unknowns are the ammonia balance over the separator

$$F_{\text{product}} = F_{\text{out}}\omega_{NH_3,\text{out}} \quad (1.14)$$

the inert balance over the separator.

$$F_{\text{out}}\omega_{I,\text{out}} = F_{\text{side}}\omega_{I,\text{recycle}} \quad (1.15)$$

and a total hydrogen balance over the entire process.

$$0.69F_{\text{feed}} = F_{\text{purge}}\omega_{H_2,\text{recycle}} + \frac{3}{2}F_{\text{product}} \quad (1.16)$$

Equation 1.1 through 1.16 constitute the model, 16 nonlinear algebraic equations with 16 unknowns. Some of the equations are arbitrary in the sense that they can be replaced by other balances while other, such as the equations for the sum of the mole fractions, must be included in the model. The model certainly looks cumbersome but it can be solved with a bit of effort, thereby confirming that the model is complete or well posed. The solution is

$$F_{\text{product}} = \frac{146\alpha + 189\alpha^2 - 43 \pm (1 + \alpha)\sqrt{50625\alpha^2 - 1350\alpha + 1849}}{182\alpha + 225\alpha^2 - 43 \pm (1 + \alpha)\sqrt{50625\alpha^2 - 1350\alpha + 1849}} \frac{F_{\text{feed}}}{2}$$

$$F_{\text{recycle}} = \alpha F_{\text{feed}}$$

$$F_{\text{in}} = F_{\text{feed}}(1 + \alpha)$$

$$F_{\text{purge}} = \frac{36}{225\alpha - 43 \pm \sqrt{50625\alpha^2 - 1350\alpha + 1849}} \alpha F_{\text{feed}}$$

$$F_{\text{side}} = \frac{225\alpha - 7 \pm \sqrt{50625\alpha^2 - 1350\alpha + 1849}}{225\alpha - 43 \pm \sqrt{50625\alpha^2 - 1350\alpha + 1849}} \alpha F_{\text{feed}}$$

$$F_{\text{out}} = \frac{450\alpha^2 + 175\alpha \pm (2\alpha + 1)\sqrt{50625\alpha^2 - 1350\alpha + 1849} - 43}{225\alpha - 43 \pm \sqrt{50625\alpha^2 - 1350\alpha + 1849}} \frac{F_{\text{feed}}}{2}$$

The result for the mole fraction can be expressed most compactly in terms of the molar flow rates

$$\omega_{I,\text{in}} = \frac{9F_{\text{out}} - 11F_{\text{product}}}{9F_{\text{in}}}$$

$$\omega_{I,\text{out}} = \frac{9F_{\text{out}} - 11F_{\text{product}}}{9F_{\text{out}}}$$

$$\omega_{I,\text{recycle}} = \frac{9F_{\text{out}} - 11F_{\text{product}}}{9F_{\text{side}}}$$

$$\omega_{N_2,\text{in}} = \frac{5F_{\text{product}}}{9F_{\text{in}}}$$

$$\omega_{N_2, \text{out}} = \frac{F_{\text{product}}}{18F_{\text{out}}}$$

$$\omega_{N_2, \text{recycle}} = \frac{9F_{\text{side}} + 11F_{\text{product}} - 9F_{\text{out}}}{36F_{\text{side}}}$$

$$\omega_{H_2, \text{in}} = \frac{2F_{\text{product}} - 3F_{\text{out}} + 3F_{\text{in}}}{3F_{\text{in}}}$$

$$\omega_{H_2, \text{out}} = \frac{F_{\text{product}}}{6F_{\text{out}}}$$

$$\omega_{H_2, \text{recycle}} = \frac{9F_{\text{side}} + 11F_{\text{product}} - 9F_{\text{out}}}{12F_{\text{side}}}$$

$$\omega_{NH_3, \text{out}} = \frac{F_{\text{product}}}{F_{\text{out}}}$$

Notice that solution of the model equations at one step required finding the roots of a second order polynomial. Formally, there are therefore two solution. Although multiple valid solutions are possible when solving non linear algebraic models, quite often some of these solutions must be discarded because they are not physically meaningful. In this case, evaluating the result for various values of the recycle ration α will show that one of the solutions have values of mole fractions that are not between zero and one. Obviously, this solution must be discarded.

The next example is a transient balance on a mixing tank. The example illustrates how models can be simplified by fully or partially dedimensionalizing them.

Example 1.2: Transient balance on mixing tank.

The contraption shown in Fig. 1.3 is used to make so-called density gradients, which are used in separation of molecular species based on the density.

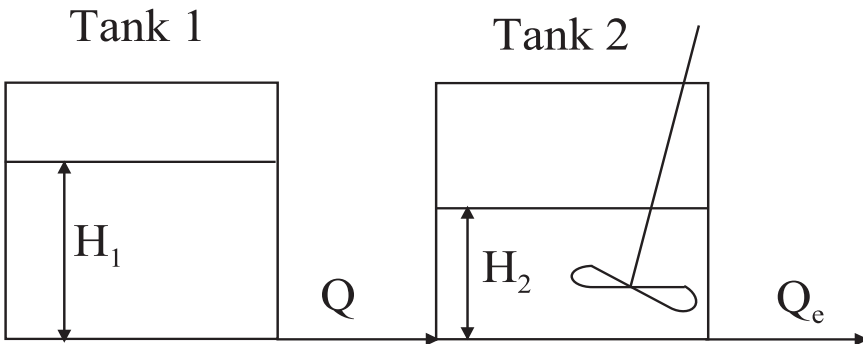


Fig. 1.3 Two connected mixing tanks used for making density gradients.

The device consists of two tanks. Tank 1 contains a less dense sucrose solution while tank 2 contains a more dense sucrose solution. A stream with volumetric flow rate Q_e is continuously withdrawn from tank 2. As the dense sucrose solution is removed from tank 2, it is replenished by the less dense solution from tank 1. The sucrose concentration in the exit stream therefore continues to drop and it can be layered carefully in a test tube to create the density gradient through the test tube. A thin layer of the mixture to be separated is then placed on top of the sucrose solution and the test tube is placed in a centrifuge. During centrifugation, the molecules in the sample will sediment through the sucrose density gradient until they reach steady state at a position where the density of the sucrose solution is equal to that of the molecule. The molecules in the sample are thus separated based on their density.

We will model the device for making the sucrose gradient and determine how the density of the exit stream depends on how the device is operated. The following assumptions will be used in the model.

- Tank 2 is well mixed, i.e. the concentration in the exit stream equals the concentration in tank 2.
- The two tanks are geometrically identical and the liquid volume in the tanks can be found as AH_n where A is the cross sectional area of the tanks and H_n the liquid level in tank n .
- The volumetric flow rate between the tanks can be expressed as $Q = (H_1 - H_2)/R$, where R is a constant resistance.

There are three unknowns in the problem, the two liquid levels, $H_1(t)$ and $H_2(t)$, and the sucrose concentration in tank 2, $C_2(t)$, so three equations are needed. Liquid volume balances on tank 1 and 2 gives

$$A \frac{dH_1}{dt} = -(H_1 - H_2)/R$$

$$A \frac{dH_2}{dt} = (H_1 - H_2)/R - Q_e$$

A sucrose balance on tank 2 gives

$$A \frac{dH_2 C_2}{dt} = C_1(H_1 - H_2)/R - C_2 Q_e$$

Notice that the accumulation terms, the time derivative, is the derivative of the total amount of sucrose inside tank 2, i.e. concentration times volume, not just concentration. Since the cross sectional area A is constant, it can be taken outside the derivative, but as the liquid height, H_2 , is a dependent variable, it cannot. The accumulation terms is therefore a derivative of a products. The model is easily simplified to the standard form for coupled ordinary differential equations with the derivatives of the dependent variables isolated on the left hand sides of the equations.

$$\frac{dH_1}{dt} = -\frac{H_1 - H_2}{AR}$$

$$\frac{dH_2}{dt} = \frac{H_1 - H_2}{AR} - \frac{Q_e}{A}$$

$$\frac{dC_2}{dt} = (C_1 - C_2) \frac{H_1 - H_2}{ARH_2}$$

and let the three initial conditions be

$$H_1(0) = H_2(0) = H, \quad C_2(0) = C_0$$

We can ask if the model can be simplified, in particular if the number of model parameters can be reduced, by making the equations fully or partially dimensionless. Doing so simplifies model analysis and solution although the effort may not be worth the while for model equations as simple as these. The model contains three parameters, A , R and Q_e , plus the values specified in the initial conditions. The product AR has dimension time and it therefore seems natural to define a dimensionless time, τ as

$$\tau = \frac{t}{AR}$$

From the chain rule, it then follows that

$$\frac{dH_1}{dt} = \frac{dH_1}{d\tau} \frac{d\tau}{dt} = \frac{1}{AR} \frac{dH_1}{d\tau}$$

Similarly for the other two derivatives. When substituted back into the model equations, these simplify to

$$\frac{dH_1}{d\tau} = H_2 - H_1$$

$$\frac{dH_2}{d\tau} = H_1 - H_2 - Q_e R$$

$$\frac{dC_2}{d\tau} = (C_1 - C_2) \frac{H_1 - H_2}{H_2}$$

Using the initial values, the following dimensionless dependent variables can be defined

$$h_1 = \frac{H_1}{H}, \quad h_2 = \frac{H_2}{H}, \quad c_1 = \frac{C_1}{C_0}, \quad c_2 = \frac{C_2}{C_0}$$

giving the fully dimensionless model

$$\frac{dh_1}{d\tau} = h_2 - h_1, \quad h_1(0) = 1$$

$$\frac{dh_2}{d\tau} = h_1 - h_2 - \frac{Q_e R}{H}, \quad h_2(0) = 1$$

$$\frac{dc_2}{d\tau} = (c_1 - c_2) \frac{h_1 - h_2}{h_2}, \quad c_2(0) = 1$$

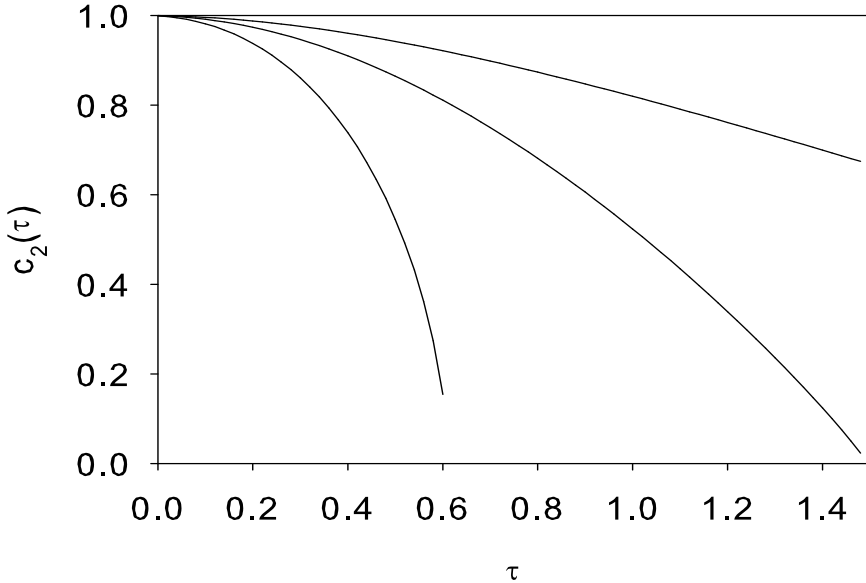


Fig. 1.4 Numerical solutions of the dimensionless sucrose concentration versus dimensionless time for $\frac{Q_e R}{H} = 0.5$ (top curve) 1 and 2 (bottom curve).

In this version, the model has only one parameter, the dimensionless group $\frac{Q_e R}{H}$. With the number of parameters this low, it is easier to e.g. plot or tabulate a numerical solution versus parameter values. Such a numerical solution is shown in Fig. 1.4 as a family of curves for different values of $\frac{Q_e R}{H}$. The concentration in tank 1 is assumed to be zero in all cases.

Although nonlinear, the model equations can in fact be partially solved. The two volume balances are linear and can be solved by methods that will be discussed later to give

$$h_1(\tau) = 1 + \frac{Q_e R}{H} \left(\frac{1}{4} - \frac{\tau}{2} - \frac{e^{-2\tau}}{4} \right)$$

$$h_2(\tau) = 1 + \frac{Q_e R}{H} \left(\frac{e^{-2\tau}}{4} - \frac{1}{4} - \frac{\tau}{2} \right)$$

Setting $c_1 = 0$ for simplicity and substituting the results for h_1 and h_2 into the dimensionless sucrose balance gives

$$\frac{1}{c_2} \frac{dc_2}{d\tau} = \frac{2 \frac{Q_e R}{H} (e^{-2\tau} - 1)}{\frac{Q_e R}{H} (e^{-2\tau} - 2\tau - 1) + 4}$$

which is a separable equation that can be solved subject to the initial condition $c_2(0) = 1$

$$\int_1^{c_2} \frac{1}{c} dc = \int_0^\tau \frac{2 \frac{Q_e R}{H} (e^{-2t} - 1)}{\frac{Q_e R}{H} (e^{-2t} - 2t - 1) + 4} dt \Rightarrow$$

$$c_2(\tau) = \exp \left(\int_0^\tau \frac{2 \frac{Q_e R}{H} (e^{-2t} - 1)}{\frac{Q_e R}{H} (e^{-2t} - 2t - 1) + 4} dt \right)$$

The solution is finished in the sense that the unknown has been isolated on one side of the equality sign but is unfinished in the sense that the integral on the right hand side does not have an explicit solution. Solutions containing unfinished expression of this type are often called *closed form solutions*, meaning that the unknown has been found in terms of some expression that is as simple as possible.

The next example, a continuous extraction unit, illustrates two things: writing balances on CVs which are not process vessels, but which change size with time and writing balances for which the “in” and “out” terms are not just process streams. The example also is a review of how to model interfacial mass transfer.

Example 1.3: Continuous extraction.

A continuous extraction process in which compounds are transferred between two phases, referred to as *I* and *II* respectively, is sketched in Fig. 1.5. The two exit streams are assumed to come from separation of a single stream but the separator will not be included explicitly in the model. The volumetric feed rates of the two phases are called $Q_{I,f}$ and $Q_{II,f}$ and are assumed known. To write the most general model possible, the solvents and solutes of the two streams will not be specified. Instead, **all** the compounds in phase *I*, irrespective of whether or not they are transferred between the phases, are labeled 1,2,3,.. etc. and their respective concentrations in phase *I* are indicated as C_n . Since the two phases appear perfectly symmetrically in this problem, the component balances on components in phase *II* will be identical in form to the balances on phase *I*, so we will not state these explicitly and therefore need not, at this point, introduce a nomenclature for the concentrations in phase *II*. The feed concentrations in stream *I* are called $C_{n,f}$ and are also assumed known. Finally, the total extractor volume, V , is assumed constant and known and the extractor and both phases in the extractor are assumed to be well mixed.

The unknowns in this problem are all the concentrations in both phases, the volumes of the two phases inside the extractor, V_I and V_{II} respectively, and the volumetric exit flow rates for both phases, Q_I and Q_{II} respectively.

The appropriate control volume for writing component balances is not the entire extractor, as one might initially expect, but the volume of each of the phases. A mole balance on compound n using the volume of phase *I* as control volume is

$$\frac{dV_I C_n}{dt} = Q_{I,f} C_{n,f} - Q_I C_n - R_n$$

Notice that the accumulation term on the left hand side is a derivative of the total number of moles of compound n , the product of the volume and the concentration.

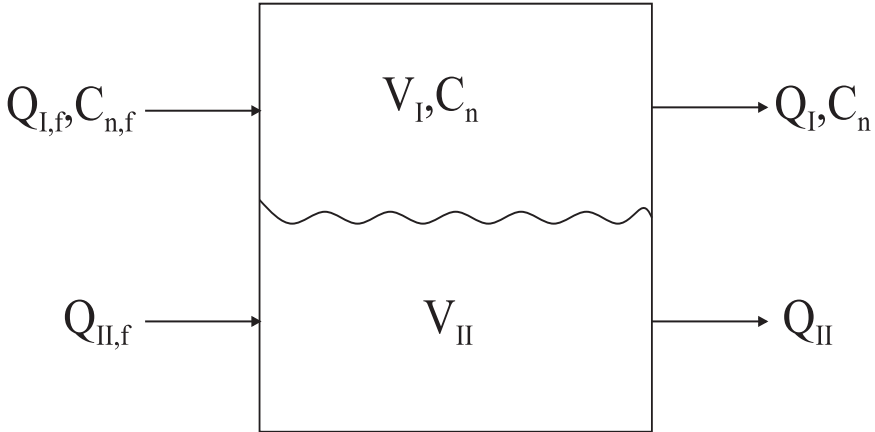


Fig. 1.5 Nomenclature for continuous extraction unit.

Since the volume of the phases may change with time, the physical volume of the control volume cannot be assumed constant and must appear inside the derivative.

The term R_n is the rate of transfer of compound n out of phase I to phase II . This transfer rate will be modeled using film theory. Simply put, in film theory, the bulk of the fluid is assumed well mixed, i.e. to have the same concentration, temperature and other physical properties throughout. However, close to an interphase the fluid is assumed stagnant, creating a film. The volume of the film is assumed negligible compared to the volume of the bulk fluid. Transfer across the film is by diffusion, conduction or some other non-convective mechanism. In the case of diffusion, the flux across the film, N , is described by means of a mass transfer coefficient, k_m , as $N = k_m \Delta C$ where ΔC is the concentration difference over the film, often referred to as *the driving force*. In the case of thermal conduction, the energy flux across the film is modeled by a similar equation using a heat transfer coefficient and a temperature difference as driving force.

The physical situation at the interface is shown in Fig. 1.6. In the well mixed bulk phases, the concentrations of the compound in question are C_I and C_{II} , respectively. Starting in phase I and moving towards the right, the concentration remains constant until the film is reached. Passing through the film, the concentration changes continuously until it reaches $C_{I,i}$ at the interface. At the interface, the concentration changes discontinuously as required by the equilibrium which will be modeled here by a linear expression as $C_{I,i} = KC_{II,i}$, where K is a partition coefficient. More complex equilibrium expressions can of course be used. Finally, the concentration in phase II changes through the film until, at the top of the film, the bulk concentration C_{II} is attained. Notice that the two films do not necessarily have the same thickness. Neither do they support the same concentration difference.

With this image established, we can model the flux through the film by using the interface as a control volume with zero physical volume. Since the CV or interface

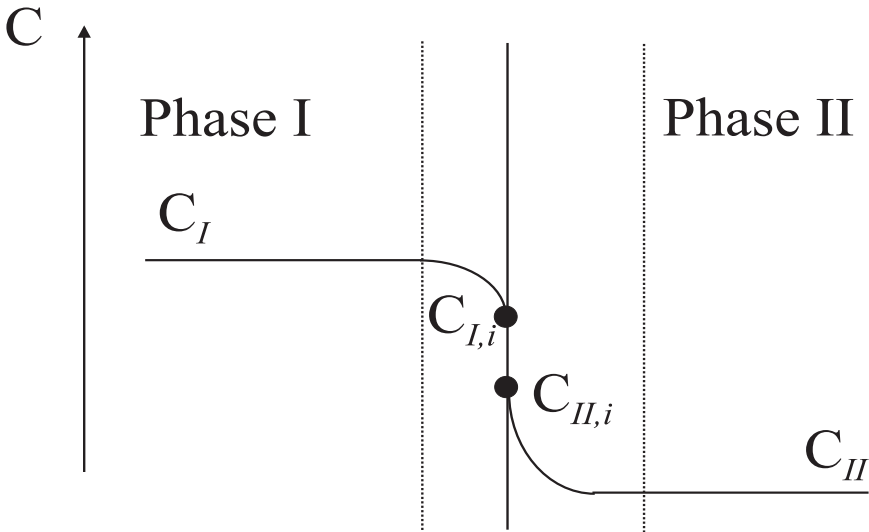


Fig. 1.6 Concentration of compound which is transferred between phase I and phase II. The interface between phase I and phase II is indicated by a solid line. The boundaries between the well mixed bulk fluids and the interfacial films are indicated by dotted lines.

has physical zero volume, there can be no accumulation taking place inside the CV and the balance simply states that the flux in equals the flux out. Modeling the fluxes through the two films by the respective single phase mass transfer coefficients, we get

$$N_n = k_{m,I}(C_I - C_{I,i}) = k_{m,II}(C_{II,i} - C_{II})$$

where N_n is the flux, mole per time per area, of compound n , from phase I to phase II. It remains to eliminate the unknown interfacial concentrations by introducing an overall mass transfer coefficient, k_m by

$$N_n = k_m(C_I - KC_{II}) \Rightarrow$$

$$\frac{N_n}{k_m} = C_I - C_{I,i} + KC_{II,i} - KC_{II} = \frac{N_n}{k_{m,I}} + \frac{KN_n}{k_{m,II}} \Rightarrow$$

$$\frac{1}{k_m} = \frac{1}{k_{m,I}} + \frac{K}{k_{m,II}}$$

The transfer rate, R_n , can therefore be written as

$$R_n = k_m(C_I - KC_{II})A = k_m(C_I - KC_{II})aV$$

where A is the total interfacial area in the extractor, usually expressed as the product of a , the specific interfacial area per volume, and V , the total volume of the vessel. This gives the final version of the component balance

$$\frac{dV_I C_n}{dt} = Q_{I,f} C_{n,f} - Q_I C_n - k_m(C_n - KC_{n,II})aV \Rightarrow$$

$$\frac{dC_n}{dt} = \frac{Q_{I,f}}{V_I} C_{n,f} - \frac{Q_I}{V_I} C_n - k_m (C_n - K C_{n,II}) \frac{aV}{V_I} - \frac{C_n}{V_I} \frac{dV_I}{dt}$$

A balance equation of this kind can be written for each compound. However, additional unknowns are the volumes of the two phases and the magnitude of the two exit streams. Four more equations are therefore needed for a complete model. Two of these are obvious. Since the total volume of the extractor is constant

$$V_I + V_{II} = V$$

and since the extractor is well mixed, the ratio of the exit volumetric flow rates must equal the ratio of the volumes of the two phases inside the extractor.

$$\frac{V_I}{V_{II}} = \frac{Q_I}{Q_{II}}$$

The remaining two equations are obtained from the mixing rules for the two phases. For ideal mixtures, the volume of the mixture is the sum over all components of the partial molar volumes multiplied by the number of moles, or

$$V_I = \sum v_n N_n = \sum v_n C_n V_I, \quad V_{II} = \sum v_n N_n = \sum v_n C_n V_{II}$$

where v_n is the partial molar volume of component n and N_n is the number of moles of component n in the phase.

