CHAPTER 17

Unsteady-State Material and Energy Balances

Unsteady-state problems in previous chapters have used the overall or integrated accumulation term in the material and energy balances. Now we focus our attention briefly on **unsteady-state** processes in which the value of the state (dependent variable) as a function of time is of interest. Recall that the term *unsteady-state* refers to processes in which quantities or operating conditions within the system *change with time.* Sometimes you will hear the words *transient state* applied to such processes. The unsteady state is somewhat more complicated than the steady state, and, in general, problems involving unsteady-state processes are somewhat more difficult to formulate and solve than those involving steady-state processes. However, a wide variety of important industrial problems fall into this category, such as the start-up of equipment, batch heating or reactions, the change from one set of operating conditions to another, and the perturbations that develop as process conditions fluctuate.

Your objectives in studying this chapter are to be able to

1. Write down the macroscopic unsteady-state material and energy balances in words and in symbols
2. Solve simple ordinary differential material or energy balance equations given the initial conditions
3. Translate a word problem into a differential equation(s)

Looking Ahead

In this section we describe how lumped macroscopic material and energy balances are developed for unsteady-state processes in which time is the independent variable.

The macroscopic balance ignores all of the detail within a system and consequently results in a balance about the entire system. Time is the independent variable in the balance. The dependent variables, such as concentration and temperature, are not functions of position but represent overall averages throughout the entire volume of the system. In effect, the system is assumed to be sufficiently well mixed so that the output concentrations and temperatures are equivalent to the concentrations and temperatures inside the system.

To assist in the translation of Equation (17.1)

$$\left\{\begin{array}{c}\text{accumulation}\\ \text{or depletion}\\ \text{within}\\ \text{the}\\ \text{system}\end{array}\right\} = \left\{\begin{array}{c}\text{transport into}\\ \text{system through}\\ \text{system}\\ \text{boundary}\end{array}\right\} - \left\{\begin{array}{c}\text{transport out}\\ \text{of system}\\ \text{through system}\\ \text{boundary}\end{array}\right\} + \left\{\begin{array}{c}\text{generation}\\ \text{within}\\ \text{system}\end{array}\right\} - \left\{\begin{array}{c}\text{consumption}\\ \text{within}\\ \text{system}\end{array}\right\} \tag{17.1}$$

into mathematical symbols, refer to Figure 17.1. Equation (17.1) can be applied to the mass of a single species or to the total amount of material or energy in the system. Let us write each of the terms in Equation (17.1) in mathematical symbols for a very small time interval Δt. Let the accumulation be positive in the direction in which time is positive, that is, as time increases from t to $t + \Delta t$. Then, using the component mass balance as an example, the accumulation will be the mass of A in the system at time $t + \Delta t$ minus the mass of A in the system at time t,

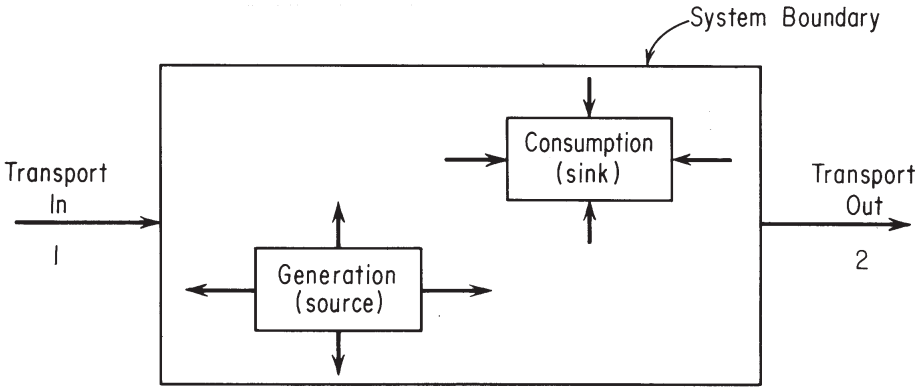


Figure 17.1 General unsteady-state process with transport in and out and internal generation and consumption

$$\text{accumulation} = \rho_A V|_{t+\Delta t} - \rho_A V|_t$$

where ρ_A = mass of component A per unit volume
V = volume of the system

and the symbol $|_t$ means that the quantities preceding the vertical line are evaluated at time t, or time $t + \Delta t$, or at surface S_1, or at surface S_2, as the case may be as denoted by the subscript. Note that the net dimensions of the accumulation term are the mass of A.

We shall split the mass transport across the system boundary into two parts, transport through defined surfaces S_1 and S_2 whose areas are known, and transport across the system boundary through other (undefined) surfaces. The net transport of A into (through S_1) and out of (through S_2) the system through defined surfaces can be written as

$$\text{Net flow across boundary via } S_1 \text{ and } S_2 = \rho_A \upsilon S\, \Delta t|_{S_1} - \rho_A \upsilon S\, \Delta t|_{S_2}$$

where υ = fluid velocity in a duct of cross section S
S_i = defined cross-sectional area perpendicular to material flow

Again note that the net dimensions of the transport term are the mass of A. Other types of transport across the system boundary can be represented by

$$\text{Net residual flow across boundary} = \dot{w}_A\, \Delta t$$

where $\dot{w}_A$ is the rate of mass flow of component A through the system boundaries other than the defined surfaces S_1 and S_2.

Finally, the net generation-consumption term will be assumed to be due to a chemical reaction $\dot{r}_A$:

$$\text{Net generation-consumption} = \dot{r}_A\, \Delta t$$

where $\dot{r}_A$ is the net rate of generation-consumption of component A by chemical reaction.

Introduction of all these terms into Equation (17.1) gives Equation (17.2). Equations (17.3) and (17.4) can be developed from exactly the same type of analysis. Try to formulate Equations (17.3) and (17.4) yourself.

The species material balance for species A is

$$\underset{\text{accumulation}}{\rho_A V|_{t+\Delta t} - \rho_A V|_t} = \underset{\text{transport through defined boundaries}}{\rho_A \upsilon S\, \Delta t|_{S_1} - \rho_A \upsilon S\, \Delta t|_{S_2}} + \underset{\substack{\text{transport}\\ \text{through}\\ \text{other}\\ \text{boundaries}}}{\dot{w}_A\, \Delta t} + \underset{\substack{\text{generation}\\ \text{or}\\ \text{consumption}}}{\dot{r}_A\, \Delta t} \quad (17.2)$$

The total material balance is

$$\rho V|_{t+\Delta t} - \rho V|_t = \rho v S\,\Delta t|_{S_1} - \rho v S\,\Delta t|_{S_2} + \dot{w}\,\Delta t \tag{17.3}$$

accumulation; transport through defined boundaries; transport through other boundaries

By an analogous procedure we can formulate the energy balance:

$$E|_{t+\Delta t} - E|_t = \left|\left(\hat{H} + \frac{v^2}{2} + gh\right)\dot{m}\,\Delta t\right|_{S_1} - \left|\left(\hat{H} + \frac{v^2}{2} + gh\right)\dot{m}\,\Delta t\right|_{S_2}$$

accumulation; transport through defined boundaries

$$+ \dot{Q}\,\Delta t + \dot{W}\,\Delta t + \dot{B}\,\Delta t \tag{17.4}$$

heat; work; transport through other boundaries

where $\dot{B}$ = rate of energy transfer accompanying $\dot{w}$
$\dot{m}$ = rate of mass transfer through defined surfaces S_1 in and S_2 out, respectively
$\dot{Q}$ = rate of heat transfer to the system
$\dot{W}$ = rate of work done on the system
$\dot{w}$ = rate of total mass flow through the system boundaries other than through the defined surfaces S_1 and S_2

The other notation for the material and energy balances is identical to that of Chapters 9 to 10; note that the work, heat, generation, and mass transport are now all expressed as rate terms (mass or energy per unit time).

If each side of Equation (17.2) is divided by Δt, we obtain

$$\frac{\rho_A V|_{t+\Delta t} - \rho_A V|_t}{\Delta t} = \rho_A v S|_{S_1} - \rho_A v S|_{S_2} + \dot{w}_A + \dot{r}_A \tag{17.5}$$

Similar relations can be obtained from Equations (17.3) and (17.4). If we take the limit of each side of Equation (17.5) as $\Delta t \to 0$, we get a differential equation

$$\frac{\mathrm{d}(\rho_A V)}{\mathrm{d}t} = -\Delta(\rho_A v S) + \dot{w}_A + \dot{r}_A \tag{17.6}$$

and analogously the total mass balance and the energy balance, respectively, are

$$\frac{\mathrm{d}(\rho V)}{\mathrm{d}t} = -\Delta(\rho v S) + \dot{w} \tag{17.7}$$

$$\frac{\mathrm{d}(E)}{\mathrm{d}t} = \dot{Q} + \dot{W} + \dot{B} - \Delta\left[\left(\hat{H} + \frac{v^2}{2} + gh\right)\dot{m}\right] \tag{17.8}$$

Can you get Equations (17.7) and (17.8) from (17.3) and (17.4), respectively? Try it.

The relation between the energy balance given by Equation (17.8), which has the units of energy per unit time, and the energy balance given by Equation (9.21), which has the units of energy, should now be fairly clear. Equation (9.21) represents the integration of Equation (17.8) with respect to time, expressed formally as follows:

$$E_{t_2} - E_{t_1} = \int_{t_1}^{t_2} \{\dot{Q} + \dot{B} + \dot{W} - \Delta[(\hat{H} + \hat{K} + \hat{P})\dot{m}]\}\, \mathrm{d}t \tag{17.9}$$

The quantities designated in Equation (9.21) without the superscript dot are the respective integrated values from Equation (17.9).

To solve one or any combination of the very general equations (17.6), (17.7), or (17.8) analytically may be quite difficult, and in the following examples we shall have to restrict our analyses to simple cases. If we make enough (reasonable) assumptions and work with simple problems, we can consolidate or eliminate enough terms of the equations to be able to integrate them and develop some analytical answers. If analytical solutions are not possible, a computer code can be used to get a numerical solution for a specific case.

In the formulation of unsteady-state equations you apply the usual procedures of problem solving discussed in previous chapters. You can set up the equation as in Equations (17.2)–(17.4) or use the differential equations (17.6)–(17.8) directly. To complete the problem formulation you must include some known value of the dependent variable (or its derivative) at a specified time, usually the **initial condition.**

We are now going to examine some very simple unsteady-state problems. You can (and will) find more complicated examples in texts dealing with all phases of mass transfer, heat transfer, and fluid dynamics.

Example 17.1 Unsteady-State Material Balance without Generation

A tank holds 100 gal of a water-salt solution in which 4.0 lb of salt are dissolved. Water runs into the tank at the rate of 5 gal/min and salt solution overflows at the same rate. If the mixing in the tank is adequate to keep the concentration of salt in the tank uniform at all times, how much salt is in the tank at the end of 50 min? Assume that the density of the salt solution is essentially the same as that of water.

Solution

We shall set up from scratch the differential equations that describe the process. The basis will be 50 min.

Step 2

Draw a picture, and put down the known data. See Figure E17.1.

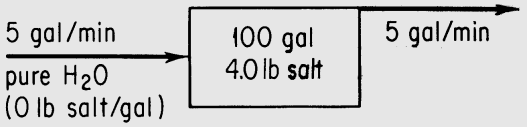


Figure E17.1

Step 3

Choose the independent and dependent variables. Time, of course, is the independent variable, and either the salt quantity or concentration of salt in the tank can be the dependent variable. Suppose that we make the mass (quantity) of salt the dependent variable. Let x = pounds of salt in the tank at time t.

Step 4

Write the known value of x at a given value of t. This is the initial condition:

$$\text{at } t = 0 \; x = 4.0 \text{ lb}$$

Steps 6–8

It is easy to make a total material balance and a component material balance on the salt. (No energy is needed because the system can be assumed to be isothermal.)

Total balance:

$$\begin{matrix} \textbf{accumulation} & & \textbf{in} \\ [m_{\text{tot}}\ \text{lb}]_{t+\Delta t} - [m_{\text{tot}}\ \text{lb}]_t = & & \dfrac{5\ \text{gal}}{\text{min}} \left| \dfrac{1\ \text{ft}^3}{7.48\ \text{gal}} \right| \left| \dfrac{\rho_{H_2O}\ \text{lb}}{\text{ft}^3} \right| \Delta t\ \text{min} \\ & & \textbf{out} \\ & & - \dfrac{5\ \text{gal}}{\text{min}} \left| \dfrac{1\ \text{ft}^3}{7.48\ \text{gal}} \right| \left| \dfrac{\rho_{\text{soln}}\ \text{lb}}{\text{ft}^3} \right| \Delta t\ \text{min} \end{matrix}$$

This equation tells us that the flow of water into the tank equals the flow of solution out of the tank if $\rho_{H_2O} = \rho_{\text{soln}}$ as assumed.

Salt balance:

$$\begin{matrix} \textbf{accumulation} & \textbf{in} & \textbf{out} \\ [x\ \text{lb}]_{t+\Delta t} - [x\ \text{lb}]_t = 0 & - & \dfrac{5\ \text{gal}}{\text{min}} \left| \dfrac{x\ \text{lb}}{100\ \text{gal}} \right| \Delta t\ \text{min} \end{matrix}$$

(*Continues*)

Example 17.1 Unsteady-State Material Balance without Generation *(Continued)*

Dividing by Δt and taking the limit as Δt approaches zero,

$$\lim_{\Delta t \to 0} \frac{[x]_{t+\Delta t} - [x]_t}{\Delta t} = -0.05x$$

or

$$\frac{dx}{dt} = -0.05x \tag{a}$$

Notice how we have kept track of the units in the normal fashion in setting up these equations. Because of our assumption of uniform concentration of salt in the tank, the concentration of salt leaving the tank is the same as that in the tank, or x lb/100 gal of solution.