Mixing rules for non-ideal mixtures can give complex equations and simpler models are often sufficient. A simple way to close the model without using mixing rules is to assume that the densities of the two phases, ρ_I and ρ_{II} are constant. Let the molecular weight of compound n be M_n , multiply each of the component balances found above by M_n and add them over all the compounds to get

$$\begin{aligned} \sum_{n=1}^N M_n \frac{dC_n}{dt} &= \frac{Q_{I,f}}{V_I} \sum_{n=1}^N M_n C_{n,f} - \frac{Q_I}{V_I} \sum_{n=1}^N M_n C_n \\ &\quad - k_m \left(\sum_{n=1}^N M_n C_{n,I} - K \sum_{n=1}^N M_n C_{n,II} \right) \frac{aV}{V_I} - \frac{\sum_{n=1}^N M_n C_n}{V_I} \frac{dV_I}{dt} \Rightarrow \\ \frac{d}{dt} \left(\sum_{n=1}^N M_n C_n \right) &= \frac{d\rho_I}{dt} = 0 \\ &= \frac{Q_{I,f}}{V_I} \rho_I - \frac{Q_I}{V_I} \rho_I - k_m (\rho_I - K \rho_{II}) \frac{aV}{V_I} - \frac{\rho_I}{V_I} \frac{dV_I}{dt} \Rightarrow \\ \frac{dV_I}{dt} &= (Q_{I,f} - Q_I) - k_m \left(1 - K \frac{\rho_{II}}{\rho_I} \right) aV \end{aligned}$$

with a similar result for the volume of phase II .

The assumption of a well mixed fluid phase, which was used in the previous examples, is very common in chemical engineering. The assumption states that

there are no concentration or temperature gradients within the fluid and that any exit stream taken from the fluid is unbiased and has the same composition as the fluid itself. The assumption may fail for various reasons, for instance if interfacial mass transfer is rapid enough to generate significant concentration gradients inside a phase or if rapid chemical reactions at the feed stream inlet create concentrations and temperatures close to the inlet that are very different from the concentration and temperatures in the bulk fluid. Models in which one assumes that concentration and temperature gradients are negligible over a region are called *lumped* models since they use values of concentrations and temperatures that are averaged or lumped over a region a space. Models that do not rely on this simplifying assumption but which treat concentrations and temperatures as variables that change with position are called *distributed models*.

The next example shows another instance of lumping and also serves to remind the reader of some of the key variables used in modeling heat transfer.

Example 1.4: Cooling of catalytic slurry reactor.

Consider a flow through reactor in which a catalytic pellets are kept in suspension by mechanical stirring of the fluid, Fig. 1.7. The volumetric flow rate of the feed and exit stream is Q and their temperatures are T_f and T , respectively. The physical properties of the fluid, density and heat capacity, are considered constant and the fluid is assumed well mixed. Thus, the temperature of the exit stream equals the fluid temperature inside the reactor.

Reactions occurring inside the catalytic pellets generate heat with a constant specific rate \dot{q} (Energy per time per volume). This generation of heat will create a temperature gradient in the pellets but the modeling problem will be simplified by lumping. It will be assumed that the rate of thermal conduction inside the pellets is fast compared to the rate of heat generation such that the temperature is uniform through the pellet and equal to the constant value T_{pellet} . For simplicity, we will also assume that all the pellets have the same shape and size. Heat transfer between pellets and fluid will be modeled using film theory with a heat transfer coefficient h .

The temperature in the reactor is controlled by a cooling jacket. The volumetric flow rate of the coolant stream is Q_{cool} and the inlet and outlet temperatures are T_{in} and T_{out} respectively. The liquid in the jacket is also assumed well mixed.

An energy balance can now be done on several possible control volumes. The first will be the fluid phase inside the reactor, i.e. excluding the catalytic pellets themselves.

$$V\rho c_p \frac{dT}{dt} = Q\rho c_p(T_f - T) + hA_{\text{pellet}}(T_{\text{pellet}} - T) - UA_{\text{cool}}(T - T_{\text{out}}) \quad (1.17)$$

where V is the volume of the fluid inside the reactor, ρ and c_p the density and heat capacity of the fluid, A_{pellet} the total surface area of the pellets, A_{cool} the surface area between the reactor and the cooling jacket and U the overall heat transfer

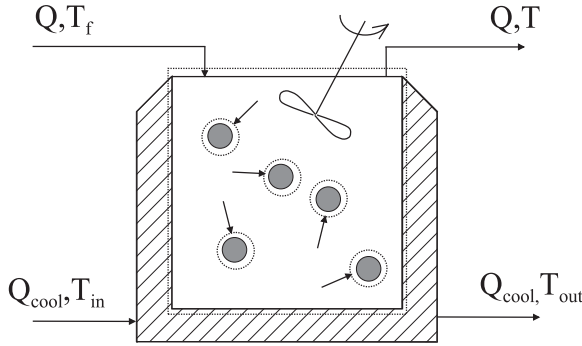


Fig. 1.7 Catalytic slurry reactor with cooling. Fluid inside the reactor is white, coolant is hatched. The dotted line indicates the control volume boundaries; between the catalytic pellets and the fluid and between the fluid inside the reactor and the cooling jacket.

coefficient between reactor and cooling jacket. An energy balance on the pellets give

$$\rho_{\text{pellet}} c_{\text{pellet}} V_{\text{pellet}} \frac{dT_{\text{pellet}}}{dt} = \dot{q} V_{\text{pellet}} - h A_{\text{pellet}} (T_{\text{pellet}} - T) \quad (1.18)$$

where ρ_{pellet} and c_{pellet} is the density and heat capacity of the pellets and V_{pellet} the total volume of the pellets. The balance on the coolant becomes

$$V_{\text{cool}} \rho_{\text{cool}} c_{\text{cool}} \frac{dT_{\text{out}}}{dt} = Q_{\text{cool}} \rho_{\text{cool}} c_{\text{cool}} (T_{\text{in}} - T_{\text{out}}) + U A_{\text{cool}} (T - T_{\text{out}}) \quad (1.19)$$

Equations 1.17 through 1.19 constitute the model. Three ordinary differential equations with three unknowns, the three temperatures.

The solution of this model depends on a huge number of model parameters, 6 material constants (densities and heat capacities), 5 geometric parameters (volumes and areas), the parameters h , U and \dot{q} and the input feed steam properties, Q , Q_{cool} , T_f and T_{in} , which may vary with time. To simplify the model, reduce the effective number of model parameters by collecting the original parameters into a smaller number of groups. Taken to the extreme, this will give a dimensionless model with the smallest possible number of dimensionless parameters. However, in this case, we will only simplify the model equations to the point where they are in standard mathematical form, with the derivatives of the unknowns isolated.

$$\frac{dT}{dt} = D(T_f - T) + \left(\frac{h A_{\text{pellet}}}{V \rho c_p} \right) (T_{\text{pellet}} - T) - \left(\frac{U A_{\text{cool}}}{V \rho c_p} \right) (T - T_{\text{out}})$$

$$\frac{dT_{\text{pellet}}}{dt} = \left(\frac{\dot{q}}{\rho_{\text{pellet}} c_{\text{pellet}}} \right) - \left(\frac{h}{\rho_{\text{pellet}} c_{\text{pellet}} L_{\text{pellet}}} \right) (T_{\text{pellet}} - T)$$

$$\frac{dT_{\text{out}}}{dt} = D_{\text{cool}} (T_{\text{in}} - T_{\text{out}}) + \left(\frac{U}{L_{\text{cool}} \rho_{\text{cool}} c_{\text{cool}}} \right) (T - T_{\text{out}})$$

where we have introduced the dilution rates $D = Q/V$ and $D_{\text{cool}} = Q_{\text{cool}}/V_{\text{cool}}$ and the characteristic lengths of the pellets and cooling jacket, $L_{\text{pellet}} = V_{\text{pellet}}/A_{\text{pellet}}$ and $L_{\text{cool}} = V_{\text{cool}}/A_{\text{cool}}$. The fractions inside the brackets are grouped parameters with dimension of inverse time or temperature per time. The number of constant parameters is thus reduced from 14 to 5 making model analysis far simpler.

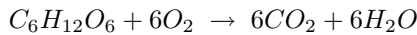
There are several ways one can proceed to make to model fully dimensionless. Both of the inlet temperatures, T_f and T_{in} , can be used to define a dimensionless temperature and time can similarly be made dimensionless two way using either the characteristic time of the reactor, $1/D$ or the characteristic time of the cooling jacket, $1/D_{\text{cool}}$.

An important point to note from the previous two examples is that the control volume used was not the entire vessel. In the case of the extractor, only a single phase was used and in the case of the slurry reactor, only the fluid phase inside the vessel was used, excluding the catalytic particles. The reason for these choices is that the best control volumes usually are those for which the dependent variables do not change value inside the control volume. Typically, this choice results in simpler balance equations. This is such an important point that we will state it formally as a rule of thumb.

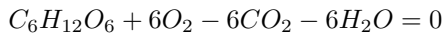
Rule of Thumb. *Pick the control volume no smaller than necessary, but so small that the variable for which the balance equation is written for does not change with position inside the control volume. Or, equivalently, pick the control volume such that it encloses the largest possible volume over which the extensive variable does not change value.*

1.1.1.2 Balances involving chemical kinetics

Chemical reactions are defined by their stoichiometry, usually given as an equation of the form



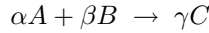
or



in which form products are recognized as the compounds with negative stoichiometric coefficients and reactants as compounds with positive coefficients. Reactions that proceed only 1 way are called irreversible while reactions that can proceed both ways are called reversible.

The specific rate of a reaction (number of moles per time per volume) will be indicated r_A where A is one of the compounds taking part in the reaction. r_A indicates the number of moles produced or consumed in the reaction in question and may be only one of several production/consumption terms in a balance equation.

Each reaction will contribute one such term. The specific reaction rate can be specified using any of the compounds taking part in the reaction and the different ways of indication the rate are related by the stoichiometry. For instance, for the reaction



it holds that

$$\frac{r_B}{\beta} = \frac{r_A}{\alpha}$$

and

$$\frac{r_C}{\gamma} = -\frac{r_A}{\alpha}$$

Reaction rates are concentration dependent and elementary reactions are often assumed to follow mass action kinetics. For this type of kinetics, the rate is proportional to concentration of the reactants raised to the power of their stoichiometric coefficient. For instance, for the reaction above

$$r_A = kC_A^\alpha C_B^\beta$$

The reaction is said to be of order α in A and of order β in B . The reaction rate constant k has whatever units are required to give r_A units of moles per time per volume and depends strongly on temperature. Other kinetic expressions are also seen. Particularly popular are expressions of the form

$$r_A = \frac{r_{\max} C_A}{K + C_A}$$

In catalysis, this expression is known as Langmuir-Hinshelwood kinetics while in enzymology it is called Michaelis-Menten kinetics. r_{\max} and K are constants, but not elemental reaction rate constants and therefore not exhibit the same temperature dependence as these. For elemental reaction rate constants, Arrhenius' law has been found to represent temperature dependence well.

$$k(T) = k_0 e^{-E/RT}$$

where R is the gas constant, T absolute temperature, E is the so-called activation energy and k_0 is called the frequency factor.

Chemical reactions are associated with energy effects and reactions that evolve heat are called *exothermic* while reactions that consume heat are called *endothermic reactions*. The energy **consumed** in a reaction is quantified by the heat of reaction, ΔH_r in energy/mole. A chemical reaction therefore contributes a consumption term in an energy balance of the form $\Delta H_r r V$ where r is the specific reaction rate and V the volume of the CV. Clearly, ΔH_r is negative for exothermic reactions and positive for endothermic reactions.

There are several idealized reactor concepts that are commonly used in chemical engineering, the plug flow reactor, the continuously stirred tank reactor (CSTR),

the well mixed batch and the well mixed fed batch reactor. The last two can be viewed as special cases of the CSTR and need therefore not be described separately.

Modeling the plug flow reactor requires the use of differential control volumes and will be covered in the next section. The well mixed CSTR however, can be modeled using the reactor vessel as a control volume, Fig. 1.8. The CSTR is a well mixed vessel with an inlet and an outlet stream. The batch reactor is obtained as a special case when both stream have zero flow rate and the fed batch when the only the exit stream has zero flow rate.

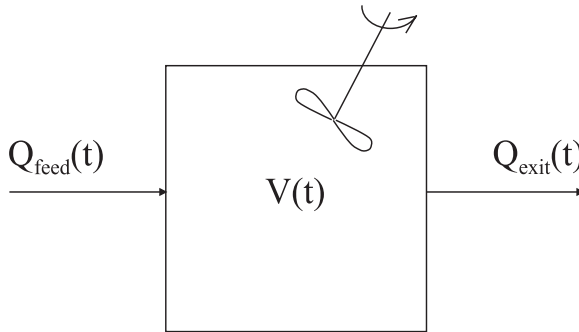


Fig. 1.8 CSTR diagram. Q represent the volumetric flow rates of the inlet and outlet streams, V is the volume of reacting solution inside the CSTR.

A general mass balance can be written over the CSTR. To identify all the reactants, let them be numbered 1 through N and let the reactions that occur inside the CSTR be numbered 1 through X . Further, let r_{xn} be the specific rate of formation of compound n in reaction x and assume kinetic expressions are known for all these rates and that there is no volume change associated with any of the reactions. A mole balance on compound n over the volume of the mixture inside the CSTR is

$$\frac{dV C_n}{dt} = Q_{\text{feed}} C_{n,\text{feed}} - Q_{\text{exit}} C_n + \sum_{x=1}^X r_{xn} V$$

Notice that since the volume of the mixture can change with time the physical volume inside the CV is not constant and must be included inside the derivative of the accumulation term. To make the model complete, an equation for this volume is needed. Obviously, this is

$$\frac{dV}{dt} = Q_{\text{feed}} - Q_{\text{exit}}$$

Using this balance, the component balances can be rearranged to standard form.

$$\frac{dC_n}{dt} = \frac{Q_{\text{feed}}}{V} (C_{n,\text{feed}} - C_n) + \sum_{x=1}^X r_{xn}$$

The next example considers a steady state continuous, stirred tank reactor (CSTR) in which an exothermic reaction takes place. This examples reviews how

to handle thermal effects of reactions. It also an example of a model for which multiple solutions can exist, in spite of the fact that the model is complete. Multiple solutions may arise in nonlinear models and when multiple steady state solutions occur, it is reasonable to ask if all the solutions are stable. Only stable solutions can be observed empirically and unstable solutions are rarely of practical interest. The steady state CSTR with an exothermic reaction is a classical chemical engineering example in stability analysis. Two of the solutions, corresponding to an extinguished reactor and an ignited reactor, can be shown to be stable, while the remaining solution is unstable.

Example 1.5: Mass and energy balances. for CSTR

Consider a CSTR of constant volume V which is cooled by a coolant with a constant temperature T_c . In the reactor, a first order exothermic reaction with reaction rate constant which obey Arrhenius law and heat of reaction ΔH_r takes place. The volumetric flow rate through the reactor is Q and the inlet reactant concentration and temperature are C_{feed} and T_{feed} respectively. Using the whole vessel as control volume, the reactant balance equation contains terms for two fluxes across the control volume surface, the inlet and outlet stream, a term for the rate of consumption of the reactant and the accumulation term

$$V \frac{dC}{dt} = QC_{\text{feed}} - QC - k_0 e^{-\frac{E}{RT}} CV$$

The energy balance contains similar terms, but in addition it will have terms for loss of energy due to cooling and due to shaft work, the work done by mechanical stirring of the vessel. The loss term due to cooling equals the product of an overall heat transfer coefficient for the vessel, U , the area available for cooling, A , and the driving force or temperature for cooling, $T - T_c$. The shaft work is clearly negative, stirring of the vessel adds energy to the system, and will just be indicated by W . The energy balance thus becomes

$$V \rho C_p \frac{dT}{dt} = Q \rho C_p T_{\text{feed}} - Q \rho C_p T + (-\Delta H_r) CV k_0 e^{-\frac{E}{RT}} - UA(T - T_c) - W$$

where it has been assumed that the density, ρ , and the heat capacity, C_p , are constant, i.e. temperature independent. The heat of reaction, ΔH_r , must be negative since we have assumed that the reaction is exothermic.

The two balances are coupled and nonlinear and, as such, difficult to solve analytically. Here, we will only be concerned with solving for the steady states, but even this simpler problem cannot be solved analytically. However, notice that the nonlinear term, $e^{-\frac{E}{RT}} C$, is the same in both the mass and the energy balance. This strongly suggests eliminating this term from one of the steady state balances with the hope that a simpler problem will be obtained. Before doing this, we will reduce the number of parameters in the problem by making the equations dimensionless. The steady state balances take the form

$$Q(C_{\text{feed}} - C) = k_0 e^{-\frac{E}{RT}} CV$$

$$0 = Q\rho C_p(T_{\text{feed}} - T) + (-\Delta H_r)CVk_0e^{-\frac{E}{RT}} - UA(T - T_c) - W$$

Now define a dimensionless concentration, Θ , and a dimensionless temperature, Ψ , by dividing each variable by its feed value.

$$\Theta \equiv \frac{C}{C_{\text{feed}}}$$

$$\Psi \equiv \frac{T}{T_{\text{feed}}}$$

In terms of these dimensionless variables, the steady state balances take the form

$$\begin{aligned} 1 - \Theta &= \Theta \left(\frac{k_0 V}{Q} \right) e^{-\frac{E}{RT_{\text{feed}} \Psi}} \\ (1 - \Psi) + \Theta \left(\frac{k_0 V}{Q} \right) e^{-\frac{E}{RT_{\text{feed}} \Psi}} &\left(\frac{(-\Delta H_r) C_f}{T_{\text{feed}} \rho C_p} \right) \\ &- \frac{AU}{Q\rho C_p} \left(\Psi - \frac{T_c}{T_{\text{feed}}} \right) - \frac{W}{T_{\text{feed}} Q\rho C_p} = 0 \end{aligned}$$

The following groups of dimensionless parameters appear

$$\alpha = \frac{k_0 V}{Q}$$

This can be thought of as the ratio of the reaction rate and the dilution rate in the vessel. A large value of α indicates that the reaction is rapid relative to the residence time in the reactor.

$$h = \frac{-\Delta H_r C_f}{T_{\text{feed}} \rho C_p}$$

which is simply a dimensionless heat of reaction. For an exothermic reaction, h must be positive. And

$$u = \frac{AU}{Q\rho C_p}, \quad \Psi_c = \frac{T_c}{T_{\text{feed}}}, \quad w = \frac{W}{T_{\text{feed}} Q\rho C_p}, \quad \epsilon = \frac{E}{RT_{\text{feed}}}$$

The steady state balances can now be written

$$1 - \Theta = \Theta \alpha \exp\left(-\frac{\epsilon}{\Psi}\right)$$

$$(1 - \Psi) + \Theta \alpha e^{-\frac{\epsilon}{\Psi}} h - u\Psi + (u\Psi_c - w) = 0$$

The group $u\Psi_c - w$ can be thought of as a single dimensionless model parameter. The number of model parameters has thus been reduced from 13 to 5, a substantial reduction in the complexity of the problem. Proceed now by eliminating the nonlinear term, $\Theta e^{-\frac{\epsilon}{\Psi}} \alpha$ from the energy balance, which becomes

$$(1 - \Psi) + (1 - \Theta)h - u\Psi + (u\Psi_c - w) = 0$$

Solving the mass and energy balances for Θ yields

$$\Theta = \frac{1}{1 + \alpha \exp(-\frac{\epsilon}{\Psi})}$$

$$\Theta = \left(1 + \frac{1}{h} + \frac{u\Psi_c - w}{h}\right) - \frac{1 + u}{h}\Psi$$

In the last result, we can again combine parameters to get the even simpler expression

$$\Theta = A - B\Psi$$

and for an exothermic reaction, B is positive so plotting Θ versus Ψ will give a straight line with a negative slope. Examining the expression for the intercept A also shows that this must be greater than 1. The line for $A = 1$ therefore shows the lower limit on where these lines can occur. The steady states are found where these straight lines intersects the curve given by the equation for the mass balance. We cannot find these points analytically but can do so graphically by plotting the two equations for various parameters values. This is done in Fig. 1.9.

Notice that there are 3 possible cases. A unique, extinguished steady state for low values of A , 3 steady states (the middle one of which can be shown to be

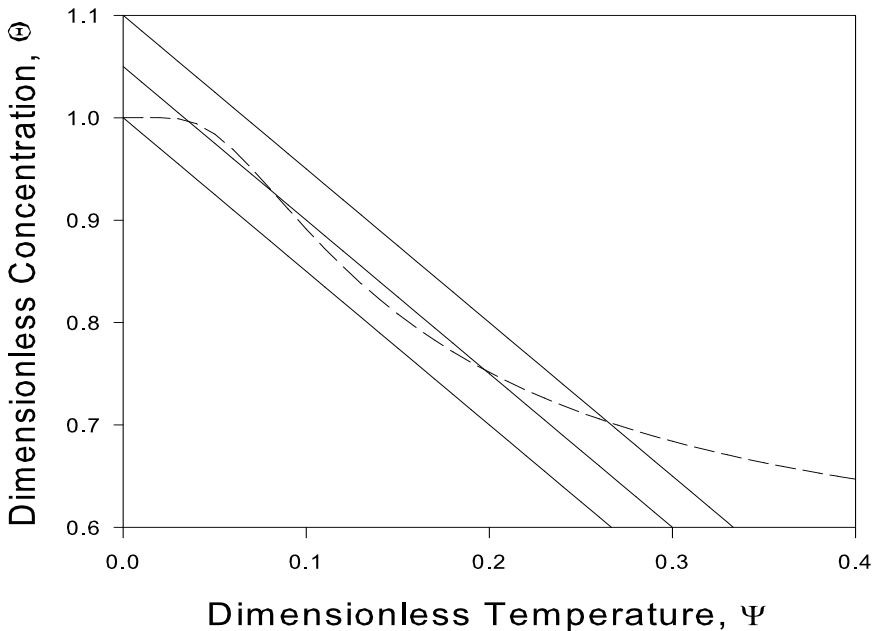


Fig. 1.9 Dimensionless mass and energy balances for a CSTR with an exothermic first order reactions. Parameter values are $\alpha = 0.9$, $\epsilon = 0.2$, $B = 1.5$. For the bottom straight line, $A = 1$, for the middle straight line $A = 1.05$ and for the top straight line $A = 1.1$.

unstable) for intermediate values of A or a unique ignited steady state for large values of A ¹.

As a last example of a macroscopic control volume, we will consider a chemical reaction taking place on a surface. The control volume is a unit area of the surface and it therefore has zero physical volume. This may seem like a paradox, but only serves to illustrate the fact that the term “control volume” must not be taken too literally.

Surface reactions play an important role in catalysis. Not just in industrial reactors, but also in environmental problems where airborne pollutants may adsorb to natural surfaces such as ice and water or on man made surfaces such as the grimy film that covers most windows, and react in ways that alter the compositions of the pollutants in the air. Adsorbed molecules often react faster than molecules in suspension because reactant molecules only need to diffuse in two dimensions to encounter one another and, all other things being equal, two dimensional diffusion is faster than three dimensional diffusion. To convince yourself of this, just think of how much quicker it is to find someone’s office if you know the floor on which the office is located as opposed to when you only know the building. Even greater rate enhancement result from restricting diffusion of reactants to 1 dimension. This effect probably plays a role in biological systems where regulatory proteins may bind to a DNA molecule and diffuse along the DNA strand to rapidly find their binding site.

Example 1.6: Surface reaction.

The situation to be considered is sketched in Fig. 1.10. Two reactants in a gas stream, call them A and B , adsorb² to a surface and react to form a product P which then detach from the surface. The surface can at most be covered by a monolayer of reacting molecules and this will be modeled by assuming that there is a finite number of sites per surface area onto which reactants can adsorb. Adsorption is then modeled as a reaction between a gas phase molecule and a free site leading to an adsorbed molecule. The number of free sites must therefore be modeled by a writing a conservation equation on the number of free sites, similar to the conservation equations on the reactants. The gas phase concentrations will be assumed constant while surface concentrations can change with time. Rates are assumed to follow mass action kinetics in both reactant concentrations and adsorption sites.

Let the gas phase concentrations be $C_{A,g}$, $C_{B,g}$ and $C_{P,g}$ and the surface concentrations be $C_{A,s}$, $C_{B,s}$ and $C_{P,s}$. The number of free sites per area will be indicated

¹The problem of the stability of the steady state is clearly of great importance and it has been analyzed in significantly more depth than the presentation given here. Readers who would like to learn more should consult: R. Aris and N.R. Amundson, An analysis of chemical reactor stability and control - I, **Chemical Engineering Science**, **7**, 3, 121-131, (1958)

²The term adsorption is often confused with the similar sounding term absorption. Adsorption refers to retention of atoms and molecules on the surface of a substance while absorption refers to retention into the bulk of a phase

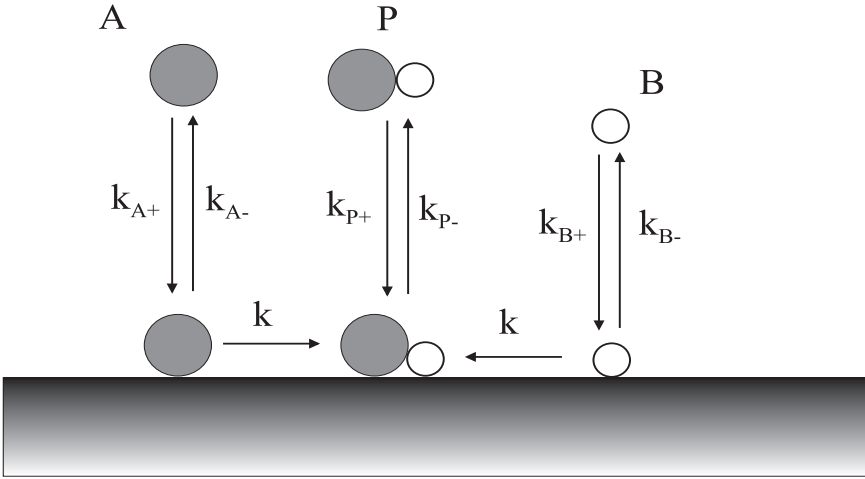


Fig. 1.10 Schematic of a surface catalyzed reaction between two molecules.

as N and, assuming that N is large, it can be approximated as a continuous variable. Reaction rate constants are as indicated in the figure. Before we can write balance equations on the reactants, we must decide how to treat surface sites in a reaction. Does the products take up a single site on the surface or does it occupy two, as one might expect since it is formed from two reactant that occupy one site each? We will assume that the product occupies two sites so the number of free sites do not change in a reaction. (The reader may want to write the balances when it is assumed that the product occupies only one site and that a free site is therefore formed in each reaction). Mass balances on the two reactants and the product give

$$\frac{dC_{A,s}}{dt} = k_{A+}C_{A,g}N - k_{A-}C_{A,s} - kC_{A,s}C_{B,s}$$

$$\frac{dC_{B,s}}{dt} = k_{B+}C_{B,g}N - k_{B-}C_{B,s} - kC_{A,s}C_{B,s}$$

$$\frac{dC_{P,s}}{dt} = kC_{A,s}C_{B,s} + k_{P+}C_{P,g}N - k_{P-}C_{P,s}$$

and a balance on the number of free sites per area gives

$$\frac{dN}{dt} = k_{A-}C_{A,s} + k_{B-}C_{B,s} + 2k_{P-}C_{P,s} - k_{A+}C_{A,g}N - k_{B+}C_{B,g}N - 2k_{P+}C_{P,g}N$$

The model consists of four coupled differential equations. But, as is often the case in kinetic problems of this kind, one of the differential equations can be replaced by an algebraic equations by taking some weighted sum of the balances. Multiply the balance for $C_{P,s}$ by two (since adsorbed product occupies two sites) and sum

this equation and the remaining three balances to get the differential equation

$$\begin{aligned} \frac{d}{dt}(C_{A,s} + C_{B,s} + 2C_{P,s} + N) &= k_{A+}C_{A,g}N - k_{A-}C_{A,s} - kC_{A,s}C_{B,s} \\ &+ k_{B+}C_{B,g}N - k_{B-}C_{B,s} - kC_{A,s}C_{B,s} \\ &+ 2kC_{A,s}C_{B,s} + 2k_{P+}C_{P,g}N - 2k_{P-}C_{P,s} \\ &+ k_{A-}C_{A,s} + k_{B-}C_{B,s} + 2k_{P-}C_{P,s} - k_{A+}C_{A,g}N - k_{B+}C_{B,g}N - 2k_{P+}C_{P,g}N \end{aligned}$$

which upon simplification gives

$$\frac{d}{dt}(C_{A,s} + C_{B,s} + 2C_{P,s} + N) = 0 \Rightarrow C_{A,s} + C_{B,s} + 2C_{P,s} + N = \text{Constant}$$

This constant is simply the total number of sites, free or filled, per area and it must be a constant since none of the reactions consume or produce sites. This result is of course so obvious that one could have written it down without the need for calculating the weighted sum of the balances. However, it is important to appreciate that this balance on the total number of sites is not independent of the four reactant balances and, when it is used in a model, one of the reactant balances can be ignored by e.g. eliminating N to get a model consisting of three coupled ordinary differential equations.

$$\frac{dC_{A,s}}{dt} = k_{A+}C_{A,g}(N_{\text{total}} - C_{A,s} - C_{B,s} - 2C_{P,s}) - k_{A-}C_{A,s} - kC_{A,s}C_{B,s}$$

$$\frac{dC_{B,s}}{dt} = k_{B+}C_{B,g}(N_{\text{total}} - C_{A,s} - C_{B,s} - 2C_{P,s}) - k_{B-}C_{B,s} - kC_{A,s}C_{B,s}$$

$$\frac{dC_{P,s}}{dt} = kC_{A,s}C_{B,s} + k_{P+}C_{P,g}(N_{\text{total}} - C_{A,s} - C_{B,s} - 2C_{P,s}) - k_{P-}C_{P,s}$$

These equations are nonlinear and will have to be solved numerically. However, significant model simplifications are possible if one can assume that the adsorption and desorption reactions are very fast compared to the chemical reaction. In this case, the concentration of the adsorbed species can be assumed to be in a so called *quasi steady state*. Steady state balances on adsorption and desorption of A , B and P gives three algebraic equations

$$k_{A+}C_{A,g}(N_{\text{total}} - C_{A,s} - C_{B,s} - 2C_{P,s}) = k_{A-}C_{A,s}$$

$$k_{B+}C_{B,g}(N_{\text{total}} - C_{A,s} - C_{B,s} - 2C_{P,s}) = k_{B-}C_{B,s}$$

$$k_{P+}C_{P,g}(N_{\text{total}} - C_{A,s} - C_{B,s} - 2C_{P,s}) = k_{P-}C_{P,s}$$

which can be solved for $C_{A,s}$, $C_{B,s}$ and $C_{P,s}$

$$C_{A,s} = \frac{k_{A+}k_{B-}k_{P-}C_{A,g}N_{\text{total}}}{k_{A+}k_{B-}k_{P-}C_{A,g} + k_{A-}k_{B+}k_{P-}C_{B,g} + 2k_{A-}k_{B-}k_{P+}C_{P,g} + k_{A-}k_{B-}k_{P-}}$$

$$C_{B,s} = \frac{k_A - k_{B+}k_{P-}C_{B,g}N_{\text{total}}}{k_{A+}k_{B-}k_{P-}C_{A,g} + k_A - k_{B+}k_{P-}C_{B,g} + 2k_A - k_{B-}k_{P+}C_{P,g} + k_A - k_{B-}k_{P-}}$$

$$C_{P,s} = \frac{k_A - k_{B-}k_{P+}C_{P,g}N_{\text{total}}}{k_{A+}k_{B-}k_{P-}C_{A,g} + k_A - k_{B+}k_{P-}C_{B,g} + 2k_A - k_{B-}k_{P+}C_{P,g} + k_A - k_{B-}k_{P-}}$$

and for most practical purposes, we are done because the interesting result, the steady rate of product formation, is easily calculated as a function of the gas phase concentrations.

$$r_P = kC_{A,s}C_{B,s}$$

$$= \frac{kk_{A+}k_A - k_{B+}k_{B-}k_{P-}^2C_{A,g}C_{B,g}N_{\text{total}}^2}{(k_{A+}k_{B-}k_{P-}C_{A,g} + k_A - k_{B+}k_{P-}C_{B,g} + 2k_A - k_{B-}k_{P+}C_{P,g} + k_A - k_{B-}k_{P-})^2}$$

Notice, that although the surface reaction itself is irreversible and independent of the adsorbed product concentration, the overall reaction rate does depend on the gas phase concentration of the product. This is caused by the fact that adsorbed product limit the number of free sites available to the reactants and therefore slows down the overall reaction. The highest reaction rate is therefore obtained when the gas phase concentration of the product equals zero, in which case the expression above simplifies to

$$r_P = \frac{kk_{A+}k_A - k_{B+}k_{B-}C_{A,g}C_{B,g}N_{\text{total}}^2}{(k_{A+}k_{B-}C_{A,g} + k_A - k_{B+}C_{B,g} + k_A - k_{B-})^2}$$

1.1.2 The quasi steady state assumption

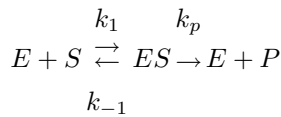
In the previous example, we made explicit use of the quasi or pseudo steady state assumption. This assumption or approximation is such an important tool for simplifying models that it deserves to be discussed at some length.

The quasi steady state assumption can be used whenever a system contains processes with very different time scales. As the difference between the time scales become larger, it becomes increasingly valid to assume that the fast processes are, for all practical purposes, at their steady state. We make use of this assumption all the time, often without explicitly stating so. For instance, when we describe a vessel as being well mixed, we are saying that the characteristic time for mixing is much shorter than the characteristic time for other processes that take place in the vessel, such as chemical reactions. Or, to take a more prosaic and everyday example, when you cook a roast in the oven, you would not care whether or not the oven is preheated before you put the roast in because the time required for the oven to heat up, a few minutes, is so small compared to the time required to cook the roast, about an hour. On the other hand, if you are making a baked Alaska, a desert made by covering a lump of ice cream with beaten egg whites and quickly baking it all at a high temperature to form a meringue without melting the ice

cream inside, then it is essential that the oven is preheated because the baking time and the oven heating time are roughly equal.

Chemical reaction rates are notorious for their wide range of values and the quasi steady state assumption is probably never invoked more than when modeling chemical kinetics. A famous case of this is the derivation of kinetics for enzyme catalyzed reactions.

Enzymes work by binding to a substrate (the reactant) to form an enzyme-substrate complex and this complex then reacts to form the free product. The reversibility of the reaction leading to formation of the enzyme-substrate complex and the irreversibility of the reaction leading to the product are both common assumptions in enzyme kinetics. The reaction can be written formally as



where E indicates the enzyme, S the substrate, ES the enzyme-substrate complex and P the product. The rate equations for a well mixed batch reactor can now be stated.

$$\frac{dC_P}{dt} = k_p C_{ES}$$

$$\frac{dC_{ES}}{dt} = k_1 C_S C_E - (k_{-1} + k_p) C_{ES}$$

$$\frac{dC_E}{dt} = k_{-1} C_{ES} - k_1 C_E C_S + k_p C_{ES}$$

$$\frac{dC_S}{dt} = k_{-1} C_{ES} - k_1 C_E C_S$$

Adding the second and third rate equations give

$$\frac{d}{dt}(C_E + C_{ES}) = 0 \Rightarrow C_E + C_{ES} = C_{E0}$$

where C_{E0} is the constant total enzyme concentration, free enzyme plus enzyme-substrate complex. This result is simply a total enzyme balance.

The rate equations above are nonlinear and cannot be solved analytically. In order to obtain a model which can be solved analytically, two simplifying assumptions have been suggested in the literature, the Michaelis-Menten³ or equilibrium assumption and the Briggs-Haldane⁴ or steady state assumption. The latter assumption is less restrictive than the former and thus models the true kinetics more accurately, but it is slightly more cumbersome to work with.

³Michaelis L. and Menten M.L. Die Kinetik der Invertinwirkung, **Biochem. Z.** **49**, 333, (1913)

⁴Briggs G.E. and Haldane J.S.B., A note on the kinetics of enzyme action, **Biochem. J.** **19**, 338-339, (1925)

The Michaelis-Menten assumption is that the product forming reaction is the rate limiting reaction in the system. In other words, the rate of formation of ES and the rate of breakdown of ES into free enzyme and substrate are fast compared to the rate at which the enzyme-substrate complex breaks down to form product. The two fast reactions can therefore be considered to be in a quasi steady state at all times. Because the assumption implies that the enzyme-substrate complex is in equilibrium with the free substrate and enzyme, Michaelis-Menten analysis is also referred to as rapid equilibrium analysis. Using the assumption of equilibrium, we obtain,

$$k_1 C_S C_E = k_{-1} C_{ES} \Rightarrow \frac{C_S C_E}{C_{ES}} = \frac{k_{-1}}{k_1} = K_m$$

and using this result to eliminate C_E from the total enzyme balance gives,

$$C_{ES} = \frac{C_S C_{E0}}{K_m + C_S}$$

Substituting this result into the rate equation for substrate formation gives the desired result.

$$\frac{dC_P}{dt} = k_p \frac{C_S C_{E0}}{K_m + C_S} = \frac{r_{\max} C_s}{K_m + C_s}$$

The Briggs-Haldane analysis is also called steady state analysis because the basic assumption is that the concentration of the enzyme-substrate complex is at a quasi steady state. This is **not** the same as the Michaelis-Menten assumption which stated that the complex was in equilibrium with the free species, but is slightly less restrictive. In fact, Michaelis-Menten results can be obtained from the Briggs-Haldane results as a special case. Mathematically, the Briggs-Haldane assumption can be stated as,

$$\frac{dC_{ES}}{dt} = k_1 C_S C_E - k_{-1} C_{ES} - k_p C_{ES} = 0$$

While in the Michaelis-Menten analysis we discarded the k_p -term, in this analysis we will keep it and the reaction leading to the product is therefore not necessarily the rate limiting reaction. Obviously, we should be able to obtain the Michaelis-Menten results from the Briggs-Haldane results by setting k_p equal to zero. To obtain the desired rate expression, we proceed essentially as before. Find C_E from the equation above and substitute the result into the total enzyme balance. Solve for C_{ES} and substitute this result into the equation for the rate of product formation.

$$\frac{dC_P}{dt} = k_p \frac{C_S C_{E0}}{\frac{k_{-1} + k_p}{k_1} + C_S}$$

Notice, that if we invoke the Michaelis-Menten assumption, then $k_p \ll k_{-1}$ and this result simplifies to the Michaelis-Menten result.

Example 1.7: Return of the density gradient device.

In the example on page 8, we looked at two connected, well-mixed tanks for making density gradients. The relevant figure is repeated here, Fig. 1.11.

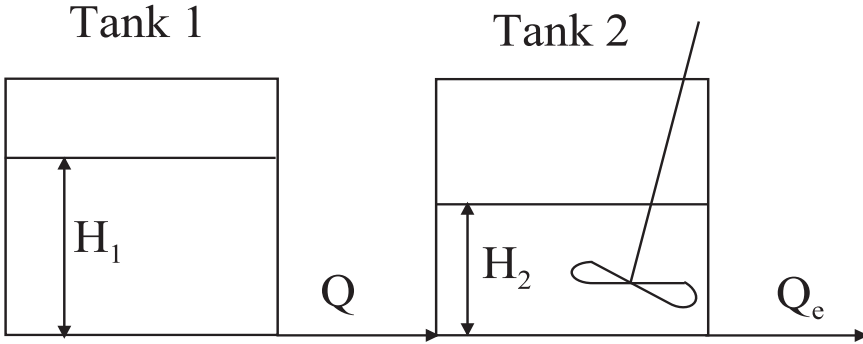


Fig. 1.11 Two connected mixing tanks used for making density gradients.

The three balance equations, two on the liquid volume and one on the concentration of sucrose in tank 2, were

$$A \frac{dH_1}{dt} = -(H_1 - H_2)/R$$

$$A \frac{dH_2}{dt} = (H_1 - H_2)/R - Q_e$$

$$A \frac{dH_2 C_2}{dt} = C_1(H_1 - H_2)/R - C_2 Q_e$$

If we now assume that the sucrose stream, Q_e , is withdrawn very slowly compared to how fast the liquid flows from tank 1 to tank 2, then it is reasonable to assume that the liquid levels in the two tanks are equal or in a quasi steady state. This quasi steady state assumption clearly implies that the volumetric flow rate from tank 1 to tank 2 equals half the flow rate out of the device, giving the model

$$A \frac{dH_1}{dt} = -\frac{Q_e}{2}$$

$$A \frac{dH_2}{dt} = -\frac{Q_e}{2}$$

$$A \frac{dH_2 C_2}{dt} = C_1 \frac{Q_e}{2} - C_2 Q_e \Rightarrow H_2 \frac{dC_2}{dt} = C_1 \frac{Q_e}{2A} - C_2 \frac{Q_e}{2A}$$

Reintroducing the previously defined dimensionless variables

$$\tau = \frac{t}{AR}, \quad h_1 = \frac{H_1}{H}, \quad h_2 = \frac{H_2}{H}, \quad c_1 = \frac{C_1}{C_0}, \quad c_2 = \frac{C_2}{C_0}$$

the dimensionless model equations become

$$\frac{dh_1}{d\tau} = -\frac{Q_e R}{2H}$$

$$\frac{dh_2}{d\tau} = -\frac{Q_e R}{2H}$$

$$h_2 \frac{dc_2}{d\tau} = c_1 \frac{Q_e R}{2H} - c_2 \frac{Q_e R}{2H}$$

which can be solved to give

$$h_1(t) = 1 - \frac{Q_e R}{2H} \tau, \quad 0 \leq \tau \leq \frac{2H}{Q_e R}$$

$$h_2(t) = 1 - \frac{Q_e R}{2H} \tau, \quad 0 \leq \tau \leq \frac{2H}{Q_e R}$$

$$c_2(t) = c_1 + (1 - c_1) \left(1 - \frac{Q_e R}{2H} \tau \right), \quad 0 \leq \tau \leq \frac{2H}{Q_e R}$$

The slow withdrawal of the solution therefore creates a linear concentration gradient in the test tube, with a bottom concentration of C_0 and a top concentration of C_1 .

The quasi steady state assumption used was that the flow out of the second vessel was slow compared to the flow between the vessels. This occurs if Q_E or if

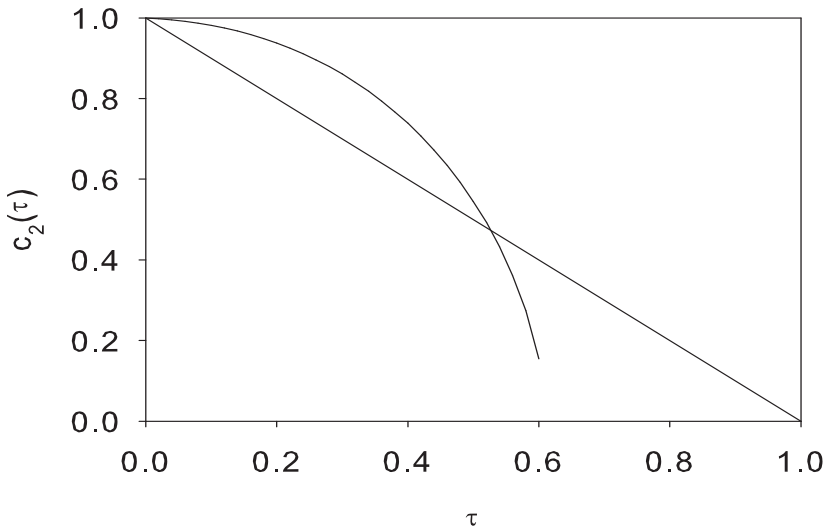


Fig. 1.12 Solutions of the dimensionless sucrose concentration versus dimensionless time for full model (curved solution) and for quasi steady state model (straight line solution). Both plots are for $\frac{Q_e R}{H} = 2$ and $c_1 = 0$.

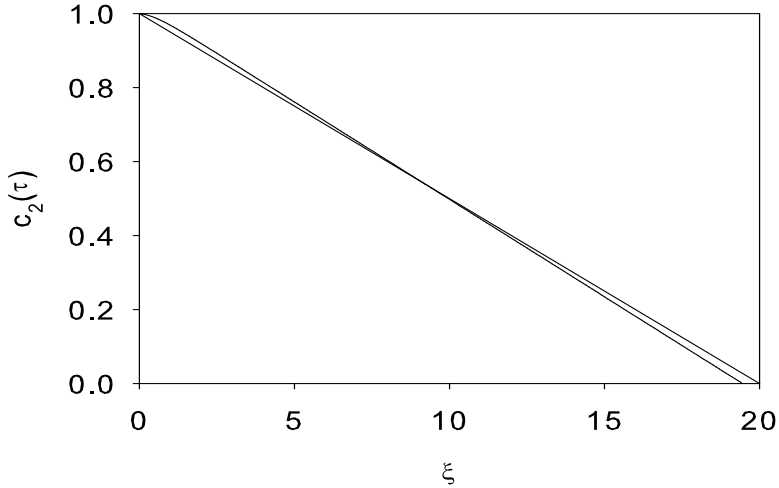


Fig. 1.13 Solutions of the dimensionless sucrose concentration versus dimensionless time for full model (curved solution) and for quasi steady state model (straight line solution). Both plots are for $\frac{Q_e R}{H} = 0.1$ and $c_1 = 0$.

R are small and plotting the quasi steady state solution against the solution of the full model confirms this. Fig. 1.12 shows the two solutions for $\frac{Q_e R}{H} = 2$ and the quasi steady state solution is obviously poor.

Figure 1.13 show the sucrose concentration for $\frac{Q_e R}{H} = 0.1$ and the solution obtained using the quasi steady state assumption is seen to be quite good.