Step 9

Solve the unsteady-state material balance on the salt. By separating the independent and dependent variables we get

$$\frac{dx}{x} = -0.05\, dt$$

This equation can be integrated between the definite limits of

$t = 0 \quad x = 4.0$

$t = 50 \quad X =$ the unknown value of x lb

$$\int_{4.0}^{X} \frac{dx}{x} = -0.05 \int_{0}^{50} dt$$

$$\ln \frac{X}{4.0} = -2.5 \qquad X = \frac{4.0}{12.2} = 0.328 \text{ lb salt}$$

An equivalent differential equation to Equation (a) can be obtained directly from the component mass balance in the form of Equation (17.6) if we let ρ_A = concentration of salt in the tank at any time t in terms of pounds per gallon:

$$\frac{d(\rho_A V)}{dt} = -\left(\frac{5 \text{ gal}}{\text{min}} \middle| \frac{\rho_A \text{ lb}}{\text{gal}}\right) - 0$$

If the tank holds 100 gal of solution at all times, V is a constant and equal to 100, so

$$\frac{d\rho_A}{dt} = -\frac{5\rho_A}{100} \tag{b}$$

The initial conditions are

$$\text{at } t = 0 \; \rho_A = 0.04$$

The solution of Equation (b) would be carried out exactly as the solution of Equation (a).

Example 17.2 Unsteady-State Material Balance without Generation

A square tank 4 m on a side and 10 m high is filled to the brim with water. Find the time required for it to empty through a hole in the bottom 5 cm^2 in area.

Solution

Step 2

Draw a diagram of the process, and write down the data. See Figure E17.2a.

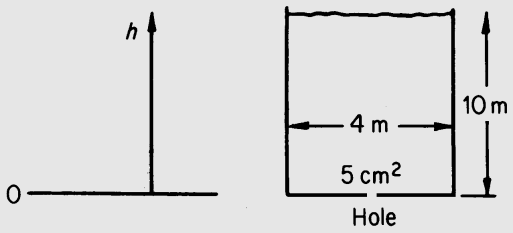


Figure E17.2a

Step 3

Select the independent and dependent variables. Again, time will be the independent variable. We could select the quantity of water in the tank as the dependent variable, but since the cross section of the tank is constant, let us choose h, the height of the water in the tank, as the dependent variable.

Step 4

Write the known value of h at the given time t:

$$\text{at } t = 0 \quad h = 10 \text{ m}$$

Steps 5–8

Develop the unsteady-state balance(s) for the process. In an elemental of time Δt, the height of the water in the tank drops Δh. The mass of water leaving the tank is in the form of a cylinder 5 cm^2 in area, and we can calculate the quantity as

$$\frac{5 \text{ cm}^2}{}\left|\left(\frac{1 \text{ m}}{100 \text{ cm}}\right)^2\right|\frac{\nu^* \text{ m}}{\text{s}}\left|\frac{\rho \text{ kg}}{\text{m}^3}\right|\frac{\Delta t \text{ s}}{} = 5 \times 10^{-4} \nu^* \rho \, \Delta t \text{ kg}$$

where ρ = density of water
ν^* = average velocity of the water leaving the tank

The depletion of water inside the tank in terms of the variable h, expressed in kilograms is

$$\frac{16 \text{ m}^2}{}\left|\frac{\rho \text{ kg}}{\text{m}^3}\right|\frac{h \text{ m}}{}\Bigg|_{t+\Delta t} - \frac{16 \text{ m}^2}{}\left|\frac{\rho \text{ kg}}{\text{m}^3}\right|\frac{h \text{ m}}{}\Bigg|_{t} = 16 \rho \Delta h \text{ kg}$$

(*Continues*)

Example 17.2 Unsteady-State Material Balance without Generation *(Continued)*

An overall material balance is

$$\begin{matrix}\textbf{accumulation} & \textbf{in} & \textbf{out}\end{matrix}$$

$$16\rho\Delta h = 0 - 5 \times 10^{-4}\,\rho v^* \Delta t \qquad \text{(a)}$$

Note that Δh will have a negative value, but our equation takes account of this automatically; the accumulation is really a depletion. You can see that the term ρ, the density of water, cancels out, and we could just as well have made our material balance on a volume of water.

Equation (a) becomes

$$\frac{\Delta h}{\Delta t} = -\frac{5 \times 10^{-4} v^*}{16}$$

Taking the limit as Δh and Δt approach zero, we get the differential equation

$$\frac{dh}{dt} = -\frac{5 \times 10^{-4} v^*}{16} \qquad \text{(b)}$$

Steps 8 and 9

Unfortunately, this is an equation with one independent variable, t, and two dependent variables, h and v^*. We must find another equation to eliminate either h or v^* if we want to obtain a solution. Since we want our final equation to be expressed in terms of h, the next step is to find some function to relate v^* to h and t, and then we can substitute for v^* in the unsteady-state equation, Equation (b).

We shall employ the steady-state mechanical energy balance equation for an incompressible fluid, discussed in Chapter 14, to relate v^* and h. See Figure E17.2b. With $W = 0$ and $E_v = 0$ the steady-state mechanical energy balances reduce to

$$\Delta\left(\frac{(v^*)^2}{2} + gh\right) = 0 \qquad \text{(c)}$$

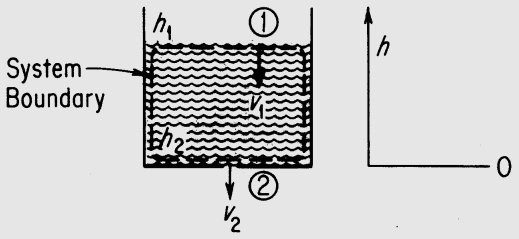


Figure E17.2b

We have assumed that the atmospheric pressure is the same at section 1—the water surface—and section 2—the hole—for the system consisting of the water in the tank. Equation (c) can be rearranged to

$$\frac{(\nu_2^*)^2 - (\nu_1^*)^2}{2} + g(h_2 - h_1) = 0 \tag{d}$$

where ν_2^* = exit velocity through the 5 cm^2 hole at boundary 2
ν_1^* = velocity of water in the tank at boundary 1

If $\nu_1^* \cong 0$, a reasonable assumption for the water in the large tank at any time, at least compared to ν_2^*, we have

$$\begin{aligned}(\nu_2^*)^2 &= -2g(0 - h_1) = 2gh \\ \nu_2^* &= \sqrt{2gh}\end{aligned} \tag{e}$$

Because the exit-stream flow is not frictionless and because of turbulence and orifice effects in the exit hole, we must correct the value of v given by Equation (e) for frictionless flow by an empirical adjustment factor as follows:

$$\nu_2^* = c\sqrt{2gh} \tag{f}$$

where c is an orifice correction that we could find (from a text discussing fluid dynamics) with a value of 0.62 for this case. Thus

$$\nu_2^* = 0.62\sqrt{2(9.80)h} = 2.74\sqrt{h}\ \text{m/s}$$

Let us substitute this relation into Equation (b) in place of ν^*. Then we obtain

$$\frac{dh}{dt} = -\frac{(5.0 \times 10^{-4})(2.74)(h)^{1/2}}{16} \tag{g}$$

Equation (g) can be integrated between

$$h = 10\ \text{m at}\ t = 0$$

and

$$h = 0\ \text{m at t} = \theta, \text{ the unknown time}$$

$$-1.17 \times 10^4 \int_{10}^{0} \frac{dh}{h^{1/2}} = \int_0^{\theta} dt$$

to yield

$$\theta = 1.17 \times 10^4 \int_0^{10} \frac{dh}{h^{1/2}} = 1.17 \times 10^4 \left[2\sqrt{h}\right]_0^{10} = 7.38 \times 10^4\ \text{s}$$

Now suppose that in addition to the loss of fluid through the hole in the bottom of the tank additional fluid is poured continuously into the top of the tank at varying rates. Numerical integration of the resulting differential equations yields a varying height of fluid as illustrated in Figure E17.2c.