1.1.3 Differential balances

We now switch to examples of distributed models. In distributed models, system properties such as temperatures and concentrations change with position. In other words, they are distributed over space as opposed to being lumped into a single value characteristic of an entire well mixed phase. The previously stated rule of thumb for picking a control volume, so small that the dependent variable does not change value inside the CV, then tells us that the CV for distributed models should be a point in space. As this is not possible, a differentially small control volume will be used. Such a control volume is usually defined using a coordinate system, so the most commonly used coordinate systems will be described first.

1.1.3.1 Coordinate systems

Defining a coordinate system means defining both the origin of the system and the positive direction of each coordinate. The type of coordinate system that is best suited for a given problem is often obvious and only in cases with fairly complex

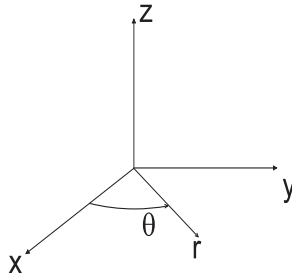


Fig. 1.14 Transformation between rectangular and cylindrical coordinate systems.

geometries is choosing a coordinate system a problem. We will look at the three most commonly used coordinate systems, rectangular, cylindrical and spherical.

The simplest differential control volume is obtained in rectangular coordinates, (x, y, z) . This control volume is a cube with edges of lengths dx , dy and dz and the areas of the sides are $dx dy$, $dx dz$ and $dy dz$. This control volume is so familiar that we will not insult the readers intelligence by spending any more time discussing it.

In cylindrical coordinate systems the coordinates are usually indicated by z , the axial coordinate, r , the radial coordinate and θ , the angular coordinate. The cylindrical coordinate system can be related to the rectangular coordinate system by letting the z -axis of the two coordinate systems coincide and placing a polar coordinate system in the xy -plane, Fig. 1.14. With this relative placement the transformation between the two coordinate systems can be written as

$$x = r \cos \theta$$

$$y = r \sin \theta$$

$$z = z$$

The coordinate surfaces, the surfaces formed by constant values of r , θ and z , are concentric cylinders around the z -axis, the planes that pivot around the z -axis and the planes at a right angle to the z -axis.

A control volume is a volume swept out by the differentials dz , dr and $d\theta$ as shown in Fig. 1.15. Notice that the arc which spans the angle θ has length $r d\theta$ and the area available for transport in the radial direction is therefore $r d\theta dz$ and the volume of the control volume is $r d\theta dz dr$.

Spherical coordinates of a point are usually indicated by a radial coordinate r , a longitudinal coordinate ϕ and a latitudinal coordinate θ , which is the angle between the position vector of the point and the position vector of the north pole, Fig. 1.16.

The transformation equations between rectangular and spherical coordinates can be written

$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta$$

where the origin of the two systems are superimposed, the $\theta=0$ -direction, the direction from the center to the north pole, is in the z -direction of the rectangular system and the $\phi=0$ -direction in the direction of the x axis.

The coordinate surfaces are concentric spheres (constant r), planes that pivot around the $\theta=0$ axis (constant ϕ) and cones with their axis of symmetry on the $\theta=0$ -axis and their tips at the center of the r =constant spheres(constant θ).

The differential control volume in spherical coordinates is shown in Fig. 1.17 and visualizing it well and figuring out the lengths of its sides does require some ability to visualize objects in 3 dimensions. The length of the arc spanned by $d\theta$ equals $r d\theta$, the length of the arc spanned by $d\phi$ equals $r \sin \theta d\phi$ so the differential area defined by $d\theta$ and $d\phi$ is $r^2 \sin \theta d\theta d\phi$. This is the area available for transport in the radial direction and is indicated by the grey square in Fig. 1.17. Similarly, the area for transport in the θ direction is $r \sin \theta dr d\phi$ and the area for transport in the ϕ direction is $r dr d\theta$. The physical volume of the differential element is $r^2 \sin \theta dr d\theta d\phi$.

Whenever the physical situation is such that the quantity being modeled does not change in one or two of the coordinate directions, one does not use the control volumes described above but instead the larger control volume swept out by the differentials of the coordinates along which the variable does change. For this kind of control volume, the coordinates for which the variable does not change pass through their entire range of possible values. For instance, in a situation with perfect spherical symmetry, variation in the θ and ϕ directions can be excluded and the control volume is defined by the distance dr and by θ taking all values between 0 and π and ϕ taking all values between 0 and 2π . In other words, the control volume is a spherical shell with thickness dr .

The three simple coordinate systems mentioned here, rectangular, cylindrical and spherical, do not exhaust all possibilities. There are an infinity of possible

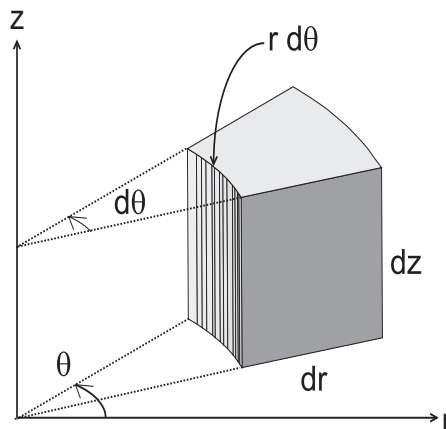


Fig. 1.15 The differential control volume in cylindrical coordinates.

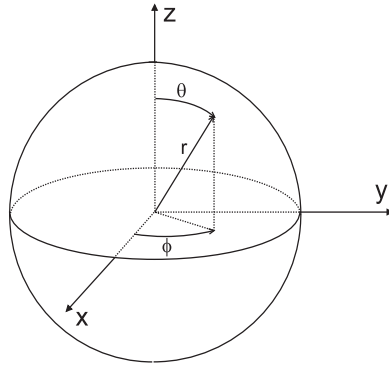


Fig. 1.16 Transformation between rectangular and spherical coordinate systems.

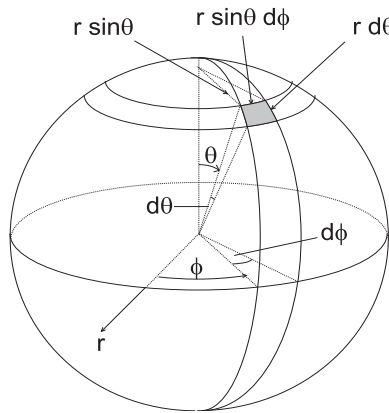


Fig. 1.17 The differential control volume in spherical coordinates. The control volume is not actually shown in the figure. It is a box of height dr sitting atop the grey square.

coordinate systems and descriptions of the more useful ones can be found in the literature⁵.

All coordinate systems are created equal and are equally valid for setting up models. However, the aim of the modeler is to obtain the simplest possible mathematical problem and here the choice of coordinate system becomes important. Usually the boundary conditions dictate the choice of coordinate system such that the system that gives the simplest boundary conditions are used in a given problem. Boundary conditions are particularly nice if they can be specified along coordinate surfaces.

⁵see e.g Morse, P.M. and H. Feshbach, *Methods of Theoretical Physics*, McGraw-Hill, 1953, Vol I or Happel, J. and Brenner, H., *Low Reynolds number hydrodynamics*, Martinus Nijhoff, 1983

1.1.3.2 Constitutive equations

When writing balance equations on a differential control volume, one must find expressions for the fluxes across the control volume surfaces. This step typically requires the use of constitutive equations. Constitutive equations are equations that model the relationship between physical quantities such as the heat flux and the temperature gradient or between a force applied and the amount of deformation it causes. Constitutive equations are not fundamental laws of nature and it does not make sense to talk about constitutive equations as being true or false; they are good or bad, depending on how well they describe reality. Picking the best constitutive equations is thus an important step in getting the best final model.

The four most important constitutive equations in chemical engineering can be stated in rectangular coordinates as follows: Fourier's law for conduction in an isotropic solid, used for calculating energy fluxes

$$q_x = -k \frac{\partial T}{\partial x}$$

where q_x is the flux in the x -direction (Energy per time per area), k is the thermal conductivity of the substance and T the temperature. Similar expressions hold for the flux in the y and z directions.

Fick's law for calculation of diffusive fluxes.

$$N_x = -D \frac{\partial C}{\partial x}$$

where N_x is the diffusive flux in the x -direction. Usually in mole/(area time) but other units can be used depending on the units used to measure concentration. D is the diffusion coefficient (area/time) and C concentration of the diffusion species. Similar expressions hold for the flux in the y and z directions.

Newton's law of viscosity which states that the stress in the fluid is proportional to a velocity gradient or a shear rate

$$\tau = \mu \frac{\partial v}{\partial x}$$

where τ is stress, μ viscosity and v velocity.

Finally Hooke's law for deformation of an elastic solid, which states that the stress in the solid is proportional to the strain

$$\tau = E \frac{\Delta l}{l}$$

where τ is stress, E Young's modulus or shear modulus, ΔL the change in length of a solid which has length L when unstressed. Thus $\Delta L/L$ is the strain.

Both Newton's law of viscosity and Hooke's law involve stress and specification of the stress in a continuum requires that all stress components be specified. Both laws are therefore considerable more complex than stated here and a proper statement of these laws require the use of tensors, a type of vector function that will be introduced in section 4.4. Both laws can also be written with a minus sign on the right hand side. The sign depends on how the positive direction for stress is defined.

Note that all four constitutive equations are proportionalities, i.e. they are linear. Consequently, when they are used they (usually) give rise to linear models. Linear models are invariably easier to solve than nonlinear models and one should therefore pick linear constitutive equations whenever this is possible.

Constitutive equations are specific to a given substance and thus make use of one or several material constants. Substances are often described by terms derived from the constitutive equations used to model them. For instance, if Newton’s law of viscosity is used to model the relationship between stress and velocity gradients in a fluid, then the fluid is called a Newtonian fluid while a power law fluid is modeled using the power law.

What concerns us here is the fact that even simple constitutive equations take different forms in different coordinate systems. Consider, for instance, a transient energy balance in rectangular coordinates on a solid in which heat is generated at the rate \dot{q} (Energy/(time volume)). The balance becomes,

$$q_x|_x dydz - q_x|_{x+dx} dydz + q_y|_y dx dz - q_y|_{y+dy} dx dz + q_z|_z dx dy - q_z|_{z+dz} dx dy = \rho C_p \frac{\partial T}{\partial t} dx dy dz - \dot{q} dx dy dz$$

where the term $q_x|_x dydz$ represent the rate of energy transport into the differential cube, through the surface parallel to the y, z -plane (or, equivalently, the surface which is at a right angle to the x -axis) and at position x . q_x is the flux and $dydz$ the area of the side of the differential cube. Similarly, the term $-q_x|_{x+dx} dydz$ represents the rate of transport out of the cube at position $x + dx$ and so forth. Density ρ and heat capacity C_p are assumed constant. This balance is rewritten using the standard method for rewriting differential balances. Divide through by the differential factors dx, dy and dz

$$-\frac{q_x|_{x+dx} - q_x|_x}{dx} - \frac{q_y|_{y+dy} - q_y|_y}{dy} - \frac{q_z|_{z+dz} - q_z|_z}{dz} = \rho C_p \frac{\partial T}{\partial t} - \dot{q}$$

and recognize that the three fractions are derivatives with respect to x, y and z respectively, to get

$$-\frac{\partial q_x}{\partial x} - \frac{\partial q_y}{\partial y} - \frac{\partial q_z}{\partial z} = \rho C_p \frac{\partial T}{\partial t} - \dot{q}$$

The flux q can now be modeled using Fourier’s law. Substitution into the energy balance gives

$$\frac{\partial}{\partial x} \left(k \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left(k \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial z} \left(k \frac{\partial T}{\partial z} \right) = \rho C_p \frac{\partial T}{\partial t} - \dot{q}$$

and if the thermal conductivity k is independent of position, it can be taken outside the derivatives and divided out to get the simplified balance, usually written

$$\frac{k}{\rho C_p} \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) + \frac{\dot{q}}{\rho C_p} = \frac{\partial T}{\partial t}$$

The fraction, $k/\rho C_p$ has dimension of area per time and is called the thermal diffusivity.

If the same balance is now done in e.g. cylindrical coordinates, one must first content with the greater complexity of the differential control volume. The size of the sides of the differential element are no longer simply products of the three differentials but are given by the expression discussed earlier and the transient energy balance becomes

$$\begin{aligned} q_r r|_r d\theta dz - q_r r|_{r+dr} d\theta dz + q_\theta|_\theta dr dz - q_\theta|_{\theta+d\theta} dr dz + q_z|_z r d\theta dr - q_z|_{z+dz} r d\theta dr \\ = \rho C_p \frac{\partial T}{\partial t} r d\theta dr dz - \dot{q} r d\theta dr dz \end{aligned}$$

which upon simplification becomes

$$-\frac{\partial r q_r}{\partial r} - \frac{\partial q_\theta}{\partial \theta} - r \frac{\partial q_z}{\partial z} = \rho C_p \frac{\partial T}{\partial t} r - \dot{q} r$$

Notice, that when you divide through by $dr d\theta dz$, you cannot divide out the r -factor at the same time because the r -factor that appears in e.g. the term $q_r r|_{r+dr} d\theta dz$ is shorthand for $r + dr$.

To continue, we need Fourier's law in cylindrical coordinates, and it is slightly more complicated looking than in rectangular coordinates.

$$q_r = -k \frac{\partial T}{\partial r}, \quad q_\theta = -\frac{k}{r} \frac{\partial T}{\partial \theta}, \quad q_z = -k \frac{\partial T}{\partial z}$$

giving

$$\frac{1}{r} \frac{\partial}{\partial r} \left(k r \frac{\partial T}{\partial r} \right) + \frac{1}{r^2} \frac{\partial}{\partial \theta} \left(k \frac{\partial T}{\partial \theta} \right) + \frac{\partial}{\partial z} \left(k \frac{\partial T}{\partial z} \right) = \rho C_p \frac{\partial T}{\partial t} - \dot{q}$$

and for constant thermal conductivity

$$\frac{k}{\rho C_p} \left(\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 T}{\partial \theta^2} + \frac{\partial^2 T}{\partial z^2} \right) + \frac{\dot{q}}{\rho C_p} = \frac{\partial T}{\partial t}$$

The point to note here is that the form of both the balance equation and the constitutive equation change with the coordinate system. The different forms can be converted to one another, but doing so between general coordinate systems is not trivial and the appropriate form of most common constitutive equations can be looked up.

1.1.3.3 Operator notation

Balance equations and constitutive equations can be stated in a coordinate system independent form using operator notation. As the example with the energy balance on a solid showed, any coordinate system can be used to specify a differential control volume. All coordinate systems are valid although they are not all equally convenient for a given problem. A model written with operator notation can be applied to any geometry by writing the explicit form of the operators for the given

coordinate system. This makes it very easy to switch between different geometries. For instance, the expression $\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2}$ which arise frequently in balance equations when rectangular coordinates are used, is written using operator notation as

$$\nabla^2 T = \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2}$$

The operator ∇^2 is called the Laplacian operator and is, in rectangular coordinates, defined as

$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

With this operator, the transient energy balance on a solid with heat generation can be written

$$\frac{k}{\rho C_p} \nabla^2 T + \frac{\dot{q}}{\rho C_p} = \frac{\partial T}{\partial t}$$

One can now look up the explicit expression for ∇^2 in any coordinate system one wants to use. For instance, in spherical coordinates, the ∇^2 operator is

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$$

and the model result obtained in rectangular coordinates can be converted to spherical coordinates by substituting this expression into the operator form of the model giving

$$\frac{k}{\rho C_p} \left(\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial T}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 T}{\partial \phi^2} \right) + \frac{\dot{q}}{\rho C_p} = \frac{\partial T}{\partial t}$$

The symbol ∇ is known as “nabla” and is used in some form in almost all operators encountered in chemical engineering problems. In rectangular coordinates it is defined as

$$\nabla = \frac{\partial}{\partial x} e_x + \frac{\partial}{\partial y} e_y + \frac{\partial}{\partial z} e_z$$

where e_x , e_y and e_z are the three basis vectors of the coordinate system. Thus ∇ is a vector and has both magnitude and direction. Taking the scalar product of ∇ with itself gives ∇^2 , the Laplacian operator.

Many of the operators that make use of the ∇ symbol have common names such as gradient (**grad**), divergence (div) and curl (**curl**) or rotation (**rot**). Curl and rotation are synonymous. The **grad**, div etc. nomenclature is found mostly in the German literature. Notice that the gradient is taken of a scalar function but is itself a vector while the divergence is taken of a vector but is itself a scalar. This is the reason for often writing **grad** in boldface, which in many texts is an indication of a vector. The different names, the different uses and the slightly different ways of writing different operators can initially be confusing, but keep in mind that the operator notation is simply a compact, coordinate free nomenclature. Working

Table 1.1 Common operators in rectangular coordinates.

Gradient of a scalar function

$$\mathbf{grad}f = \nabla f(x, y, z) = \frac{\partial f}{\partial x}e_x + \frac{\partial f}{\partial y}e_y + \frac{\partial f}{\partial z}e_z$$

Laplacian of a scalar function

$$\nabla^2 f(x, y, z) = \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2}$$

Divergence of a vector function

$$\text{div}f = \nabla \cdot v = \frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z}$$

Laplacian of a vector function

$$\nabla^2 v = \nabla^2 v_x e_x + \nabla^2 v_y e_y + \nabla^2 v_z e_z$$

Rotation or curl of a vector function

$$\mathbf{rot}v = \mathbf{curl}v = \nabla \times v = \left(\frac{\partial v_z}{\partial y} - \frac{\partial v_y}{\partial z} \right) e_x + \left(\frac{\partial v_x}{\partial z} - \frac{\partial v_z}{\partial x} \right) e_y + \left(\frac{\partial v_y}{\partial x} - \frac{\partial v_x}{\partial y} \right) e_z$$

with operators only requires knowledge of what a given symbol stands for. The most commonly used operators, their definitions and names, are given in Tables 1.1 through 1.3 for the three basic coordinate systems.

It is possible to find the explicit expression for an operator in any coordinate system if an explicit expression is known in a reference coordinate system and if the transformations which convert the reference coordinates to the new coordinates are known. The reference coordinates are usually rectangular coordinates. However, doing so is tedious and not straight forward. So unless one works in a very unusual coordinate system which is not described in the literature, expressions for operators are looked up in tables rather than derived.

Using operator notation, we can now restate Fourier's and Fick's laws. They are, Fourier's law

$$q = -k\nabla T$$

and Fick's law

$$N = -D\nabla C$$

Notice that both fluxes are vectors and that Fourier's and Fick's laws are mathematically identical, which is at the root of the famous Chilton-Colburn analogy⁶. Strictly speaking, Fick's law is only valid for diffusion of a dilute solute through the solvent and one should be cautious about using it to model multicomponent diffusion or diffusion in concentrated solutions. As stated here, both Fourier's law

⁶T.H. Chilton and A.P. Colburn, *Mass Transfer (Absorption) Coefficients, Prediction from Data on Heat Transfer and Fluid Friction*, **Ind. Eng. Chem.**, **26**, 1183-1187 (1934)

Table 1.2 Common operators in cylindrical coordinates.

Gradient of a scalar function

$$\mathbf{grad}f = \nabla f(r, \theta, z) = \frac{\partial f}{\partial r} e_r + \frac{1}{r} \frac{\partial f}{\partial \theta} e_\theta + \frac{\partial f}{\partial z} e_z$$

Laplacian of a scalar function

$$\nabla^2 f(r, \theta, z) = \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial f}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 f}{\partial \theta^2} + \frac{\partial^2 f}{\partial z^2}$$

Divergence of a vector function

$$\text{div}f = \nabla \cdot v = \frac{1}{r} \frac{\partial r v_r}{\partial r} + \frac{1}{r} \frac{\partial v_\theta}{\partial \theta} + \frac{\partial v_z}{\partial z}$$

Laplacian of a vector function

$$\begin{aligned} \nabla^2 v = & \left(\frac{\partial}{\partial r} \left(\frac{1}{r} \frac{\partial r v_r}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 v_r}{\partial \theta^2} - \frac{2}{r^2} \frac{\partial v_\theta}{\partial \theta} + \frac{\partial^2 v_r}{\partial z^2} \right) e_r \\ & + \left(\frac{\partial}{\partial r} \left(\frac{1}{r} \frac{\partial r v_\theta}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 v_\theta}{\partial \theta^2} + \frac{2}{r^2} \frac{\partial v_r}{\partial \theta} + \frac{\partial^2 v_\theta}{\partial z^2} \right) e_\theta \\ & + \left(\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial v_z}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 v_z}{\partial \theta^2} + \frac{\partial^2 v_z}{\partial z^2} \right) e_z \end{aligned}$$

Rotation or curl of a vector function

$$\mathbf{rot}v = \mathbf{curl}v = \nabla \times v = \left(\frac{1}{r} \frac{\partial v_z}{\partial \theta} - \frac{\partial v_\theta}{\partial z} \right) e_r + \left(\frac{\partial v_r}{\partial z} - \frac{\partial v_z}{\partial r} \right) e_\theta + \left(\frac{1}{r} \frac{\partial r v_\theta}{\partial r} - \frac{1}{r} \frac{\partial v_r}{\partial \theta} \right) e_z$$

and Fick’s law are for isotropic substances, i.e. substances in which properties are independent of direction. In non isotropic substances such as crystals, either solid or liquid, properties change with direction and the thermal conductivity of or diffusion coefficient inside a crystal will depend on the direction of transport. Stating the relevant constitutive equations for such substances requires the use of tensors. Both equations must also be used with caution when modeling transport in porous media and the coefficients should more correctly be called effective conductivity and effective diffusivity. The value of the effective transport coefficients will not equal that of the coefficients in an unrestricted medium due to the convoluted path of the pores that serve as transport conduits.

Diffusion in porous media is particularly complex and may involve both Fickian diffusion and Knudsen and surface diffusion. Estimation of the effective diffusion coefficient in porous media is an important problem when modeling catalysts and an extensive literature exists on this topic⁷.

⁷The reader interested in learning more may want to consult the old but still valuable monograph: “Transport in porous catalysts”, Roy Jackson. Elsevier, Amsterdam, 1977

Table 1.3 Common operators in spherical coordinates.