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Example 17.2 Unsteady-State Material Balance without Generation *(Continued)*

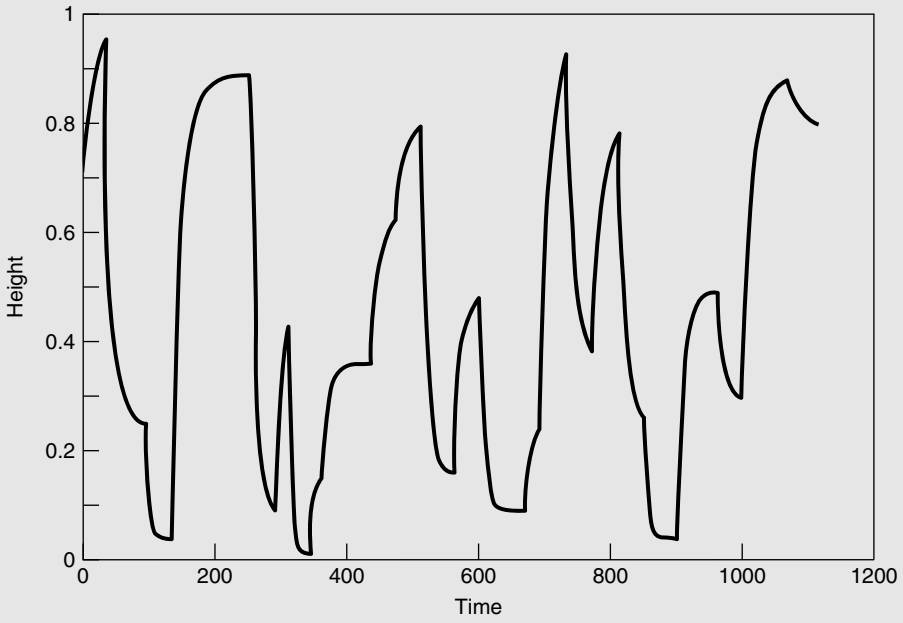


Figure E17.2c

Example 17.3 Material Balance in Batch Distillation

A small still is separating propane and butane at 135°C and initially contains 10 kg mol of a mixture whose composition is $x = 0.30$ (x = mole fraction butane). Additional mixture ($x_F = 0.30$) is fed at the rate of 5 kg mol/hr. If the total volume of the liquid in the still is constant, and the concentration of the vapor from the still (x_D) is related to x_S as follows:

$$x_D = \frac{x_S}{1 + x_S} \tag{a}$$

how long will it take for the value of x_S to change from 0.3 to 0.4? What is the steady-state ("equilibrium") value of x_S in the still (i.e., when x_S becomes constant)? See Figure E17.3.

Solution

Since butane and propane form ideal solutions, we do not have to worry about volume changes on mixing or separation. Only the material balance is needed to answer the questions posed. If t is the independent variable and x_S is the dependent variable, we can say:

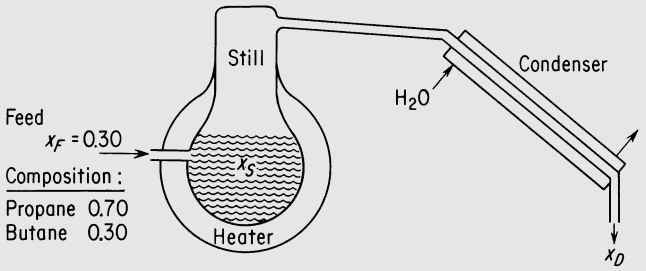


Figure E17.3

Butane balance (C_4): The input to the still is:

$$\frac{5 \text{ mol feed}}{\text{hr}} \left| \frac{0.30 \text{ mol } C_4}{\text{mol feed}} \right.$$

The output from the still is equal to the amount condensed:

$$\frac{5 \text{ mol cond.}}{\text{hr}} \left| \frac{x_D \text{ mol } C_4}{\text{mol condensed}} \right.$$

The accumulation is $\dfrac{10\, dx_S}{dt}$

Our unsteady-state equation is then

accumulation in out

$$\frac{dx_S}{dt} = 0.15 - 0.5x_D \tag{b}$$

As in Example 17.2, it is necessary to reduce the equation to one dependent variable by substituting for x_D from Equation (a) in Equation (b):

$$\frac{dx_S}{dt} = 0.15 - \frac{x_S}{1 + x_S}(0.5) \tag{c}$$

Integration of Equation (c) between the following limits

$$\begin{aligned} \text{at } t &= 0 \quad x_S = 0.30 \\ t &= \theta \quad x_S = 0.40 \end{aligned}$$

$$\int_{0.30}^{0.40} \frac{dx_S}{0.15 - [0.5x_S/(1 + x_S)]} = \int_0^{\theta} dt = \theta$$

$$\int_{0.30}^{0.40} \frac{(1 + x_S)\, dx_S}{0.15 - 0.35x_S} = \theta = \left[-\frac{x_S}{0.35} - \frac{1}{(0.35)^2} \ln(0.15 - 0.35x_S) \right]_{0.30}^{0.40}$$

gives $\theta = 5.85$ hr.

(*Continues*)

Example 17.3 Material Balance in Batch Distillation *(Continued)*

If you only had experimental data for x_D as a function of x_S instead of the given equation, you could always integrate the equation numerically.

The steady-state value of x_S is established at infinite time or, alternatively, when the accumulation is zero. At that time,

$$0.15 = \frac{0.5x_S}{1 + x_S} \qquad \text{or} \qquad x_S = 0.428$$

The value of x_S could never be any greater than 0.428 for the given conditions.

Example 17.4 Oscillating Reactions

In an isothermal reactor the following reactions take place:

$$\mathrm{A} + \mathrm{X} \xrightarrow{k_1} 2\mathrm{X}$$

$$\mathrm{X} + \mathrm{Y} \xrightarrow{k_2} 2\mathrm{Y}$$

$$\mathrm{Y} \xrightarrow{k_3} \mathrm{B}$$

where A is the initial reactant, X and Y are intermediate species, and B is the final product of the reaction. A is maintained at a constant value by starting with so much A that only X, Y, and B vary with time.

Develop the unsteady-state material balance equations that predict the change of X and Y as a function of time for the initial conditions $c_X(0) = 30$ and $c_Y(0) = 90$ (c designates concentration).