Gradient of a scalar function

$$\mathbf{grad}f = \nabla f(r, \theta, \phi) = \frac{\partial f}{\partial r} e_r + \frac{1}{r} \frac{\partial f}{\partial \theta} e_\theta + \frac{1}{r \sin \theta} \frac{\partial f}{\partial \phi} e_\phi$$

Laplacian of a scalar function

$$\nabla^2 f(r, \theta, \phi) = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial f}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial f}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 f}{\partial \phi^2}$$

Divergence of a vector function

$$\text{div}f = \nabla \cdot v = \frac{1}{r^2} \frac{\partial r^2 v_r}{\partial r} + \frac{1}{r \sin \theta} \frac{\partial v_\theta \sin \theta}{\partial \theta} + \frac{1}{r \sin \theta} \frac{\partial v_\phi}{\partial \phi}$$

Laplacian of a vector function

$$\begin{aligned} \nabla^2 v = & \left(\nabla^2 v_r - \frac{2v_r}{r^2} - \frac{2}{r^2} \frac{\partial v_\theta}{\partial \theta} - \frac{2v_\theta \cot \theta}{r^2} - \frac{2}{r^2 \sin \theta} \frac{\partial v_\phi}{\partial \phi} \right) e_r \\ & + \left(\nabla^2 v_\theta + \frac{2}{r^2} \frac{\partial v_r}{\partial \theta} - \frac{v_\theta}{r^2 \sin^2 \theta} - \frac{2 \cos \theta}{r^2 \sin^2 \theta} \frac{\partial v_\phi}{\partial \phi} \right) e_\theta \\ & + \left(\nabla^2 v_\phi - \frac{v_\phi}{r^2 \sin^2 \theta} + \frac{2}{r^2 \sin \theta} \frac{\partial v_r}{\partial \phi} + \frac{2 \cos \theta}{r^2 \sin^2 \theta} \frac{\partial v_\theta}{\partial \phi} \right) e_\phi \end{aligned}$$

Rotation or curl of a vector function

$$\begin{aligned} \mathbf{rot}v = \mathbf{curl}v = \nabla \times v = & \left(\frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} (v_\phi \sin \theta) - \frac{1}{r \sin \theta} \frac{\partial v_\theta}{\partial \phi} \right) e_r \\ & + \left(\frac{1}{r \sin \theta} \frac{\partial v_r}{\partial \phi} - \frac{1}{r} \frac{\partial r v_\phi}{\partial r} \right) e_\theta + \left(\frac{1}{r} \frac{\partial r v_\theta}{\partial r} - \frac{1}{r} \frac{\partial v_r}{\partial \theta} \right) e_\phi \end{aligned}$$

1.1.3.4 Mass and energy balances

Of the three coordinate systems presented so far, the most difficult one to visualize and use is the spherical coordinate system. The next example shows how to write a balance in this system by carefully accounting for transport terms in each of the three coordinate directions.

Example 1.8: Spherical catalytic pellet.

Consider a spherical catalytic particle of radius R . Transport of the reactant through the pellet is given by Fick's law with an effective diffusion coefficient D and the reactant is consumed in a first order reaction with reaction rate constant k . The concentration of the reactant at the pellet surface, $C_s(\theta, \phi)$, is assumed known. Write a model for the concentration of the reactant through the catalytic particle as a function of time. Assume that there are no heat effects associated with the reaction.

The balance equation must account for the diffusive flux in all three coordinate directions. In all cases, the rate of transport in and out of the control volume is the product of the flux given by Fick's law and the area of the surface of the control volume that is at a right angle to the coordinate direction. In cylindrical coordinates, Fick's law takes the form

$$N_r = -D \frac{\partial C}{\partial r}, \quad N_\theta = -D \frac{1}{r} \frac{\partial C}{\partial \theta}, \quad N_\phi = -D \frac{1}{r \sin \theta} \frac{\partial C}{\partial \phi}$$

where the three N 's are the fluxes in the radial, θ and ϕ directions, respectively. For transport in the radial direction, the area available for the flux equals $rd\theta r \sin \theta d\phi$ at a radial distance of r . Thus

$$\text{In - out} = -D \frac{\partial C}{\partial r} rd\theta r \sin \theta d\phi \Big|_r - \left(-D \frac{\partial C}{\partial r} rd\theta r \sin \theta d\phi \Big|_{r+dr} \right)$$

where the subscript r indicates that the expression in parentheses is evaluated at r . For the θ direction, the area for transport equals $r \sin \theta d\phi dr$, giving

$$\text{In-out} = -D \frac{1}{r} \frac{\partial C}{\partial \theta} (r \sin \theta d\phi dr) \Big|_\theta - \left(-D \frac{1}{r} \frac{\partial C}{\partial \theta} (r \sin \theta d\phi dr) \Big|_{\theta+d\theta} \right)$$

and, finally, for transport in the ϕ direction, the area for transport is $rd\theta dr$.

$$\text{In-out} = -D \frac{1}{r \sin \theta} \frac{\partial C}{\partial \phi} (rd\theta dr) \Big|_\phi - \left(-D \frac{1}{r \sin \theta} \frac{\partial C}{\partial \phi} (rd\theta dr) \Big|_{\phi+d\phi} \right)$$

The accumulation term is the rate of change or time derivative of the concentration inside the control volume multiplied by the physical volume of the control volume, $r^2 \sin \theta dr d\phi d\theta$.

$$\text{Accumulation} = \frac{\partial}{\partial t} (Cr^2 \sin \theta dr d\phi d\theta) = r^2 \sin \theta dr d\phi d\theta \frac{\partial C}{\partial t}$$

Similarly, the generation term equals the specific reaction rate inside the control volume multiplied by the physical volume of the control volume.

$$\text{Generation} = -kCr^2 \sin \theta dr d\phi d\theta$$

Putting everything together gives the following expression.

$$\begin{aligned} & -D \frac{\partial C}{\partial r} r^2 \sin \theta d\phi d\theta \Big|_r + D \frac{\partial C}{\partial r} r^2 \sin \theta d\phi d\theta \Big|_{r+dr} \\ & -D \frac{\partial C}{\partial \theta} \sin \theta d\phi dr \Big|_\theta + D \frac{\partial C}{\partial \theta} \sin \theta d\phi dr \Big|_{\theta+d\theta} \\ & -D \frac{1}{\sin \theta} \frac{\partial C}{\partial \phi} d\theta dr \Big|_\phi + D \frac{1}{\sin \theta} \frac{\partial C}{\partial \phi} d\theta dr \Big|_{\phi+d\phi} \\ & = r^2 \sin \theta dr d\phi d\theta \frac{\partial C}{\partial t} + kCr^2 \sin \theta dr d\phi d\theta \end{aligned}$$

Dividing through by $r^2 \sin \theta dr d\phi d\theta$ and recognizing derivatives, one obtains

$$\begin{aligned} \frac{1}{r^2} \frac{\partial}{\partial r} \left(D r^2 \frac{\partial C}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(D \sin \theta \frac{\partial C}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial}{\partial \phi} \left(D \frac{\partial C}{\partial \phi} \right) \\ = \frac{\partial C}{\partial t} + kC \end{aligned}$$

One can do the same problem in rectangular coordinates. In that case the governing differential equation will be (convince yourself of this)

$$\left(\frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial y} \left(D \frac{\partial C}{\partial y} \right) + \frac{\partial}{\partial z} \left(D \frac{\partial C}{\partial z} \right) \right) = \frac{\partial C}{\partial t} + kC$$

The big difference between models in the two coordinate systems become apparent when the boundary condition at the surface is written. In spherical coordinates, this boundary condition is

$$r = R \Rightarrow C = C_s(\theta, \phi)$$

which is a condition along a coordinate surface. Because of this, the surface concentration is a function of, at most, two coordinates, θ and ϕ . In rectangular coordinates the same boundary condition is written as

$$x^2 + y^2 + z^2 = R^2 \Rightarrow C = C_s(\theta(x, y, z), \phi(x, y, z))$$

This condition is not specified on a coordinate surface and the specified surface condition is now in general a function of three coordinates, x, y, z . The difference between the two models become even greater when one considers the steady state problem with the simplifications that are possible if the surface concentration has spherical symmetry. In that case, the concentration is independent of θ and ϕ so all derivatives with respect to these variables vanish and the model in spherical coordinates becomes

$$\frac{1}{r^2} \frac{d}{dr} \left(D r^2 \frac{dC}{dr} \right) = kC \quad (1.20)$$

Given the spherical symmetry, one could have derived this balance equation from a reactant balance using a control volume which is a spherical shell of thickness dr .

Similar simplifications are not possible in rectangular coordinates. Thus, in spherical coordinates the model is an ordinary differential equation while it is a partial differential equation in rectangular coordinates. There can be little disagreement that the model in spherical coordinates is far simpler and easier to solve than the model in rectangular coordinates even though both models are valid and give the same solution.

In order to solve Eq. 1.20 for the steady state concentration profile, two boundary conditions are needed. However, it is possible to write more than just two conditions.

For instance some possible boundary conditions in spherical coordinates are

$$r = R \Rightarrow C = C_s$$

$$r = 0 \Rightarrow \frac{dC}{dr} = 0$$

$$r = 0 \Rightarrow C \text{ finite}$$

$$\int_0^R kC(r)4\pi r^2 dr = D4\pi R^2 \left(\frac{dC}{dr} \right)_R$$

The first boundary condition is a specification of the concentration at the pellet surface, the second follows from the assumption of spherical symmetry which requires the solution to be an even function. The third condition state that concentrations, since they are physical, measurable quantities, must be finite. The last is a total pellet balance equating the flux through the surface of the pellet to the total rate of conversion inside the pellet. All these boundary conditions must be satisfied by the solution. If they are not, the boundary conditions, the balance equation or the solution must be wrong. With a little experience, it is usually easy to pick the two boundary conditions that give the simplest solution procedure. The complete solution to Eq. 1.20 is

$$C(r) = C_1 \frac{\cosh\left(\sqrt{\frac{k}{D}}r\right)}{r} + C_2 \frac{\sinh\left(\sqrt{\frac{k}{D}}r\right)}{r}$$

where C_1 and C_2 are arbitrary constants. The $\frac{\cosh}{r}$ -term goes to infinity as r goes to zero so the constant C_1 must be zero to avoid a physically absurd solution. The other arbitrary constant is most easily found from the boundary condition at the surface and the solution is

$$C(r) = C_s \frac{R}{r} \frac{\sinh\left(\sqrt{\frac{k}{D}}r\right)}{\sinh\left(\sqrt{\frac{k}{D}}R\right)}$$

which is usually written as

$$\frac{C(\zeta)}{C_s} = \frac{1}{\zeta} \frac{\sinh(3\Phi\zeta)}{\sinh(3\Phi)}$$

where $\zeta = r/R$ is the dimensionless radial coordinate and $\Phi = \frac{R}{3}\sqrt{\frac{k}{D}}$ is the so-called Thiele modulus for a first order reaction in a spherical pellet⁸. The reason for defining the modulus this way, with the peculiar choice of $R/3$ as the characteristic length, is that this characteristic length equals the volume of the particle divided by its surface area. This definition of the characteristic length makes comparison between results for different shapes or geometries much easier. The Thiele modulus

⁸Thiele, E.W., Relation Between Catalytic Activity and Size of Particle, **Ind. Eng. Chem.** **31**, 916-920 (1939)

is basically a dimensionless measure of the rate of reaction relative to the rate of diffusion. Its definition depends on both the geometry of the catalytic pellet and on the rate expression for the catalyzed reaction. However, it is possible to avoid the confusion caused by this situation dependent definition by defining a generalize Thiele modulus which can be applied to any type of kinetics in any catalytic pellet⁹.

One often want to find the effectiveness factor, η , of catalytic particles. This is defined as the observed reaction rate over the pellet divided by the rate one would observe with no diffusional resistance, i.e. the rate one would observe if the concentration of the reactant equaled the surface concentration throughout the pellet. Thus, for a first order reaction

$$\eta = \frac{\int_V kC dV}{\int_V kC_s dV}$$

Evaluation of the integral in the denominator is straight forward. It obviously equals $kC_s \frac{4}{3}\pi R^3$. The integral in the numerator is more cumbersome to evaluate and it is easier to calculate the observed rate from the flux into the pellet. A reactant balance over the whole pellet states that the observed rate of reaction over the pellet equals the rate of diffusion from the pellet surface into the pellet, i.e.

$$\int_V kC dV = -(-D4\pi R^2) \left(\frac{dC}{dr} \right)_R$$

The minus sign outside the parentheses is needed because the flux into the pellet is a flux in the negative radial direction. The expression on the right hand side is easier to evaluate because differentiation is usually simpler to carry out than integration. The result for the effectiveness factor becomes

$$\eta = \frac{1}{\Phi} \left(\frac{1}{\tanh(3\Phi)} - \frac{1}{3\Phi} \right)$$

This result is plotted in Fig. 1.18 together with the similar results for a first order reaction in rectangular and cylindrical geometries. In all geometries, the length that appears in the Thiele modulus is defined as the volume of the particle divided by its surface area. In rectangular geometry, the result is

$$\eta = \frac{1}{\Phi} \tan \Phi$$

while in cylindrical geometry

$$\eta = \frac{I_1(2\Phi)}{\Phi I_0(2\Phi)}$$

where I_1 and I_0 are the modified Bessel functions of first kind of order 1 and zero respectively. Bessel functions will be covered in section 6.5.2.

The graphs for the three geometries are shown in Fig. 1.18 and they are seen to be very similar. Most importantly, they share the same asymptotes: at large

⁹Bischoff, K.B., Effectiveness Factors for General Reaction Rate Forms, **AICHE J.** **11**, 351-355 (1965)

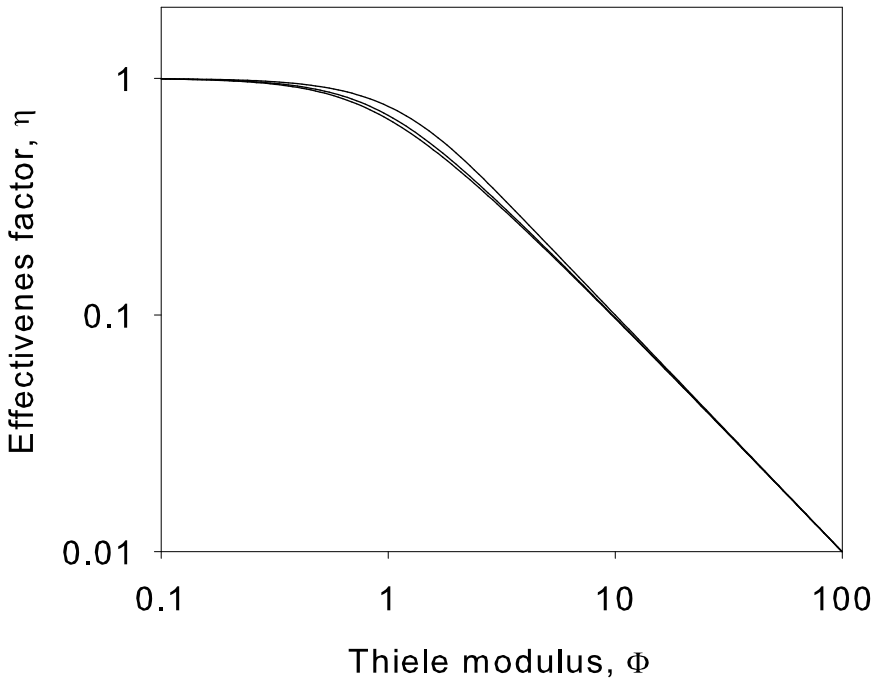


Fig. 1.18 The effectiveness factor, η , versus the Thiele modulus, Φ , for a first order reaction in rectangular, cylindrical and spherical geometries. The top curve is for rectangular geometry, the curve in the middle for cylindrical geometries and the curve at the bottom for spherical geometry.

values of the Thiele modulus, when the reaction is diffusion limited, $\eta \simeq 1/\Phi$ while at small values when the reaction rate is limiting, $\eta \simeq 1$. The Thiele modulus for different rate expressions is usually defined in such a way that this limiting behavior is maintained. The graphs also illustrate that, in this case at least, models based on different geometries but otherwise equivalent give close to the same results. This suggests that approximate modeling can often be done in the easier to handle rectangular coordinates than in curvilinear coordinates.

A more realistic model is obtained if mass transfer resistance is assumed at the surface of the pellet. In this case, the boundary condition at the pellet surface states that the flux through the film equals the flux into the pellet at the pellet surface

$$r = R \Rightarrow -D \frac{\partial C}{\partial r} = k_m (C_s - C_\infty)$$

where k_m is a mass transfer coefficient, C_s the unknown concentration of the reactant at the surface of the pellet and C_∞ the concentration of the reactant outside the film. Of course, the previous boundary condition at the surface still holds and, therefore, so does the solution. However, the surface concentration, C_s is now an

unknown which must be found from the condition above. One finds

$$C_s = \frac{k_m}{D} \frac{C_\infty}{\sqrt{\frac{k}{D}} \coth\left(\sqrt{\frac{k}{D}} R\right) - \frac{1}{R} + \frac{k_m}{D}}$$

The analysis done so far is only valid for reactions for which temperature effects are not important. To model the effects of temperature, one must account for the amount of heat produced or consumed by the reaction and the effect of temperature on the rate of reaction. The mole balance remains the same when temperature effects are taken into account, however, the reaction rate constant is now temperature dependent and this dependence is modeled by Arrhenius' law. In spherical coordinates, at steady state

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 D \frac{dC}{dr} \right) = k_0 e^{-\frac{E}{RT}} C$$

The diffusion coefficient has not been taken outside the differentiation operation because diffusion coefficients are usually temperature sensitive and therefore, for this situation, dependent on position.

The energy produced or consumed by a reaction is accounted for by the heat of reaction ΔH_r . A steady state energy balance on a spherical shell of thickness dr gives

$$\left(-4\pi r^2 k_T \frac{dT}{dr} \right)_r - \left(-4\pi r^2 k_T \frac{dT}{dr} \right)_{r+dr} = k \Delta H_r C 4\pi r^2 dr$$

where k_T is the thermal conductivity of the pellet. The two flux terms on the left hand side are straight forward applications of Fourier's law. The right hand side represent the rate of energy consumption. From the definition of the heat of reaction, this term equals the volume of the spherical shell times the heat of reaction times the rate of conversion of the reactant. Dividing through by dr and rearranging gives

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 k_T \frac{dT}{dr} \right) = k_0 e^{-\frac{E}{RT}} \Delta H_r C$$

subject to boundary conditions similar to those for the concentration. The two coupled model equations are nonlinear and too complex to solve analytically. However, numerical solutions have been obtained and presented in the literature¹⁰.

The main purpose of the next example is to illustrate the need to examine a solution to a model to determine if the result is reasonable. In the case of a zero order reaction, the reaction does not slow down as the reactant concentration approach zero so one will expect the reactant to become zero abruptly at some point in time or space. However, this fact is not reflected in a model that uses a rate expression

¹⁰Weisz, P.B. and J.S. Hicks, The Behavior of Porous Catalysts Particles in View of Internal Mass and Heat Diffusion Effects, **Chem. Eng. Sci.** **17**, 265 (1962)

which simply sets the rate equal to a constant and, in such naive models, the reactant concentration can become negative, a result that is not physically meaningful.

Example 1.9: Catalytic pellet with a zero order reaction.

Enzymes are the protein based catalysts that carry out and regulate cellular metabolism. Many enzymes are used industrially such as in production of syrups and flavors and in food processing or appear in consumer products such as in laundry detergents. Due to their cost, enzymes are most often used in immobilized form for easy recovery. Analysis of a simple enzyme reaction mechanism shows the reaction rate to be of so-called Michaelis-Menten form

$$r(C) = \frac{r_m C}{K + C}$$

where C is the concentration of the reactant and r the rate of consumption of the reactant. (In enzyme catalysis, the reaction rate is commonly called the velocity of the reaction, thus v is often used to indicate the reaction rate). The two constant parameters, r_m and K , are the maximum reaction rate and the Michaelis-Menten constant respectively.

For obvious reasons, enzyme catalyzed reactions are carried out most efficiently at high reactant concentrations when the reaction rate is approximately equal to the maximum reaction rate, r_m , i.e. when the reactant is, to a good approximation, consumed in a zero order reaction. When this assumption is valid, a mass balance on the reactant in a flat immobilized enzyme pellet is

$$D \frac{d^2 C}{dx^2} = r_m$$

Placing the origin of the x -axis in the center of the particle, the boundary conditions are

$$x = 0 \Rightarrow \frac{dC}{dx} = 0$$

$$x = L \Rightarrow C = C_s$$

where L is half the pellet thickness and also the characteristic length of the pellet. C_s is the surface concentration of the reactant. Make this model dimensionless by introducing the following dimensionless variables and parameters.

$$\zeta = \frac{\xi}{L}, \quad \Theta = \frac{C}{C_s}, \quad \Phi = \sqrt{\frac{r_m L^2}{2C_s D}}$$

where ξ is the dimensionless spatial coordinate, Θ the dimensionless concentration and Φ the Thiele modulus for a zero order reaction. This gives the dimensionless model

$$\frac{d^2 \Theta}{d\zeta^2} = 2\Phi^2, \quad \Theta(1) = 1, \quad \left. \frac{d\Theta}{d\zeta} \right|_0 = 0$$

The reason for defining the Thiele modulus this way for a zero order reaction, creating the factor of 2 in the mass balance, is not obvious. However, we will not discuss the reasons for this other than to point out that this choice gives a result for the effectiveness factor with the desired limiting behavior at large values of the Thiele modulus, $\eta \approx 1/\Phi$. Solving for Θ

$$\Theta = \Phi^2 \xi^2 + C_1 \xi + C_2$$

and applying boundary conditions gives

$$\Theta(\xi) = \Phi^2(\xi^2 - 1) + 1$$

It is now very important to note that the solution becomes negative at the center, a physical impossibility, if $\Phi > 1$. It is tempting to dismiss this problem by resetting the negative values of Θ to zero. However, this is not a valid solution to the problem of negative concentrations. To see this, note that at the distance at which the concentration becomes zero, call this distance x_c , one can write a reactant balance stating that the flux of reactant to this point equals the flux of reactant away from this point, i.e.

$$0 = -D \left. \frac{dC}{dx} \right|_{x_c}$$

but it is easily checked that the solution above does not have a zero derivative at the point where Θ becomes zero. The solution is still valid when $\Phi \leq 1$, but a different approach is needed for $\Phi \geq 1$.