Solution

The macroscopic balance for both species X and Y is

accumulation = in − out + generation − consumption

For a batch (closed) system, the reactor, the in and out terms are zero. The generation and consumption terms are formulated by using concepts from chemical kinetics:

	X	Y
Generation:	$k_1 c_A c_X$	$k_2 c_X c_Y$
Consumption:	$k_2 c_X c_Y$	$k_3 c_Y$

and the derivatives represent the accumulation. We can merge $k_1 c_A$ into a constant k_1^* since c_A is constant. Then the differential equations for X and Y are

$$\frac{dc_X}{dt} = k_1^* c_X - k_2 c_X c_Y \qquad \text{(a)}$$

$$\frac{dc_Y}{dt} = k_2 c_X c_Y - k_3 c_Y \tag{b}$$

Figure E17.4a shows the concentrations of X and Y for the values $k_1^* = 70$, $k_2 = 1$, and $k_3 = 70$ when (a) and (b) are solved using a computer code.

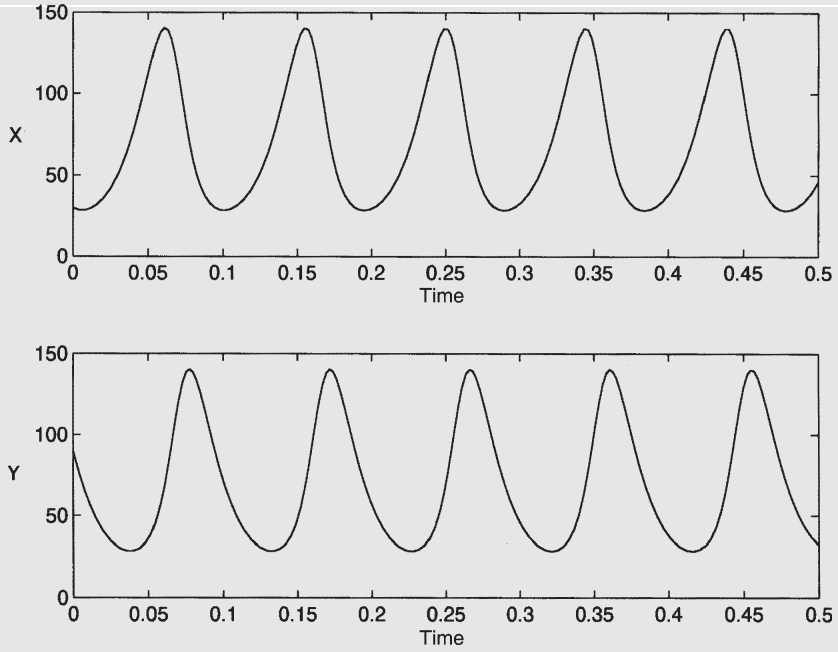


Figure E17.4a

In the steady state, the intermediates exhibit an interesting phenomenon. Divide Equation (b) by Equation (a) to get

$$\frac{dc_Y}{dc_X} = \frac{c_Y[k_2 c_X - k_3]}{c_X[k_1^* - k_2 c_Y]}$$

which can be arranged to

$$\frac{\left(k_1^* - k_2 c_Y\right)}{c_Y} dc_Y = \frac{(k_2 c_X - k_3)}{c_X} dc_X \tag{c}$$

Integration of Equation (c) yields

$$k_1^* \ln c_Y - k_2 c_Y + k_3 \ln c_X - k_2 c_X = \text{constant} \tag{d}$$

Equation (d) represents a series of closed loops when c_Y is plotted against c_X; the constant can be evaluated from the initial conditions for c_X and c_Y. Examine Figure E17.4b.

(*Continues*)

Example 17.4 Oscillating Reactions *(Continued)*

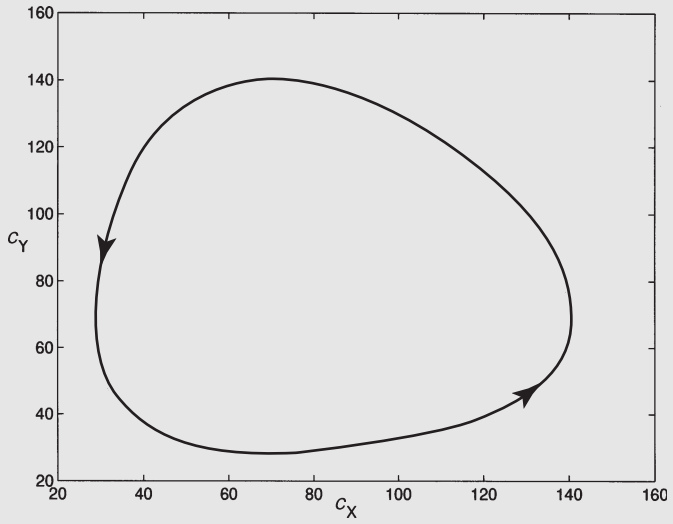


Figure E17.4b

Example 17.5 Unsteady-State Energy Balance

Oil initially at 60°F is being heated in a stirred (perfectly mixed) tank by saturated steam which is condensing in the steam coils at 40 psia. If the rate of heat transfer is given by Newton's heating law,

$$\dot{Q} = \frac{dQ}{dt} = h(T_{\text{steam}} - T_{\text{oil}})$$

where Q is the heat transferred in British thermal units and h is the heat transfer coefficient in the proper units, how long does it take for the discharge from the tank to rise from 60°F to 90°F? What is the maximum temperature that can be achieved in the tank?

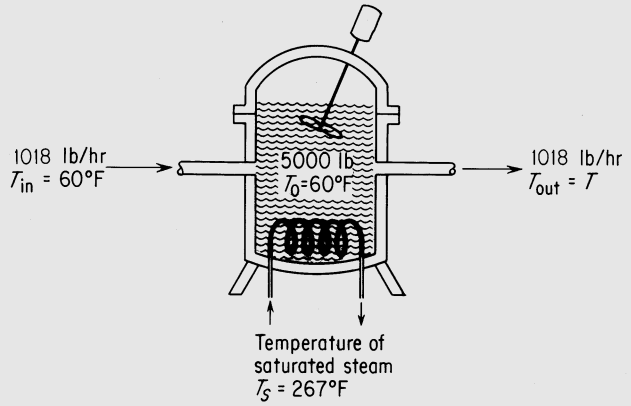


Figure E17.5

Additional data:

Motor horsepower	=	1 hp; efficiency is 0.75
Initial amount of oil in tank	=	5000 lb
Entering oil flow rate	=	1018 lb/hr at a temperature of 60°F
Discharge oil flow rate	=	1018 lb/hr at a temperature of T
h	=	291 Btu/ (hr)(°F)
$C_{p\text{oil}}$	=	0.5 Btu/ (lb)(°F)

Solution

The process is shown in Figure E17.5. The system is the oil in the tank. The independent variable will be t, the time; the dependent variable will be the temperature of the oil in the tank, which is the same as the temperature of the oil discharged. The material balance is not needed because the process, insofar as the quantity of oil is concerned, is assumed to be in the steady state.

The first step is to set up the unsteady-state energy balance. Let T_S = the steam temperature and T = the oil temperature. The balance per unit time is

$$\textbf{accumulation} = \textbf{input} - \textbf{output}$$

$$\frac{dE}{dt} = \frac{dU}{dt} = Q - \Delta H$$

The rate of change of energy inside the tank is nothing more than the rate of change of internal energy, which, in turn, is essentially the same as the rate of change of enthalpy (i.e., $dE/dt = dU/dt = dH/dt$) because $d(pV)/dt \cong 0$.

A good choice for a reference temperature for the enthalpies is 60°F because the choice makes the input enthalpy zero.

$$\left.\begin{array}{rl} \text{Rate of enthalpy of the input stream:} & \dfrac{1018 \text{ lb}}{\text{hr}}\left|\dfrac{0.5 \text{ Btu}}{(\text{lb})\ (°\text{F})}\right|\dfrac{60°\text{F} - 60°\text{F}}{T_{\text{in}} - T_{\text{ref}})} = 0 \\ \text{Rate of heat transfer:} & h(T_s - T) = \dfrac{291 \text{ Btu}}{(\text{hr})\ (°\text{F})}\left|\dfrac{(267 - T)°\text{F}}{}\right. \end{array}\right\} \textbf{input (Btu)}$$

$$\text{Rate of enthalpy of the output stream:} \quad \frac{1018 \text{ lb}}{\text{hr}}\left|\frac{0.5 \text{ Btu}}{(\text{lb})(°\text{F})}\right|\frac{(T - 60)°\text{F}}{} \quad \textbf{output (Btu)}$$

$$\text{Rate of enthalpy change inside the tank:} \quad \frac{5000 \text{ lb}}{}\left|\frac{0.5 \text{ Btu}}{(\text{lb})(°\text{F})}\right|\frac{dT(°\text{F})}{dt(\text{hr})} \quad \textbf{accumulation (Btu)}$$

The energy introduced by the motor enters the tank as rate of work, $\dot{W}$.

$$\textbf{Rate of work:} \quad \dot{W} = \frac{3 \text{ hp}}{4}\left|\frac{0.7608 \text{ Btu}}{(\text{sec})(\text{hp})}\right|\frac{3600 \text{ sec}}{1 \text{ hr}} = \frac{1910 \text{ Btu}}{\text{hr}}$$

(*Continues*)

Example 17.5 Unsteady-State Energy Balance (*Continued*)

Then

$$2500 = 291(267 - T) - 509(T - 60) + 1910$$

$$\frac{dT}{dt} = 44.1 - 0.32T$$

$$\int_{60}^{90} \frac{dT}{44.1 - 0.32T} = \int_0^{\theta} dt = \theta$$

$\theta = 1.52$ hr.

Example 17.6 Modeling a Calcination Process

The process flowsheet illustrated in Figure E17.6a is a fluidized bed in which granular solids are calcinated. Water vapor and gaseous decomposition products leave the bed with the fluidizing gas while metallic oxide products deposit on the particles in the fluidized bed. In Figure E17.6a, x is the mass concentration of the component of interest; F is the mass flow rate of the feed; x_0 is the concentration of x in F; Q is the mass flow rate of stream 1 or 2, respectively; P is the mass flow rate of product; and V is the mass of inventory at time t in vessel 1 or 2, respectively. The overlay dots (·) have been suppressed.

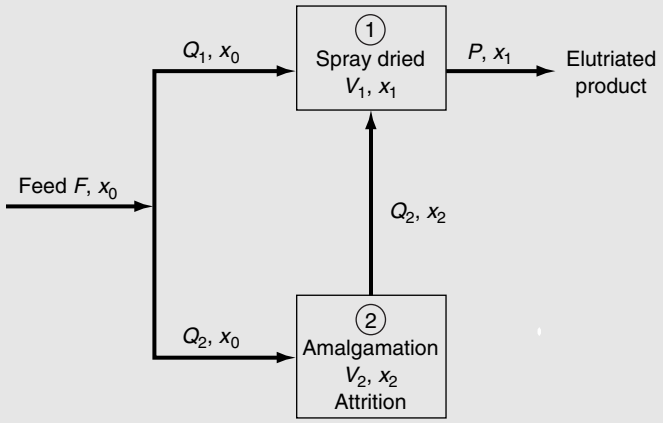


Figure E17.6a

The mass balances for each vessel after introduction of x_0 into stream F become accumulation = in − out if we ignore any reactions.

Vessel 1

Total mass:
$$\frac{dV_1}{dt} = Q_1 + Q_2 - P = 0 \qquad \text{(a)}$$

Component mass: $$V_1\frac{dx_1}{dt} = Q_1x_0 + Q_2x_2 - Px_1 \quad \text{(b)}$$

Initial condition: $x_1(0) = 0$

Vessel 2

Total mass: $$\frac{dV_2}{dt} = Q_2 - Q_2 = 0 \quad \text{(c)}$$

Component mass: $$V_2\frac{dx_2}{dt} = Q_2x_0 - Q_2x_2 \quad \text{(d)}$$

Initial condition: $x_2(0) = 0$

After x_0 is removed from stream F, the concentration of x_0 becomes 0 in the model.

Figure E17.6b shows the value of x_1 as a function of time t for the values $P = 16.5$ g/min, $Q_2 = 6.5$ g/min, $V_1 = 600$ g, and $V_2 = 2.165 \times 10^4$ g when the component of interest is added and then removed from the feed F, and the stated values of the parameters were obtained from experiments.

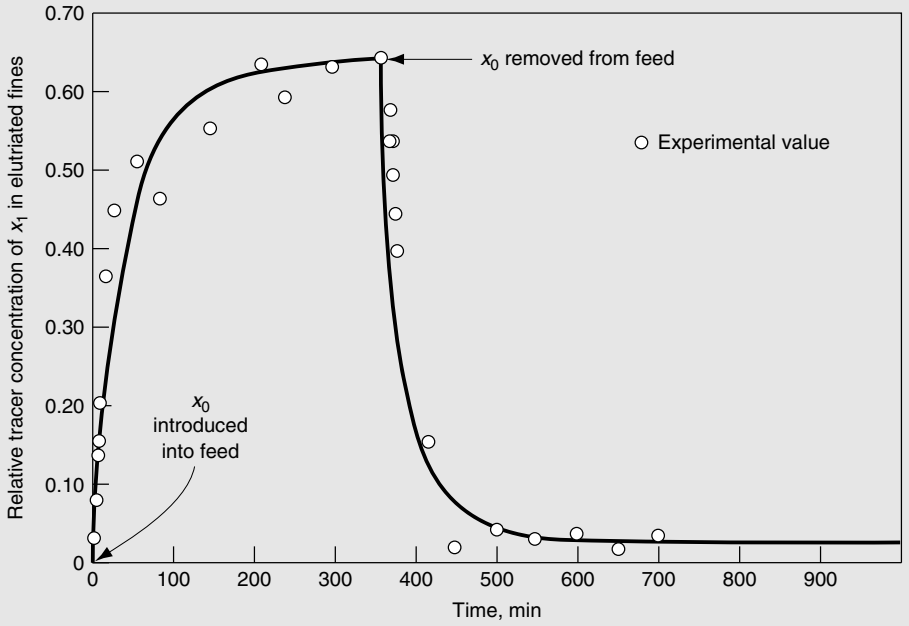


Figure E17.6b

Looking Back

In this chapter we explained how to formulate unsteady-state material and energy balances in which the variation with time is of interest.