The problem with the case $\Phi \geq 1$ is that the reactant concentration does become zero at some point inside the pellet and the boundary condition at $\xi = 0$ is therefore no longer applicable. In its place, one can use the reactant balance stated above, the balance at the point at which the concentration becomes zero. In dimensionless form, this is

$$\left. \frac{d\Theta}{d\xi} \right|_{\xi_c} = 0$$

which must be used in conjunction with a defining equation for ξ_c .

$$\Theta(\xi_c) = 0$$

The following solution is obtained

$$\Theta(\xi) = \begin{cases} \Phi^2(\xi^2 + (1 - \frac{1}{\Phi})^2 - 2\xi(1 - \frac{1}{\Phi})) , & \xi \geq 1 - \frac{1}{\Phi} \\ 0 , & \xi \leq 1 - \frac{1}{\Phi} \end{cases}$$

and

$$\xi_c = 1 - \frac{1}{\Phi}$$

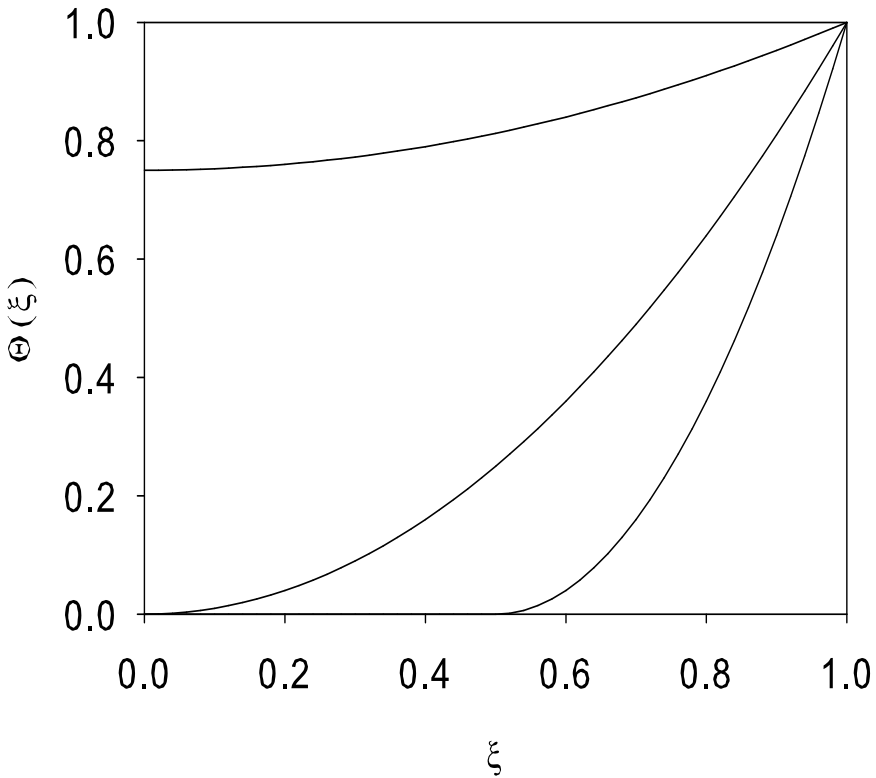


Fig. 1.19 Dimensionless concentration profiles for a zero order reaction with $\Phi = 0.5, 1, 2$, top graph to bottom graph.

As this solution is only valid when $\Phi \geq 1$, the complete solution can be written as

$$\Theta(\xi) = \begin{cases} \Phi^2(\xi^2 - 1) + 1, & \Phi \leq 1 \\ \begin{cases} \Phi^2(\xi^2 + (1 - \frac{1}{\Phi})^2 - 2\xi(1 - \frac{1}{\Phi})) & , \xi \geq 1 - \frac{1}{\Phi} \\ 0, & \xi \leq 1 - \frac{1}{\Phi} \end{cases} & , \Phi \geq 1 \end{cases}$$

and graphs of these solutions are shown in Fig. 1.19.

The effectiveness factor is found to be

$$\eta = \begin{cases} \int_0^L v_m dx / (v_m L), & \Phi \leq 1 \\ \int_{x_c}^L v_m dx / (v_m L), & \Phi \geq 1 \end{cases}$$

or

$$\eta = \begin{cases} 1, & \Phi \leq 1 \\ \frac{1}{\Phi}, & \Phi \geq 1 \end{cases}$$

Thus, the effectiveness factor curve for the zero order reaction consists of the two asymptotes of the curves of the effectiveness factors for a first order reaction, Fig. 1.18.

The next example illustrates a differential balance in which fluid flow with a known velocity profile pass through the control volume surface. When this occurs, fluxes are most easily calculated if the coordinate systems is chosen such that streamlines are at a right angle to the surface.

Example 1.10: Tubular reactor with laminar flow.

Write a model for the concentration of the reactant in a tubular reactor in which the fluid flow is laminar and diffusion occurs in both the radial and axial direction. Assume that the reactant is converted by an n 'th order reaction with reaction constant k .

The obvious choice of coordinate system is a cylindrical coordinate system with the origin at the center of the reactor inlet and the z -axis pointing in the direction of the flow. Let the radius of the reactor be R , the laminar profile then is given by

$$v_z(r) = v_m \left(1 - \left(\frac{r}{R} \right)^2 \right)$$

The reactant concentration will be a function of r and z but not a function of the angle θ (unless of course the inlet concentration is a function of θ). The control volume will therefore be an annular ring of length dz and thickness dr . The area available for transport in the axial and radial directions are $2\pi r dr$ and $2\pi r dz$ respectively and the volume of the ring has the volume $2\pi r dr dz$. See Fig. 1.20.

The following transport terms will appear in the mass balance for the reactant. The term for convective transport in the axial direction:

$$2\pi r dr v(r) C(r, z)|_z - (2\pi r dr v(r) C(r, z))|_{z+dz}$$

The term for diffusional transport in the axial direction:

$$\left(2\pi r dr \left(-D \frac{\partial C}{\partial z} \right) \right)_z - \left(2\pi r dr \left(-D \frac{\partial C}{\partial z} \right) \right)_{z+dz}$$

The term for diffusional transport in the radial direction:

$$\left(2\pi r dz \left(-D \frac{\partial C}{\partial r} \right) \right)_r - \left(2\pi r dz \left(-D \frac{\partial C}{\partial r} \right) \right)_{r+dr}$$

where D is the diffusion coefficient and $C(r, z)$ the concentration of the reactant. Substituting all this into the conservation equation gives

$$\begin{aligned} & (2\pi r dr v(r) C(r, z))_z - (2\pi r dr v(r) C(r, z))_{z+dz} \\ & + (2\pi r dr \left(-D \frac{\partial C}{\partial z} \right))_z - (2\pi r dr \left(-D \frac{\partial C}{\partial z} \right))_{z+dz} \\ & + (2\pi r dz \left(-D \frac{\partial C}{\partial r} \right))_r - (2\pi r dz \left(-D \frac{\partial C}{\partial r} \right))_{r+dr} = \frac{\partial}{\partial t} (C 2\pi r dr dz) + k C^n 2\pi r dr dz \end{aligned}$$

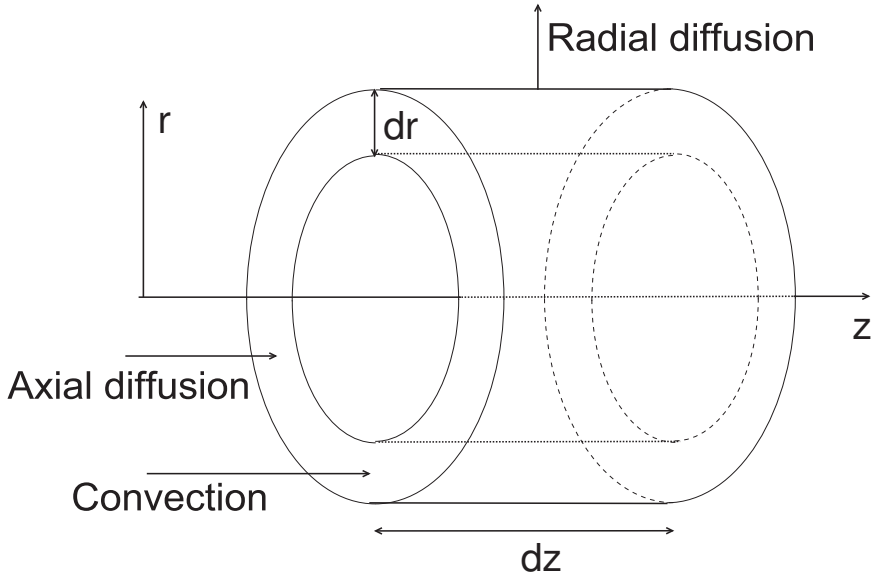


Fig. 1.20 Control volume and fluxes for the tubular reactor.

dividing through by $drdz$ and recognizing derivatives gives

$$D \frac{\partial^2 C}{\partial z^2} + \frac{D}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C}{\partial r} \right) - v_m \left(1 - \left(\frac{r}{R} \right)^2 \right) \frac{\partial C}{\partial z} = \frac{\partial C}{\partial t} + kC^n$$

where a constant diffusion coefficient has been assumed.

The boundary conditions in the radial direction are straight forward.

$$r = 0 \Rightarrow C \text{ finite and } \frac{\partial C}{\partial r} = 0$$

$$r = R \Rightarrow \frac{\partial C}{\partial r} = 0$$

We will not attempt to write the boundary conditions in the z -direction here.

The main difficulty in the next example lies in the fact that the content of a packed bed reactor is not a single phase. The usual CV, an annular ring of thickness dr and length dz , will therefore not work because the concentration of the reactant is not constant inside this CV. The best control volume includes matter from one phase only and is therefore the fluid content of a differential annular ring.

Example 1.11: Packed bed reactor.

Consider a packed bed, tubular reactor in which a reactant in the fluid phase is converted instantaneously on the surface of catalytic pellets. The reactant must diffuse through a stagnant film surrounding the catalyst in order to react. The mass transfer coefficient across the film is k_m . The fluid flow is approximately plug flow

and the mixing which occurs due to the deviation from plug flow can be modeled by assuming that back mixing of the reactant follows a law similar to Fick's law with a so-called dispersion coefficient taking the place of the diffusion coefficient. To account for the difference between radial and axial mixing, different dispersion coefficients are used in the radial and axial directions, D_r and D_z respectively. The volumetric flow rate through the reactor is Q , the cross sectional area of the reactor is A and the void fraction in the bed is ϵ . Write a model for this reactor assuming a negligible heat of reaction.

The best control volume is the fluid phase inside an annular ring of length dz and thickness dr . One cannot draw such a control volume but must think of it in more abstract terms. The surfaces of the control volume can be partitioned into two types: the surfaces of the annular ring which are covered by fluid and the interface between the fluid and the catalytic particles inside the control ring. Fluxes across all these surfaces must be accounted for when setting up the balance on the reactor.

Since the volumetric flow rate through the reactor is Q and the cross sectional area of the reactor is A , the fluid velocity based on an empty tube is Q/A . The interstitial fluid velocity, the fluid velocity between the catalyst particles, is the empty tube velocity divided by the void fraction of the bed, i.e. it equals $Q/(A\epsilon)$. This is the velocity needed in the convective term. The area available for flow in the axial direction is the area of the control volume surface at a right angle to the axial direction, $2\pi r dr$, multiplied by the void fraction, ϵ . Thus, convective transport in the axial direction is given by

$$\left(2\pi r dr \epsilon \frac{Q}{A\epsilon} C(r, z)\right)_z - \left(2\pi r dr \epsilon \frac{Q}{A\epsilon} C(r, z)\right)_{z+dz}$$

The term for transport by dispersion in the axial direction must similarly take into account the fact that fluid phase diffusion is restricted to the void volume.

$$\left(2\pi r \epsilon dr \left(-D_z \frac{\partial C}{\partial z}\right)\right)_z - \left(2\pi r \epsilon dr \left(-D_z \frac{\partial C}{\partial z}\right)\right)_{z+dz}$$

Likewise for the term for transport by dispersion in the radial direction.

$$\left(2\pi r \epsilon dz \left(-D_r \frac{\partial C}{\partial r}\right)\right)_r - \left(2\pi r \epsilon dz \left(-D_r \frac{\partial C}{\partial r}\right)\right)_{r+dr}$$

Finally, the flux across the film surrounding the catalytic pellets must be determined. The area available for transport across the film inside a control volume must be proportional to the physical volume of the control volume. The proportionality constant is the specific surface area of the bed, call it a . The rate of transport through the film now is

$$a2\pi r dr dz k_m (C - C_s)$$

where C_s is the concentration of the reactant at the solid surface. However, since the reaction is instantaneous, this concentration must be zero, i.e. the rate of transport through the film simply is

$$a2\pi r dr dz k_m C$$

The accumulation term is

$$\frac{\partial}{\partial t}(C2\pi r\epsilon dr dz)$$

and since there is no reaction the fluid phase, the generation term is zero. Putting the terms into the mass balance and carrying out the standard rearrangement of dividing through by $dr dz$ and recognizing derivatives gives

$$\frac{\partial}{\partial z} \left(\epsilon D_z \frac{\partial C}{\partial z} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left(r \epsilon D_r \frac{\partial C}{\partial r} \right) - \frac{\partial}{\partial z} \left(\frac{Q}{A} C \right) = \epsilon \frac{\partial C}{\partial t} + a k_m C$$

Assuming constant properties though the bed, this simplifies to

$$\epsilon D_z \frac{\partial^2 C}{\partial z^2} + \epsilon D_r \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C}{\partial r} \right) - \frac{Q}{A} \frac{\partial C}{\partial z} = \epsilon \frac{\partial C}{\partial t} + a k_m C$$

The boundary conditions in the radial direction are straight forward.

$$r = 0 \Rightarrow C \text{ finite and } \frac{\partial C}{\partial r} = 0$$

The boundary condition at the wall is a no-flux condition indicating that the reactant does not diffuse through the reactor wall.

$$r = R \Rightarrow \frac{\partial C}{\partial r} = 0$$

where R is the radius of the reactor.

The boundary conditions in the axial or z -direction are difficult to state, if for no other reason that the problem is not well defined in the axial direction. Dispersion in the z -direction will cause mixing of fluid that has already reacted with unreacted fluid and the entrance concentration at $z = 0$ is therefore not the same as the feed concentration to the reactor. Similarly, the concentration at the very end of the bed will not be the same as the exit concentration from the reactor due to the dispersion and mixing at the exit. Neither the entrance nor the exit mixing effects can be modeled unless the geometry of the entrance and exit regions are known, yet such detailed modeling is usually excessively detailed and complex. In most cases, it is reasonable to assume that the reactor performance is not strongly dependent on how the entrance and exit regions are shaped as long as mixing of the reactants is fast and most of the reaction occurs inside the reactor rather than in the entrance and exit regions. So how does one write boundary conditions that reflect this? Different conditions have been proposed and a generally accepted solution has emerged. These generally accepted boundary conditions can be obtained as follows. (Interested readers are referred to the original paper by Wehner and Wilhelm ¹¹ where different proposed boundary conditions are discussed and a more detailed derivation is given.)

¹¹Wehner, J.F. and R.H. Wilhelm, Boundary conditions of flow reactor, **Chem. Eng. Sci.** **6**, 89-93 (1956)

Make the assumption that there is no dispersion for $z < 0$. A balance over the surface $z = 0$ gives

$$\frac{Q}{A}C \Big|_{-dz} = \frac{Q}{A\epsilon}C \Big|_{dz} + \left(-D_z\epsilon \frac{\partial C}{\partial z} \Big|_{dz} \right)$$

If there is no dispersion for $z < 0$, i.e. no mixing of the feed with the reactor content, then $C(-dz)$ must equal the feed concentration C_{feed} and the boundary condition takes the form

$$z = 0 \Rightarrow C_{feed} = C - \frac{D_z A \epsilon}{Q} \frac{\partial C}{\partial z}$$

is obtained. C_{feed} is a specified feed concentration to the reactor. The concentration in the entrance region before the reactive bed, $z < 0$, equals C_{feed} , so this boundary condition does not require that the concentration or the concentration gradient be continuous across $z = 0$. In a rigorous sense, this is obviously not possible, but what the boundary condition states is that at the bed entrance, concentrations change so fast or over such short distances that they can be adequately modeled assuming a discontinuous concentration and concentration gradient. In other words, this boundary condition is not dictated by some law of nature but is an approximate model of the bed entrance.

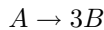
The commonly used boundary condition at the end of the bed is simply

$$z = L \Rightarrow \frac{\partial C}{\partial z} = 0$$

The next example makes use of a basis, i.e. a control volume which is a well defined lump a matter which may or may not retain its volume and position. The use a basis when doing calculation on process streams in macroscopic balance models is well known. The example below illustrates the use of a basis in a differential balance model.

Example 1.12: Plug flow reactor with volume change.

A plug flow reactor is a tubular reactor through which the fluid moves with a flat velocity profile. Consider a plug flow reactor for which diffusion is negligible, i.e. transport is purely convective, and in which the first order reaction



with the reaction rate constant k takes place. All components in the reactor can be considered as ideal gasses and the reactor operates at a constant pressure and temperature. The inlet mixture to the reactor consists of 75% inert and 25% A and the inlet volumetric flow rate, $Q(0)$, is given. What can be said about the size of reactor needed to obtain a given outlet concentration C_A ?

Start solving this problem by deriving a differential equation model for the concentration through the reactor. Place a z -axis pointing in the direction of flow

with the origin at the reactor inlet. A balance on component A in a reactor slice between z and $z + dz$ gives

$$Q(z)C_A(z)|_z - Q(z)C_A(z)|_{z+dz} = kC_A A dz$$

where $Q(z)$ is the volumetric flow rate at position z , $C_A(z)$ the concentration of the reactant and A the cross sectional area of the reactor. The balance simplifies to

$$\frac{d}{dz}(QC_A) = -kC_A A$$

so we have two unknowns, $Q(z)$ and $C_A(z)$, but so far only one equation. Another equation relating $Q(z)$ and $C_A(z)$ can be obtained as follows: First note that for ideal gasses, the total molar concentration is

$$C = \frac{N}{V} = \frac{p}{RT} = \text{Constant}$$

and because the reactor operates at a constant pressure and temperature, the total molar concentration is constant through the reactor.

Take as a basis for further calculations the amount of matter which enters the reactor during the period t . Conservation of mass requires that this matter must take the same amount of time to go past any point in the reactor. Let the number of moles in the basis be N , let the basis have the volume V , and one has

$$Ct = \frac{Nt}{V} = \frac{N}{V/t} = \frac{N}{Q} = \text{Constant}$$

We can therefore write

$$\frac{N(0)}{Q(0)} = \frac{N(z)}{Q(z)} \Rightarrow$$

$$Q(z) = Q(0) \frac{N(z)}{N(0)}$$

The stoichiometry allows us to relate $N(z)$ to the number of moles of the reactant, $N_A(z)$, as

$$N(z) = \frac{3}{4}N(0) + N_A(z) + 3 \left(\frac{1}{4}N(0) - N_A(z) \right)$$

The first term on the right hand side represents the amount of inert, the second term is the unconverted reactant and the last term is the amount of product form, i.e. three times the amount of converted reactant. Multiplying through by $Q(0)/N(0)$ and simplifying gives

$$Q(z) = Q(0) \left(\frac{3}{2} - 2 \frac{N_A(z)}{N(0)} \right)$$

Now we must relate C_A and N_A . This is fairly straight forward. Using the ideal gas law, we get

$$\begin{aligned} C_A(z) &= \frac{N_A(z)}{V} = \frac{N_A(z)}{N(z)} \frac{p}{RT} \\ &= \frac{N_A(z)}{\frac{3}{4}N(0) + N_A(z) + 3\left(\frac{1}{4}N(0) - N_A(z)\right)} \frac{p}{RT} \\ &= \frac{N_A(z)/N(0)}{\frac{3}{2} - 2N_A(z)/N(0)} \frac{p}{RT} \Rightarrow \\ \frac{N_A(z)}{N(0)} &= \frac{3/2C_A(z)}{\frac{p}{RT} + 2C_A(z)} \end{aligned}$$

Substitute this result into the equation between $Q(z)$ and $Q(0)$

$$Q(z) = Q(0) \left(\frac{3}{2} - \frac{3C_A(z)}{\frac{p}{RT} + 2C_A(z)} \right)$$

and substitute this result into the differential balance

$$\begin{aligned} Q(0) \frac{d}{dz} \left(\frac{3}{2}C_A - \frac{3C_A^2}{\frac{p}{RT} + 2C_A} \right) &= -kC_A A \Rightarrow \\ \left(\frac{3}{2} - \frac{6C_A}{\frac{p}{RT} + 2C_A} + \frac{6C_A^2}{\left(\frac{p}{RT} + 2C_A\right)^2} \right) \frac{dC_A}{dz} &= -kC_A A/F_0 \end{aligned}$$

This is a separable equation which can be solved subject to the boundary condition that C_A equals C_{A0} at the reactor inlet. One obtains

$$\ln \frac{\frac{p}{RT} + 2C_A}{\frac{p}{RT} + 2C_{A0}} - \ln \frac{C_A}{C_{A0}} - \left(\frac{\frac{p}{RT}}{\frac{p}{RT} + 2C_A} - \frac{\frac{p}{RT}}{\frac{p}{RT} + 2C_{A0}} \right) = \frac{2}{3} \frac{kzA}{Q(0)}$$

Notice that the length of the reactor cannot be determined, only the length times the cross sectional area, zA , i.e. the volume of the reactor.

An alternate way of formulating a model for this system is to write the rate equations for all the components in the system.

$$\begin{aligned} \frac{dQC_A}{dz} &= -kC_A A \\ \frac{dQC_B}{dz} &= 3kC_A A \\ \frac{dQC_I}{dz} &= 0 \end{aligned}$$

where C_B and C_I are the concentrations of B and inert, respectively. Summing these three equations and applying the ideal gas law for the total concentration gives the last equation of the model.

$$\frac{dQC}{dz} = \frac{p}{RT} \frac{dQ}{dx} = 2kC_A A$$

However, in this form, the model is somewhat harder to solve.

1.1.3.5 Problems in fluid mechanics

The equations that govern fluid motion and fluid statics are force or momentum balances. These balances are combined with constitutive equations that model the rate of momentum transport as a function of the velocity of the fluid to give the complete equation of motion for the fluid. The process is illustrated in the next example.

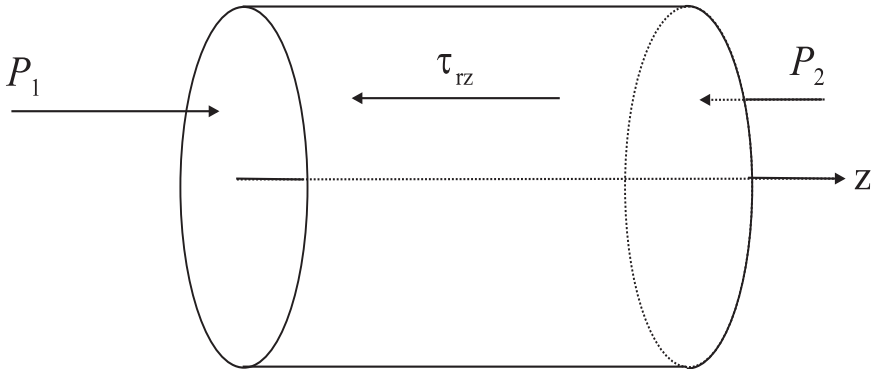


Fig. 1.21 Forces on a cylinder. Pressures, P_1 and P_2 are applied on the two ends of the cylinder, both with area πr^2 and a shear force τ_{rz} is applied to the curved surface of the cylinder with the area $2\pi rL$.

Example 1.13: Laminar flow in a cylindrical pipe.

Consider a fluid inside a cylindrical pipe of radius R subjected to a pressure gradient of $\Delta P/L$. If we assume that the flow is laminar and that entrance and exit effects of the flow pattern can be ignored, then the flow is purely in the axial or z -direction, i.e. parallel to the walls of the pipe. A force balance, Fig. 1.21, on a control volume which is a cylinder of radius r and length L gives

$$\Delta P \pi r^2 = \tau_{rz} 2\pi r L$$

where τ_{rz} is the shear stress (force per area) on the cylindrical wall of the CV and in the z -direction. To proceed, we need a constitutive equation for the stress in the fluid. The most common constitutive equation, by far, is the already mentioned Newton's law of viscosity which, for the situation at hand, can be stated

$$\tau_{rz} = -\mu \frac{dv_z}{dr}$$

where μ is the viscosity of the fluid and v_z the fluid velocity in the axial or z -direction. The following differential equation for the velocity profile is now obtained

$$\begin{aligned} \frac{dv_z}{dr} &= -\frac{\Delta P}{2L\mu} r \Rightarrow \\ v_z(r) &= C_1 - \frac{\Delta P}{4L\mu} r^2 \end{aligned}$$

The common boundary condition is the no-slip condition stating the fluid velocity at the solid wall is equal to the velocity of the solid; zero in this case. I.e., $v_z(R) = 0$, giving the well known parabolic velocity profile.

$$C_1 = \frac{\Delta P}{4L\mu} R^2 \Rightarrow$$

$$v_z(r) = \frac{\Delta P R^2}{4L\mu} \left(1 - \left(\frac{r}{R} \right)^2 \right)$$

Many fluids are non-Newtonian and are modeled using alternate constitutive equations for the fluid stress. For instance, many polymers exhibit shear thinning, meaning that the apparent viscosity decreases at higher flow rates. This behavior can be described with the power law model which, in cylindrical coordinates takes the form

$$\tau_{rz} = -m \left| \frac{dv_z}{dr} \right|^{n-1} \frac{dv_z}{dr}$$

where the parameter m is called the modulus of viscosity and n is the power law index. The modulus is usually a strong function of temperature while the power law index is not. With this model, the differential equation for the velocity profile becomes

$$\frac{dv_z}{dr} = - \left(\frac{\Delta P}{2Lm} \right)^{1/n} r^{1/n} \Rightarrow$$

$$v_z(r) = \left(\frac{\Delta P R}{2Lm} \right)^{1/n} \frac{nR}{n+1} \left(1 - \left(\frac{r}{R} \right)^{\frac{n+1}{n}} \right)$$

Another frequently used rheological model is the Bingham model. This model is used for fluids such as ketchup, toothpaste and paints which exhibit a yield stress; a minimum stress required for the fluid to flow. The fluid may still move if the stress is below the yield stress, however, in this case it will move as a solid, without internal velocity gradients. When the stress in the substance exceeds the yields stress, flow is governed by

$$\tau_{rz} = -\mu_0 \frac{dv_z}{dr} \pm \tau_0 \quad (1.21)$$

where τ_0 is the yield stress and μ_0 the Bingham plastic constant. Both are empirical parameters and may be functions of temperature. For flow in a pipe, the stress is given by

$$\tau_{rz} = \frac{\Delta P r}{2L}$$

and there is a radius, r_0 , below which the stress is less than the yield stress and the fluid therefore moves as a solid

$$r_0 = \frac{\tau_0 2L}{\Delta P} \Rightarrow v_z = C_1$$

where C_1 is an arbitrary constant, the velocity of the fluid which moves as a solid.

For $r > r_0$, the differential equation for the velocity profile is

$$\frac{dv_z}{dr} = \frac{\tau_0}{\mu_0} - \frac{\Delta P r}{\mu_0 2L} \Rightarrow$$

$$v_z(r) = \frac{\tau_0 r}{\mu_0} - \frac{\Delta P r^2}{\mu_0 4L} + C_2$$

The arbitrary constants are found using the no-slip boundary condition at the pipe wall, $v_z(R) = 0$ and continuity of velocity at r_0 .

$$v_z = \begin{cases} \frac{\tau_0 R}{\mu_0} \left(\frac{r}{R} - 1 \right) + \frac{\Delta P R^2}{4\mu_0 L} \left(1 - \left(\frac{r}{R} \right)^2 \right), & r > r_0 \\ \frac{\tau_0 R}{\mu_0} \left(\frac{r_0}{R} - 1 \right) + \frac{\Delta P R^2}{4\mu_0 L} \left(1 - \left(\frac{r_0}{R} \right)^2 \right), & r < r_0 \end{cases}$$

The flat velocity profile in the center of the Bingham fluid is often called a plug flow.

Momentum balances can be derived just as mass and energy balances by using differential control volumes. Doing so may be necessary for complex fluids and is a good exercise when first learning about fluid mechanics. But no person in their right mind would re-derive the momentum balance for a Newtonian fluid, the Navier-Stokes equation, each time it is used. The Navier-Stokes equation is not easy to derive but it is tabulated for all common coordinate systems. More important than being able to derive this equation is the ability to simplify it to the maximum extent possible for a given physical situation.

The fluid mechanical problems we will now consider are laminar flow problems of linear or Newtonian fluids governed by the Navier-Stokes equation, which, in spite of its complicated appearance, is nothing but a momentum balance or Newton's second law of motion

$$\rho \frac{Dv}{Dt} = -\nabla p + \mu \nabla^2 v + \rho g$$

and the continuity equation

$$\nabla \cdot v = 0$$

These equations hold for fluids of constant density, ρ , and constant viscosity, μ . The operator D/Dt , called the substantial time derivative, is listed for the three basic coordinate systems in table 1.4.

Boundary conditions for Newtonian fluids are often obtained from the requirement of continuity of velocity and continuity of stress. Making use of the latter requires the use of Newton's law of viscosity. In particular, these two continuity requirements give the no-slip condition at a fluid-solid interphase and the condition of zero fluid shear stress at a fluid-gas interphase, derived assuming that the gas viscosity is negligible compared to the fluid viscosity.

Table 1.4 The operator D/Dt in the three common coordinate systems.

 Rectangular coordinates

$$\begin{aligned} \frac{Dv}{Dt} &= \left(\frac{\partial v_x}{\partial t} + v_x \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_x}{\partial y} + v_z \frac{\partial v_x}{\partial z} \right) e_x \\ &+ \left(\frac{\partial v_y}{\partial t} + v_x \frac{\partial v_y}{\partial x} + v_y \frac{\partial v_y}{\partial y} + v_z \frac{\partial v_y}{\partial z} \right) e_y \\ &+ \left(\frac{\partial v_z}{\partial t} + v_x \frac{\partial v_z}{\partial x} + v_y \frac{\partial v_z}{\partial y} + v_z \frac{\partial v_z}{\partial z} \right) e_z \end{aligned}$$

Cylindrical coordinates

$$\begin{aligned} \frac{Dv}{Dt} &= \left(\frac{\partial v_r}{\partial t} + v_r \frac{\partial v_r}{\partial r} + \frac{v_\theta}{r} \frac{\partial v_r}{\partial \theta} - \frac{v_\theta^2}{r} + v_z \frac{\partial v_r}{\partial z} \right) e_r \\ &+ \left(\frac{\partial v_\theta}{\partial t} + v_r \frac{\partial v_\theta}{\partial r} + \frac{v_\theta}{r} \frac{\partial v_\theta}{\partial \theta} + \frac{v_r v_\theta}{r} + v_z \frac{\partial v_\theta}{\partial z} \right) e_\theta \\ &+ \left(\frac{\partial v_z}{\partial t} + v_r \frac{\partial v_z}{\partial r} + \frac{v_\theta}{r} \frac{\partial v_z}{\partial \theta} + v_z \frac{\partial v_z}{\partial z} \right) e_z \end{aligned}$$

Spherical coordinates

$$\begin{aligned} \frac{Dv}{Dt} &= \left(\frac{\partial v_r}{\partial t} + v_r \frac{\partial v_r}{\partial r} + \frac{v_\theta}{r} \frac{\partial v_r}{\partial \theta} + \frac{v_\phi}{r \sin \theta} \frac{\partial v_r}{\partial \phi} - \frac{v_\theta^2 + v_\phi^2}{r} \right) e_r \\ &+ \left(\frac{\partial v_\theta}{\partial t} + v_r \frac{\partial v_\theta}{\partial r} + \frac{v_\theta}{r} \frac{\partial v_\theta}{\partial \theta} + \frac{v_\phi}{r \sin \theta} \frac{\partial v_\theta}{\partial \phi} + \frac{v_r v_\theta}{r} - \frac{v_\phi^2 \cot \theta}{r} \right) e_\theta \\ &+ \left(\frac{\partial v_\phi}{\partial t} + v_r \frac{\partial v_\phi}{\partial r} + \frac{v_\theta}{r} \frac{\partial v_\phi}{\partial \theta} + \frac{v_\phi}{r \sin \theta} \frac{\partial v_\phi}{\partial \phi} + \frac{v_\phi v_r}{r} + \frac{v_\theta v_\phi \cot \theta}{r} \right) e_\phi \end{aligned}$$

Like any other models, momentum balances can be simplified using symmetry considerations and additional simplifications are possible if one can conclude that some of the velocity components must be zero. This is usually concluded from physical insight but it can be difficult to do so if the geometry is complex and it is especially difficult for people who do not easily visualize objects in 3 dimensions.

Example 1.14: Simplification of Navier-Stoke's equation.

Consider steady, laminar flow of a Newtonian fluid in a cylindrical bearing for which the inner rod rotates with an angular velocity ω and the outer bearing is stationary, Fig. 1.22. Assume that gravity can be ignored.

Place a cylindrical coordinate system with the z -axis located on the axis of rotation. The boundary conditions in this coordinate system are

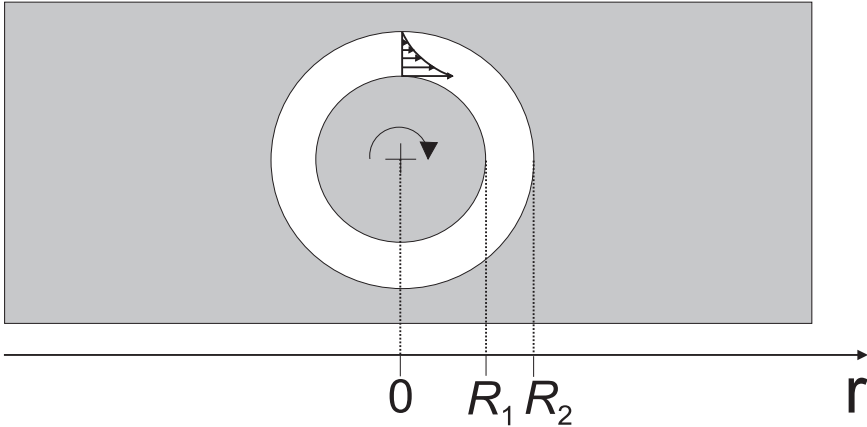


Fig. 1.22 Laminar flow in a cylindrical bearing.

$$v_z = 0 \text{ at } r = R_1, r = R_2$$

$$v_r = 0 \text{ at } r = R_1, r = R_2$$

$$v_\theta = \omega R_1 \text{ at } r = R_1 \text{ and } v_\theta = 0 \text{ at } r = R_2$$

There are two symmetry operations one can perform, rotation around and translation along the center line. In other words: the physical situation is not changed by a rotation of the entire bearing around the z -axis nor is the situation changed by a translation along the z -axis. This is also shown by the fact that the origin of the z -axis is completely arbitrary and can be placed anywhere without affecting the problem and similarly for the $\theta = 0$ direction. For laminar flow one can therefore assume that the solution is independent of the angular coordinate θ and the axial coordinate z and all derivatives with respect to these two coordinates must be zero. Using this, the Navier-Stokes and continuity equations simplify to

$$\rho \left(v_r \frac{dv_r}{dr} - \frac{v_\theta^2}{r} \right) = -\frac{dp}{dr} + \mu \frac{d}{dr} \left(\frac{1}{r} \frac{d}{dr} (rv_r) \right)$$

$$\rho \left(v_r \frac{dv_\theta}{dr} + \frac{v_r v_\theta}{r} \right) = \mu \frac{d}{dr} \left(\frac{1}{r} \frac{d}{dr} (rv_\theta) \right)$$

$$\rho v_r \frac{dv_z}{dr} = \mu \frac{1}{r} \frac{d}{dr} \left(r \frac{dv_z}{dr} \right)$$

$$\frac{1}{r} \frac{d}{dr} (rv_r) = 0$$

The last of these equations is the simplified continuity equation. It is solved in combination with the boundary conditions on v_r , to yield $v_r = 0$, an expected result. Substituting this result into the remaining equations give the even simpler model

$$\rho \frac{v_\theta^2}{r} = \frac{dp}{dr}$$

$$0 = \mu \frac{d}{dr} \left(\frac{1}{r} \frac{d}{dr} (rv_\theta) \right)$$

$$0 = \mu \frac{1}{r} \frac{d}{dr} \left(r \frac{dv_z}{dr} \right)$$

The last two equations are solved to give

$$v_z = 0$$

as expected, and

$$v_\theta = \frac{R_1^2}{R_2^2 - R_1^2} \frac{\omega}{r} (R_2^2 - r^2)$$

Finally, the remaining equation, which is the simplified θ -component of the Navier-Stokes equation, can be solved for the pressure.

$$p(r) = \rho\omega^2 R_1^4 \frac{r^2 - R_2^4/r^2 - 4R_2^2 \ln(r)}{2(R_1 - R_2)^2 (R_1 + R_2)^2} + C_1$$

where C_1 is an arbitrary constant.

1.1.3.6 Summary of common boundary conditions

Boundary conditions are required for balances on differential control volumes. Almost always, these conditions are derived from physical arguments using balances over a control volume surface or from symmetry considerations. The most frequently encountered boundary conditions are summarized below.

From physical arguments.

Continuity: It is usually taken for granted that most physical variables such as temperature, concentration and velocity are continuous functions of position. Thus, if there is no film transport resistance at an interface, the value of the dependent variable at an interface is the same in the two phases.

Film resistance: The concept of a film at a solid/fluid surface implies that the magnitude of the quantity being transported changes rapidly across a stagnant, fluid phase film adjacent to the solid phase. The fluid film is assumed so thin that accumulation in the film can be neglected and a balance over the film states that the flux through the film towards the interphase equals the flux away from the interphase in the other phase. The film flux is usually modeled using a mass or heat transfer coefficient. Thus for e.g. a heat flux, the film condition becomes

$$-k \left. \frac{dT}{dx} \right|_{surface} = h(T_{surface} - T_{infinity})$$

where h is the heat transfer coefficient, $T_{infinity}$ is the fluid temperature "far away" from the solid surface and x represents the direction of the outward normal at the solid surface.

Boundedness: Physical quantities must remain bounded. This requirement can sometimes be used as a boundary condition because it allows one to discard solutions which have singularities, i.e. points at which the solution become infinite.

Symmetry: Many physical situations exhibit some sort of symmetry in the sense that the geometry of the object being model has a plane, axis or point of symmetry and the boundary conditions are such that they do not break this symmetry. When this is the case, the solution for the dependent variable may be assumed to exhibit the same symmetry. This requirement can be used as a boundary condition since it leads one to eliminate those solutions which do not exhibit the required symmetry. However, the assumption that the solution possesses the symmetry imposed by the physical situation, can be wrong. Most importantly, symmetry breaking occurs at the onset of turbulent flow.

Approximate models: The example with the packed bed reactor showed that when the conditions at a boundary are very complex and difficult to account for, approximate boundary conditions, derived from models using simplifying assumptions, can be used.

From differential equations: In cases where a single model equation governs the whole domain of interest, boundary conditions at interfaces in the interior of the domain can be derived directly from the governing equation. Usually this is more trouble than obtaining the boundary conditions from physical arguments but, for the sake of completeness, an example of how it is done is given here.

Example 1.15: Boundary conditions from balance equation.

The one-dimensional energy balance for a solid, without internal heat generation is

$$\frac{\partial}{\partial x} \left(k \frac{\partial T}{\partial x} \right) = \rho C_p \frac{\partial T}{\partial t}$$

and this is valid even when the thermal conductivity, k , is a function of position. Consider now an interface between two solids with different physical properties and ask what the boundary condition is along this interface. The energy equation is valid at all points in the solids, i.e. also at the solid-solid interface, so we can integrate the energy equation over any control volume inside the solid. Place an x -axis normal to the surface with the origin at the surface and use a control volume which is a box of thickness 2δ and placed such that the center plane of the box is at $x = 0$, Fig. 1.23.

Let the thermal conductivities of the solids be k_1 and k_2 respectively and let the surface areas of the control volume which are parallel to the interface be A_1 and A_2 respectively. Integrating the energy equation over this control volume gives

$$\int_V \frac{\partial}{\partial x} \left(k \frac{\partial T}{\partial x} \right) dV = \rho C_p \int_V \frac{\partial T}{\partial t} dV$$

Using the divergence theorem or Gauss's theorem¹² on the integral on the left hand side gives

¹²This theorem can be found in any decent textbook on multidimensional calculus. It states that

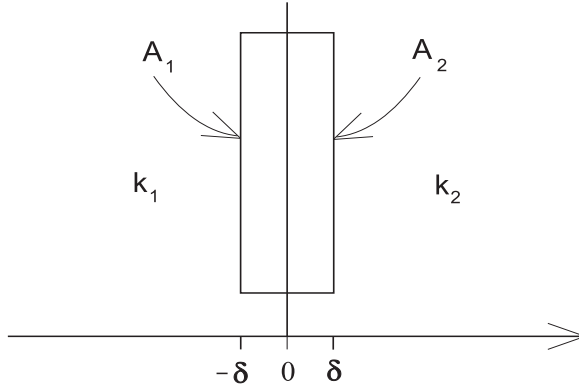


Fig. 1.23 Control volume at interface used for obtaining the boundary condition at the interface.

$$\int_V \frac{\partial}{\partial x} \left(k \frac{\partial T}{\partial x} \right) dV = - \int_{A_1} k_1 \frac{\partial T}{\partial x} d\sigma + \int_{A_2} k_2 \frac{\partial T}{\partial x} d\sigma = \rho C_p \frac{\partial}{\partial t} \int_V T dV$$

Letting δ go to zero makes A_1 and A_2 approach the same value A and makes V go to zero so that the integral on the right hand side vanishes, leaving only

$$\int_A k_1 \frac{\partial T}{\partial x} d\sigma = \int_A k_2 \frac{\partial T}{\partial x} d\sigma \Rightarrow$$

$$k_1 \frac{\partial T}{\partial x} = k_2 \frac{\partial T}{\partial x}$$

at $x = 0$. The boundary condition which states that the flux is continuous across the interface.

1.1.3.7 Symmetry

Symmetry in the boundary conditions usually translates into symmetry of the solution, the important exception to this being turbulent flow. In cases with symmetries, a rigorous analysis of the symmetries of the problem can be helpful in simplifying the model. Therefore, with the aim of making it easier to analyze symmetries and their consequences, both in terms of model simplifications and boundary conditions, this section provides a brief introduction to group theory, a beautiful mathematical abstraction of the symmetry concept.

When we say that an object is symmetric, we mean that it is possible to perform so-called symmetry operations with the object. A symmetry operation is an act that a volume integral of the divergence of a vector field, ∇F , equals the surface integral of the vector field times the outward normal, n .

$$\int_S F n d\sigma = \int_V \nabla F dV$$

moves an object away from its location in space and puts it back such that it fits perfectly in the space it occupied previously. For instance, a circle can be rotated any amount around its center or reflected in any diagonal and still fit perfectly in its original location. These operations, rotations around the center and reflection in a diagonal, are therefore symmetry operations on a circle. A plane can be translated any amount in a direction parallel to the plane, so these translations are symmetry operations on the plane. As another example, consider a rectangle with height h and width $w \neq h$. The symmetry of the rectangle is embodied by all the different ways one can move it around and return it to a position that covers the original rectangle perfectly. There are 4 ways this can be done for the rectangle: One can rotate it 180° in the plane (call this operation R_{180}), one can reflect it in either of the two lines of symmetry passing through the mid points of opposite sides (call these operations R_w and R_h) or one can simply do nothing, call this operation R_0), Fig. 1.24.

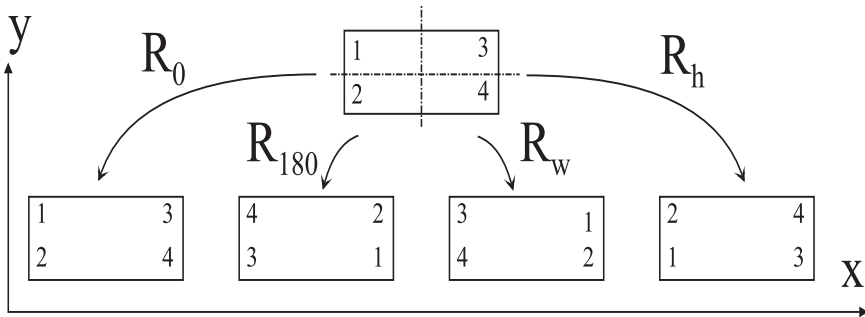


Fig. 1.24 Symmetry operations on a rectangle.

Symmetry operations can be combined. For instance, two applications of R_{180} is equivalent to R_0 and so forth. The set of all possible symmetry operations together with the rule that specifies how to combine operations form a so-called group. For finite groups, the combinations of operations are often summarized in a *Cayley table*. For the rectangle, the Cayley table is given in Table 1.5.

Table 1.5 Cayley table of the symmetry operations of a rectangle. Columns indicate the first factor, rows the second factor.

	R_0	R_w	R_h	R_{180}
R_0	R_0	R_w	R_h	R_{180}
R_w	R_w	R_0	R_{180}	R_h
R_h	R_h	R_{180}	R_0	R_w
R_{180}	R_{180}	R_h	R_w	R_0

A group is defined rigorously as a set (the set of symmetry operations) and a binary operations between the elements of the set such that i) The operation is associative, that is, $R_x(R_yR_z) = (R_xR_y)R_z$, ii) The set contains an identity element, R_0 , such that $R_0R_x = R_xR_0 = R_x$ for all R_x . (This simply states that one can always do nothing) and iii) Each element has an inverse. (This states that one can always undo a change in the orientation of an object). Using this abstract definition, one can readily find groups that do not correspond to any physical objects that normal, sane people can visualize. At the risk of departing too far from the main topic of this chapter, it deserves to be mentioned that polynomials have symmetry properties and each polynomial can be identified with a unique group. For instance, the two roots of the polynomial $x^2 = -1$, i and $-i$, are interchangeable in the sense that there is no way to distinguish i from $-i$ based on their algebraic properties, the difference between them is one of nomenclature, not of substance. This reflects a symmetry of the polynomial $x^2 = -1$ that is not possessed by e.g. $x^2 = 1$ for which the roots, -1 and 1 , are not exchangeable. The group of a polynomial has great theoretical significance and it can be shown that the group determines whether or not a solution for the roots of the polynomial can be found in terms of algebraic operations and radicals.

The group of symmetries of the rectangle is commutative, i.e. for any two elements it always holds that $R_xR_y = R_yR_x$. This is not true in general. For instance the group that represent the symmetries of an equilateral triangle is easy to construct and it is seen not to be commutative. The group of symmetries of the rectangle is also finite, it has only 4 elements, but not all groups are finite. A circle can be rotated around its center any number of radians between 0 and 2π and reflected in any diagonal. The group of the circle is therefore infinite.