Self-Assessment Test

Questions

1. In a batch type of chemical reactor, do you have to have the starting conditions to predict the yield?
2. Is time the independent or dependent variable in macroscopic unsteady-state equations?
3. How can you obtain the steady-state balances from Equations (17.6)–(17.8)?
4. Which of the following plots in Figure SAT17Q4 of response versus time are not transient-state processes?

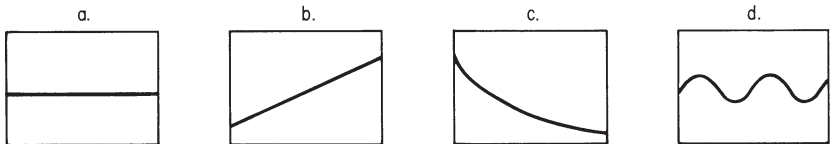


Figure SAT17Q4

5. Group the following words in sets of synonyms: (a) response, (b) input variable, (c) parameter, (d) state variable, (e) system parameter, (f) initial condition, (g) output, (h) independent variable, (i) dependent variable, (j) coefficient, (k) output variable, (l) constant.

Problems

1. A chemical inhibitor must be added to the water in a boiler to avoid corrosion and scale. The inhibitor concentration must be maintained between 4 and 30 ppm. The boiler system always contains 100,000 kg of water and the blowdown (purge) rate is 15,000 kg/hr. The makeup water contains no inhibitor. An initial 2.8 kg of inhibitor are added to the water and thereafter 2.1 kg are added periodically. What is the maximum time interval (after the 2.8 kg) until the first addition of the inhibitor should take place?
2. In a reactor a small amount of undesirable by-product is continuously formed at the rate of 0.5 lb/hr when the reactor contains a steady inventory of 10,000 lb of material. The reactor inlet stream contains traces of the by-product (40 ppm), and the effluent stream is 1400 lb/hr. If on start-up, the reactor contains 5000 ppm of the by-product, what will be the concentration in parts per million at 10 hr?

Thought Problems

1. Refer to the tank in Example 17.2. If the square tank is replaced by (a) a vertical cylindrical tank, (b) a conical tank with vertex at the bottom, (c) a horizontal cylindrical tank, or (d) a spherical tank with the parameters shown in Figure SAT17TP1, if h and D are the same in each tank at $t = 0$, which tank will be the first to drain completely?

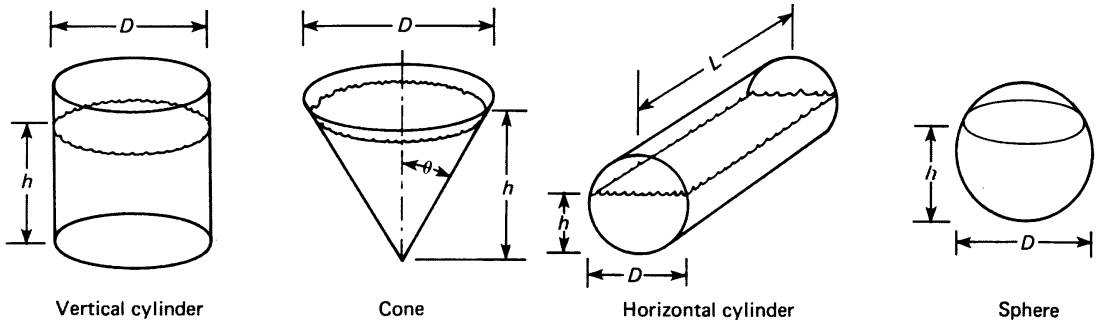


Figure SAT17TP1

2. Many chemical plant operations require that vessels and piping be inerted or purged. If a vessel is to be opened for maintenance or repair, for example, and if the vessel has contained either toxic or flammable materials, purging is required before workers can enter the vessel. For vessel entry, piping leading to or from the vessel will have to be blanked off and at least the portions of the vessels that are open to the pipe will have to be purged as well. Purging must be continued until the atmosphere in the vessel is safe for entry.

If the chemical in the vessel is flammable, purging must be accomplished in two steps: First, the flammable material is purged from the vessel with an inert gas such as nitrogen, and the nitrogen is then purged with air. When a vessel that is to be used for storing or processing flammable chemicals is initially put into service, it must be purged with an inert gas before flammable chemicals are put in the vessel. This step is required to assure that a flammable mixture of the chemical and the air in the tank does not form.

Regardless of the method used to purge the equipment, the final step should be to check the atmosphere in the equipment to make certain that the concentration of the flammable or toxic material has been reduced to safe levels. For tank entry, the oxygen concentration must also be checked before the tank is entered. The measurement of residual concentrations is sometimes required by law; it is always needed for good practice.

Suppose that a 150 ft^3 tank containing air is to be inerted to a 1% oxygen concentration. Pure nitrogen is available for the job. The tank has a maximum allowable working pressure of 150 psia, so either of two methods is possible. In the first method, air is purged by a continuous sweep of nitrogen. The nitrogen is simply allowed to flow into the tank at essentially atmospheric pressure. It is assumed that the nitrogen mixes rapidly and completely with the air in the tank, so the gas leaving the tank has the same concentration of oxygen as the gas in the tank.

In the second technique, the tank is pressurized, the pure nitrogen inlet stream is turned off, and the gas mixture in the tank is then exhausted, lowering the pressure in the tank to atmospheric pressure. If the pressurization technique is used, multiple pressurization cycles may be required, with the tank returned to atmospheric pressure at the end of each cycle. Complete mixing is assumed for each cycle.

In this problem, you may assume that both nitrogen and air behave as ideal gases and that the temperature remains constant at 80°F throughout the process. Determine the volume of nitrogen (measured at standard conditions of 1.0 atm and 0°C) required to purge the tank using each purging technique. For the pressurization technique, assume the pressure in the tank is raised to 140 psig (a little below its maximum working pressure) with nitrogen and then vented to 0 psig. This problem was adapted from the publication *Safety, Health, and Loss Prevention in Chemical Processes,* American Institute of Chemical Engineers, New York (1990).

Supplementary References

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Clements, W. C. *Unsteady-State Balances,* AIChE Chemi Series No. F5.6, American Institute of Chemical Engineers, New York (1986).

Himmelblau, D. M., and K. B. Bischoff. *Process Analysis and Simulation,* Swift Publishing Co., Austin, TX (1980).

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Russel, T. W. F., and M. M. Denn. *Introduction to Chemical Engineering Analysis,* American Institute of Chemical Engineers, New York (1968).

Web Sites

www.aspentech.com
www.hyprotech.com
www.intergraph.com

Problems

Problems in this chapter will not be rated according to the degree of difficulty.

17.1 A tank containing 100 kg of a 60% brine (60% salt) is filled with a 10% salt solution at the rate of 10 kg/min. Solution is removed from the tank at the rate of 15 kg/min. Assuming complete mixing, find the kilograms of salt in the tank after 10 min.

17.2 A defective tank of 1500 ft^3 volume containing 100% propane gas (at 1 atm) is to be flushed with air (at 1 atm) until the propane concentration reduces to less

than 1%. At that concentration of propane the defect can be repaired by welding. If the flow rate of air into the tank is 30 ft^3/min, for how many minutes must the tank be flushed out? Assume that the flushing operation is conducted so that the gas in the tank is well mixed.