With regard to boundary conditions, consider as an example steady thermal conduction in the rectangle in Fig. 1.24, assume a constant thermal conductivity and let the temperature at the top equal the temperature at the bottom and the temperature on the left hand side equal the temperature on the right hand side. The specified surface temperatures gives enough boundary conditions for a well posed problem, but sometimes it is more convenient to use boundary conditions based on the symmetry of the problem. Assuming rectangular symmetry of the solution, the solution at any point must equal the solution at other points that are mapped to this point by the symmetry operation. The temperature is therefore an even function relative to the planes of reflection. Using the coordinate system shown in Fig. 1.24, the temperature, T , at a point (x, y) must therefore satisfy

$$T(x, y) = T(2x_r - x, y) = T(x, 2y_r - y) = T(2x_r - x, 2y_r - y)$$

where x_r and y_r are the x and y coordinates of the vertical and horizontal planes of reflection, respectively. The equations above are particularly nice if x_r and y_r equal zero, stating that temperature is an even function with respect to x and y . This is the reason for placing coordinate axis in the symmetry planes whenever possible. Since the temperature must be finite at the planes of reflection, it can only be an

even function if its derivatives with respect to x and y equal zero. An equivalent statement of the symmetry boundary conditions is therefore

$$\left. \frac{\partial T}{\partial x} \right|_{x=x_r} = 0, \quad \left. \frac{\partial T}{\partial y} \right|_{y=y_r} = 0$$

which is often the most convenient boundary condition to use when solving the balance equation.

All this is of course quite trivial and no one in their right mind would worry about what particular group represents the symmetry of a given object in order to simplify a differential balance or write down symmetry based boundary conditions. However, if you are having problems simplifying a balance or stating the boundary conditions that arise from symmetry, it can be helpful to think very systematically about the possible symmetry operation and what their derived boundary conditions are.

1.2 Abstract control volumes

Lest the reader should be left with the impression that differential balances in chemical engineering are only applicable to transport problems (mass, energy and momentum transport), this section provides some examples of differential balances from other areas. This often require the use of control volumes that are volumes in some abstract space as opposed to physical space. However, the general method for deriving and manipulating the balance remains the same. The main difficulty in writing models for many of these non classical chemical engineering systems is the lack of familiarity with the expressions for the fluxes. Well known constitutive equations may not be available to describe the flux terms and expressions for the fluxes may therefore have to be modeled from first principles; a difficult task unless one is familiar with the system being modeled.

Example 1.16: Population balance equations.

When modeling biological populations, whether they are cells in a bioreactor or the human population on planet Earth, one is often interested in finding the so called distribution of states. This is a function that describes how a property such as size, mass, age, or any other meaningful measure, is distributed among the individuals in the population. Distributions of states can be multidimensional such as the age and mass distribution, etc. The balance equations that govern the distribution of states are called population balance equations. We will derive a population balance for the simple case of cells growing in a CSTR, using a differential control volume over the abstract state space to formulate the model. The state space parameter will be indicated m to suggest mass, and we will assume that the parameter m increases with cell age so that divisions of cells in state m results in formation of cells with smaller m and such that the sum of the m 's of the newborn cells equal

the m of the dividing cell. However, derivation of the population balances for other state parameters is quite similar to the derivation shown here.

Let the distribution we seek be $C(m)$. This distribution can be scaled various ways and we will define $C(m)$ such that

$$C(m)dm = \text{Number concentration of cells in the population for which the parameter indicated by } m \text{ takes a value between } m \text{ and } m + dm.$$

To anyone familiar with distributions it is obvious that one can divide $C(m)$ by the volume of the CSTR and obtain an equally valid distribution, the cell number concentration distribution. Or one can divide through by the total number of cells and obtain the frequency of cell states; a true distribution in the sense that the zeroth moment of the frequency is unity. In the latter case, $C(m)dm$ can be viewed as the probability that a randomly picked cell or individual has a value of the state parameter m that lie between m and $m + dm$.

To do a cell number balance on the differential control volume dm , Fig. 1.25, consider the processes through which cells can enter or leave the control volume. Cells can both enter and leave by growth, they can leave by dividing to become smaller cells and by being washed out of the CSTR and they can enter the control volume by birth or division of a larger cell.

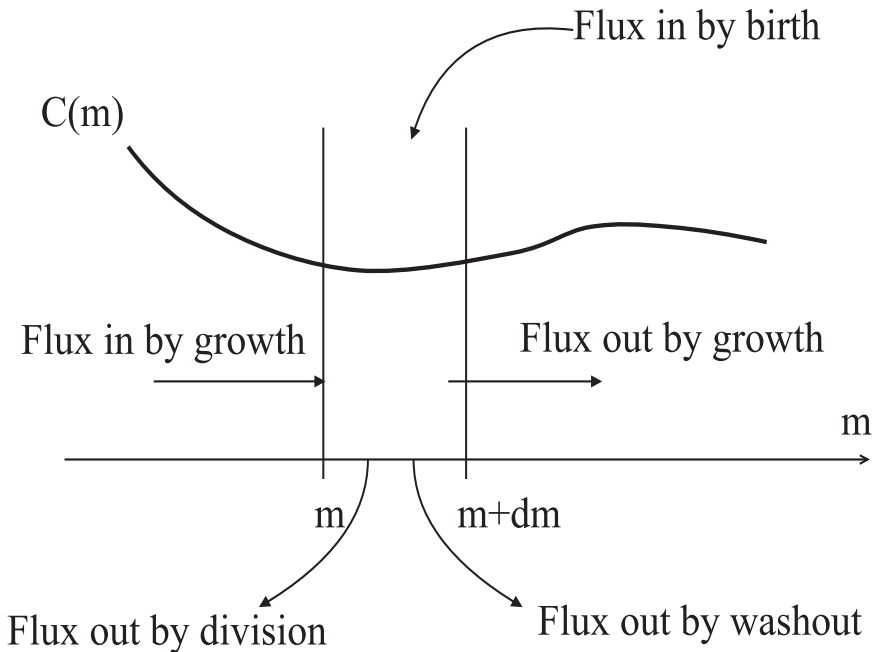


Fig. 1.25 Control volume and fluxes in m -space.

The number of cells inside the control volume equals $C(m)dm$ and the cell number balance becomes

$$\frac{\partial C(m)dm}{\partial t} = \text{Flux in by growth} - \text{Flux out by growth}$$

$$\text{Flux in by birth} - \text{Flux out by division} - \text{Flux out by washout}$$

These fluxes must be accounted for in order to finish the model but now there are no applicable constitutive equations. Each flux must be modeled.

The flux out of the control volume by washout is the easiest of the fluxes to calculate. Assuming that the dilution rate in the CSTR equals D (equal to the volumetric flow rate through the reactor divided by the reactor volume), then the rate of washout of cells from the control volume simply equals the dilution rate times the number of cells inside the control volume or $DC(m)dm$.

The growth flux into the control volume at m is the value of the distribution at m , basically equal to the number of cells immediately smaller than the cells in the control volume, multiplied by the rate at which cells grow into the control volume. This is the single cell growth rate with respect to m and will be indicated $r(m)$ and it must be determined from some additional model of single cell growth such as a metabolic model. Modeling $r(m)$ requires some idea of how fast cells grow as a function of the cell state m and of the concentration of the nutrients in the medium. So the growth flux into the control volume equals $r(m)C(m)$ and, similarly, the growth flux out of the control volume equals $r(m + dm)C(m + dm)$.

The flux out of the control volume by cell division can be described by a function specifying the rate at which cells in a given state divide. This function is called the division intensity and will be indicated $\Gamma(m)$. It is defined as

$$\Gamma(m)dt = \text{Fraction of cells in state } m \text{ that divide in the next } dt \text{ time interval}$$

The rate at which cells leave the control volume is therefore equal to the division intensity multiplied by the number of cells inside the control volume, $\Gamma(m)C(m)dm$.

Since cells split into two new cells in a division, the rate at which cells are born must equal twice the rate at which all cells divide. But the rate at which all cells divide is simply the rate of division discussed above, integrated over all cell states, $\int_0^\infty \Gamma(m)C(m)dm$. However, to find the flux of newborn cells into the control volume, the rate of division must be multiplied by the probability that a division gives rise to a newborn cell with an m -value between m and $m + dm$. Let this probability be $p(m, \tilde{m})$

$$p(m, \tilde{m})dm = \text{Probability that division of a cell in state } \tilde{m} \text{ results} \\ \text{in a new cell with state between } m \text{ and } m + dm$$

The flux of new cells into the control volume must therefore equal $2 \int_0^\infty p(m, \tilde{m})dm\Gamma(\tilde{m})C(\tilde{m})d\tilde{m}$.

Putting all these flux expressions into the balance equation gives

$$\frac{\partial C(m)dm}{\partial t} = r(m)C(m) - r(m+dm)C(m+dm) \\ 2 \int_0^\infty p(m, \tilde{m})dm\Gamma(\tilde{m})C(\tilde{m})d\tilde{m} - \Gamma(m)C(m)dm - DC(m)dm$$

This result is then treated like any other differential balance, by dividing by the volume of the control volume, dm , and recognizing derivatives to get the population balance equation

$$\frac{\partial C}{\partial t} + \frac{\partial rC}{\partial m} = 2 \int_0^\infty p(m, \tilde{m})\Gamma(\tilde{m})C(\tilde{m})d\tilde{m} - (D + \Gamma(m))C(m)$$

The next example shows an alternate method for deriving a population balance. The purpose of this is to demonstrate how it is sometimes possible to derive differential balances using macroscopic control volumes. This is perhaps an odd approach, but the method does have its proponents who see the method as more rigorous than derivations that use questionable algebraic manipulations with differential quantities.

Example 1.17: Alternate derivation a population balance.

We will base the balance on the control volume defined by the bracket from cell state b to state c where $c - b$ is not a differential quantity. We will assume without loss of generality that the cell state parameter m increases with cell age and that $b < c$. The number of cells in the control volume is

$$\int_b^c C(m) dm$$

The sum of the growth fluxes in and out of the control volume is

$$r(b)C(b) - r(c)C(c)$$

The division and washout fluxes of cells out of the control volume are

$$D \int_b^c C(m)dm + \int_b^c \Gamma(m)C(m)dm$$

and the birth flux into the control volume is

$$\int_b^c 2 \int_0^\infty p(m, \tilde{m})\Gamma(\tilde{m})C(\tilde{m})d\tilde{m}dm$$

Putting the flux and accumulation terms together, the balance becomes.

$$\frac{\partial}{\partial t} \int_b^c C(m) dm = r(b)C(b) - r(c)C(c) + \int_b^c 2 \int_0^\infty p(m, \tilde{m})\Gamma(\tilde{m})C(\tilde{m})d\tilde{m}dm \\ - \int_b^c (D + \Gamma(m))C(m)dm \Rightarrow$$

$$\int_b^c \frac{\partial C(m)}{\partial t} dm + \int_b^c \frac{\partial r(m)C(m)}{\partial m} dm = \int_b^c 2 \int_0^\infty p(m, \tilde{m})\Gamma(\tilde{m})C(\tilde{m})d\tilde{m}dm$$

$$- \int_b^c (D + \Gamma(m))C(m)dm \Rightarrow$$

$$\int_b^c \left(\frac{\partial C}{\partial t} + \frac{\partial rC}{\partial m} - 2 \int_0^\infty p(m, \tilde{m})\Gamma(\tilde{m})C(\tilde{m})d\tilde{m} - (D + \Gamma(m))C \right) dm = 0$$

The key argument that allows one to obtain a differential balance from this macroscopic balance is as follows: As the limits on the integral are arbitrary, the integrand must be identically zero, giving us the population balance.

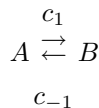
$$\frac{\partial C}{\partial t} + \frac{\partial rC}{\partial m} - 2 \int_0^\infty p(m, \tilde{m})\Gamma(\tilde{m})C(\tilde{m})d\tilde{m} - (D + \Gamma(m))C = 0$$

The population balance equation derived in the previous two examples is a simple case of the more general situation where the cell state is characterized by a large number of parameters and where the population balance is coupled to balances on the microbial substrates and products. Reader who would like to learn more on this should consult the paper by Fredrickson, Ramkrishna, and Tsuchiya¹³. Population balance models are in fact a huge topic and they are important not just when modeling living cells, but when modeling any particulate system, such as aerosols, emulsions and crystallizers¹⁴.

The next example shows a situation in which the control volume is a single point in state space and where the flux terms are stochastic and must be modeled using probabilistic arguments.

Example 1.18: Stochastic chemical kinetics.

Chemical reactions are commonly modeled with the assumption that concentration can be treated as a continuous variable. This is a valid approximation in most cases but it fails when only a small number of molecules react. In this case, the state of the system must be indicated by specifying the numbers of each of the participating molecules as a function of time and reactions rates are no longer deterministic but stochastic. Similarly, the result is not deterministic, but is a probability function describing the likelihood of finding the system in a state with a given number of molecules of each of the reactants. To illustrate how to write a model for such a system, consider the very simple reaction



¹³Fredrickson A. G., D. Ramkrishna, and H.M. Tsuchiya, Statics and Dynamics of Procarvotic Cell Populations, **Mathematical Biosciences**, **1**, 327-374, (1967)

¹⁴D. Ramkrishna, Population Balances, Academic Press, San Diego, CA, USA, 2000

where c_1 and c_{-1} are the stochastic equivalents of reaction rate constants, they are known as reaction propensities.

The state space is the set of point of the form (N_A, N_B) where N_A and N_B are the number of molecules of A and B respectively and the probability of finding the system in the state (N_A, N_B) at time t will be indicated $P(t, N_A, N_B)$. To write a model of this system, pick a *single point* (N_A, N_B) in the state space as control volume and write a balance for the probability measure of that state.

For readers who have not studied probability calculus this is unfamiliar territory and it may be more convenient to consider instead a very large number of independent realizations, say \mathcal{N} , of this reaction system. Some number, \mathcal{N}_{N_A, N_B} , of these systems will be in the state specified by the control volume, and for a large enough number of realizations, the probability $P(t, N_A, N_B)$ equals $\mathcal{N}_{N_A, N_B}/\mathcal{N}$. We can therefore do a balance on the number of systems which are in the state (N_A, N_B) and divide the balance equation by \mathcal{N} to get the model for the probability.

Systems that are in the state equivalent to the control volume can leave the state through two possible reactions: A reacting to form B or $(N_A, N_B) \rightarrow (N_A - 1, N_B + 1)$ and B reacting to form A or $(N_A, N_B) \rightarrow (N_A + 1, N_B - 1)$.

Similarly, systems in the state $(N_A - 1, N_B + 1)$ can enter the control volume if B reacts to form A and systems in the state $(N_A + 1, N_B - 1)$ can enter the control volume if A reacts to form B .

The fluxes corresponding to each of these reactions are proportional to the number of systems in the required reactive state and to the number of molecules that can react. The proportionality constants are the reaction propensities c_1 and c_{-1} defined above. For the four reactions that affect our control volume, we can therefore write

$$(N_A, N_B) \rightarrow (N_A - 1, N_B + 1) : \text{Flux out} = c_1 \mathcal{N}(t, N_A, N_B) N_A$$

$$(N_A, N_B) \rightarrow (N_A + 1, N_B - 1) : \text{Flux out} = c_{-1} \mathcal{N}(t, N_A, N_B) N_B$$

$$(N_A - 1, N_B + 1) \rightarrow (N_A, N_B) : \text{Flux in} = c_{-1} \mathcal{N}(t, N_A - 1, N_B + 1) (N_B + 1)$$

$$(N_A + 1, N_B - 1) \rightarrow (N_A, N_B) : \text{Flux in} = c_1 \mathcal{N}(t, N_A + 1, N_B - 1) (N_A + 1)$$

We hasten to add that the flux terms are only this simple because the reactions are all simple first order reactions. If several molecules are required for a reaction to proceed, then the rate is not proportional to the number of reactant molecules, but to the number of distinct molecular combinations for the reaction. For instance, had the reaction $A \rightarrow B$ been second order in A , then the factor N_A in the first flux term would have to be replaced by $N_A(N_A - 1)/2!$ since the first molecule can be picked N_A different ways, the second molecule $N_A - 1$ different ways and the product is divided by $2!$ since this particular sample of reactant molecules can be

obtained 2! different ways. Substituting the flux terms into the conservation balance yield the equation

$$\begin{aligned} \frac{d\mathcal{N}(t, N_A, N_B)}{dt} &= c_1\mathcal{N}(t, N_A, N_B)N_A + c_{-1}\mathcal{N}(t, N_A, N_B)N_B \\ &\quad - c_{-1}\mathcal{N}(t, N_A - 1, N_B + 1)(N_B + 1) \\ &\quad - c_1\mathcal{N}(t, N_A + 1, N_B - 1)(N_A + 1) \end{aligned}$$

and dividing through by \mathcal{N} gives the model in terms of the fractions or probabilities of each state.

$$\begin{aligned} \frac{dP(t, N_A, N_B)}{dt} &= c_1P(t, N_A, N_B)N_A + c_{-1}P(t, N_A, N_B)N_B \\ &\quad - c_{-1}P(t, N_A - 1, N_B + 1)(N_B + 1) \\ &\quad - c_1P(t, N_A + 1, N_B - 1)(N_A + 1) \end{aligned}$$

which is known by the non-descriptive term *the master equation*¹⁵. For all but the simplest cases, the master equation must be solved numerically by Monte Carlo methods¹⁶. The few cases that are amenable to analytical methods are given in the literature¹⁷. Here, we will restrict ourselves to find the analytical solution for the probability distributions at steady state. Start by setting $N_A + N_B = N$, where N , the total number of molecules, is clearly constant and eliminate N_B from the master equation.

$$\begin{aligned} \frac{dP(t, N_A)}{dt} &= c_1P(t, N_A + 1)(N_A + 1) + c_{-1}P(t, N_A - 1)(N + 1 - N_A) \\ &\quad - c_1P(t, N_A)N_A - c_{-1}P(t, N_A)(N - N_A) \end{aligned}$$

where $0 \leq N_A \leq N$. It is illustrative to write the equations for $N_A = 0$ and $N_A = N$ as these are special cases.

$$\begin{aligned} \frac{dP(t, 0)}{dt} &= c_1P(t, 1) - c_{-1}P(t, 0)N \\ \frac{dP(t, N)}{dt} &= c_{-1}P(t, N - 1) - c_1P(t, N)N \end{aligned}$$

A quick investigation of these equations reveal that each flux term appears twice in the system, but with opposite sign. Thus, summing all the equations give.

$$\frac{d \sum P}{dt} = 0 \Rightarrow \sum_{n=0}^N P(t, n) = 1$$

where the sum of the probabilities necessarily must equal 1. Now, let $c = c_1/c_{-1}$ and set the derivatives equal to zero to get the set of equations.

$$0 = cP(1) - P(0)N$$

¹⁵For a rigorous derivation of the master equation for chemical kinetics, see: D.T. Gillespie, A rigorous derivation of the chemical master equation, **Physica A** **188**, 404-425, (1992)

¹⁶D.T. Gillespie, A General Method for Numerically Simulating the Stochastic Time Evolution of Coupled Chemical Reactions, **J. Comp. Phys.** **22**, 403-434, (1976)

¹⁷D.A. McQuarrie, Stochastic approach to chemical kinetics, **J. Appl. Prob.** **4**, 413-478, (1967)

$$0 = cP(N_A + 1)(N_A + 1) + P(N_A - 1)(N + 1 - N_A) - cP(N_A)N_A - P(N_A)(N - N_A)$$

$$0 = cP(N - 1) - P(N)N$$

$$\sum_{n=0}^N P(n) = 1$$

The model has $N + 2$ equations for $N + 1$ unknowns, but the steady state master equations are not independent, any one of them can be obtained from the others. We therefore can discard the master equation for $N_A = N$ from the model. Now take the master equation for $N_A = 0$ and subtract it from the master equation for $N_A = 1$. Take this equation and subtract it from the master equation for $N_A = 3$ etc. (Doing this is much easier if the set of equations are written in vector matrix notation. A topic of chapter 3). The following set of equations is obtained

$$\begin{aligned} 0 &= cP(1) - P(0)N \\ 0 &= cP(2)2 - P(1)(N - 1) \\ &\vdots \\ 0 &= cP(n)n - P(n - 1)(N - (n - 1)) \\ &\vdots \\ 0 &= cP(N)N - P(N - 1) \end{aligned}$$

or as a recursive relationship, we can write

$$P(n) = P(n - 1) \frac{N - (n - 1)}{n} \frac{1}{c}$$

which is a very simple difference equation (chap. 5) with the solution

$$P(n) = P(0) \frac{1}{c^n} \prod_{x=1}^n \frac{N - (x - 1)}{x} = \frac{P(0)}{c^n} \frac{N!}{n!(N - n)!}$$

which can be substituted into the normalization equation to give

$$1 = P(0) \sum_{x=0}^N \frac{N!}{c^n n!(N - n)!} = P(0) \left(1 + \frac{1}{c}\right)^N \Rightarrow$$

$$P(0) = \left(\frac{c}{c + 1}\right)^N$$

The problem is essentially solved since the remaining $P(n)$ values can easily be found recursively. A few distributions are plotted in Fig. 1.26 and they exhibit exactly the trends one would expect. For $c = 1$, the two reactions have the same rate and a symmetric distribution is obtained. As c decreases, the rate of the forward reaction, $A \rightarrow B$ decreases relative to the reverse reaction and the probability of finding a large number of molecules of A therefore increases and the distributions shift to the right.

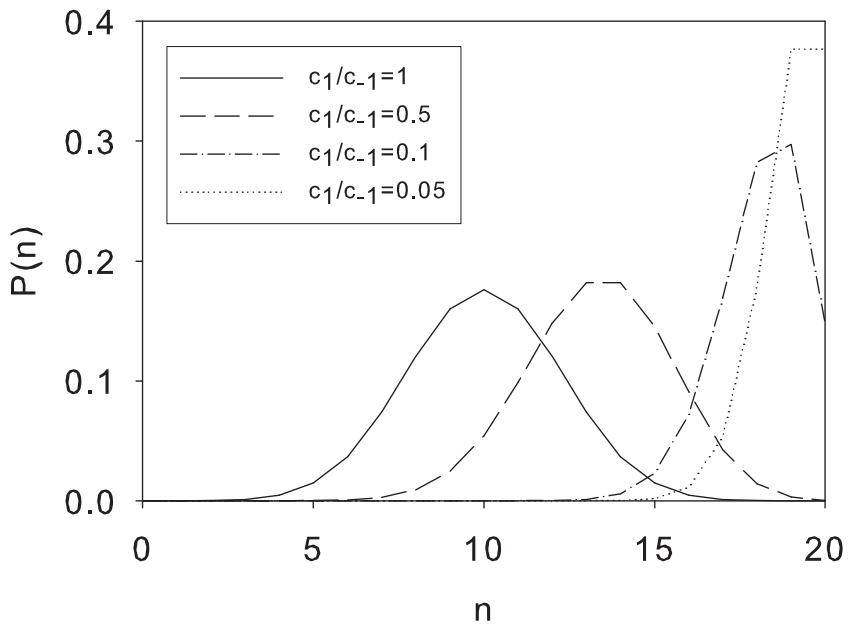


Fig. 1.26 Distributions of number of molecules of A for $N = 20$ and for different values of $c = c_1/c_{-1}$.