17.3 A 2% uranium oxide slurry (2 lb UO_2/100 lb H_2O) flows into a 100 gal tank at the rate of 2 gal/min. The tank initially contains 500 lb of H_2O and no UO_2. The slurry is well mixed and flows out at the same rate at which it enters. Find the concentration of slurry in the tank at the end of 1 hr.

17.4 The catalyst in a fluidized-bed reactor of 200 m^3 volume is to be regenerated by contact with a hydrogen stream. Before the hydrogen can be introduced in the reactor, the O_2 content of the air in the reactor must be reduced to 0.1%. If pure N_2 can be fed into the reactor at the rate of 20 m^3/min, for how long should the reactor be purged with N_2? Assure that the catalyst solids occupy 6% of the reactor volume and that the gases are well mixed.

17.5 An advertising firm wants to get a special inflated sign out of a warehouse. The sign is 20 ft in diameter and is filled with H_2 at 15 psig. Unfortunately, the door frame to the warehouse permits only 19 ft to pass. The maximum rate of H_2 that can be safely vented from the balloon is 5 ft^3/min (measured at room conditions). How long will it take to get the sign small enough to just pass through the door?

a. First assume that the pressure inside the balloon is constant so that the flow rate is constant.
b. Then assume the amount of H_2 escaping is proportional to the volume of the balloon and initially is 5 ft^3/min.

Could a solution to this problem be obtained if the amount of escaping H_2 were proportional to the pressure difference inside and outside the balloon?

17.6 A plant at Canso, Nova Scotia, makes fish-protein concentrate (FPC). It takes 6.6 kg of whole fish to make 1 kg of FPC, and therein is the problem—to make money, the plant must operate most of the year. One of the operating problems is the drying of the FPC. It dries in the fluidized dryer at a rate approximately proportional to its moisture content. If a given batch of FPC loses one-half of its initial moisture in the first 15 min, how long will it take to remove 90% of the water in the batch of FPC?

17.7 Water flows from a conical tank at the rate of $0.020(2 + h^2)$ m^3/min, as shown in Figure P17.7. If the tank is initially full, how long will it take for 75% of the water to flow out of the tank? What is the flow rate at that time?

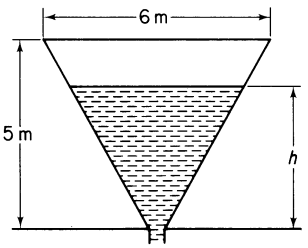


Figure P17.7

17.8 A sewage disposal plant has a big concrete holding tank of 100,000 gal capacity. It is three-fourths full of liquid to start with and contains 60,000 lb of organic material in suspension. Water runs into the holding tank at the rate of 20,000 gal/hr and the solution leaves at the rate of 15,000 gal/hr. How much organic material is in the tank at the end of 3 hr?

17.9 Suppose that in problem 17.8 the bottom of the tank is covered with sludge (precipitated organic material) and that the stirring of the tank causes the sludge to go into suspension at a rate proportional to the difference between the concentration of sludge in the tank at any time and 10 lb of sludge/gal. If no organic material were present, the sludge would go into suspension at the rate of 0.05 lb/(min) (gal solution) when 75,000 gal of solution are in the tank. How much organic material is in the tank at the end of 3 hr?

17.10 In a chemical reaction the products X and Y are formed according to the equation

$$C \rightarrow X + Y$$

The rate at which each of these products is being formed is proportional to the amount of C present. Initially: $C = 1$, $X = 0$, $Y = 0$. Find the time for the amount of X to equal the amount of C.

17.11 A tank is filled with water. At a given instant two orifices in the side of the tank are opened to discharge the water. The water at the start is 3 m deep and one orifice is 2 m below the top while the other one is 2.5 m below the top. The coefficient of discharge of each orifice is known to be 0.61. The tank is a vertical right circular cylinder 2 m in diameter. The upper and lower orifices are 5 and 10 cm in diameter, respectively. How much time will be required for the tank to be drained so that the water level is at a depth of 1.5 m?

17.12 Suppose that you have two tanks in series, as diagrammed in Figure P17.12. The volume of liquid in each tank remains constant because of the design of the overflow lines. Assume that each tank is filled with a solution containing 10 lb of A, and that each tank contains 100 gal of aqueous solution of A. If freshwater enters at the rate of 10 gal/hr, what is the concentration of A in each tank at the end of 3 hr? Assume complete mixing in each tank and ignore any change of volume with concentration.

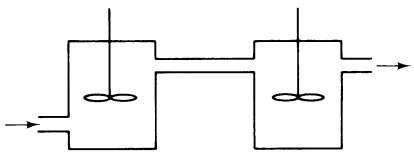


Figure P17.12

17.13 A well-mixed tank has a maximum capacity of 100 gal and it is initially half full. The discharge pipe at the bottom is very long and thus it offers resistance to the flow of water through it. The force that causes the water to flow is the

height of the water in the tank, and in fact that flow is just proportional to the height. Since the height is proportional to the total volume of water in the tank, the volumetric flow rate of water out, q_o, is

$$q_o = kV$$

The flow rate of water into the tank, q_i, is constant. Use the information given in Figure P17.13 to decide whether the amount of water in the tank increases, decreases, or remains the same. If it changes, how much time is required to completely empty or fill the tank, as the case may be?

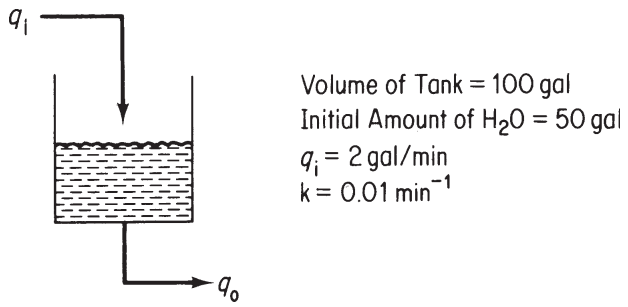


Figure P17.13

17.14 A stream containing a radioactive fission product with a decay constant of 0.01 hr^{-1} (i.e., $dn/dt = 0.01\ n$) is run into a holding tank at the rate of 100 gal/hr for 24 hr. Then the stream is shut off for 24 hr. If the initial concentration of the fission product was 10 mg/L and the tank volume is constant at 10,000 gal of solution (owing to an overflow line), what is the concentration of fission product (a) at the end of the first 24 hr period and (b) at the end of the second 24 hr period?

What is the maximum concentration of fission product? Assume complete mixing in the tank.

17.15 A radioactive waste that contains 1500 ppm of ^{92}Sr is pumped at the rate of 1.5×10^{-3} m^3/min into a holding tank that contains 0.40 m^3. ^{92}Sr decays as follows:

$$^{92}Sr \longrightarrow {}^{92}Y \longrightarrow {}^{92}Zr$$

half-life: 2.7 hr 3.5 hr

If the tank contains clear water initially and the solution runs out at the rate of 1.5×10^{-3} m^3/min, assuming perfect mixing:

a. What is the concentration of Sr, Y, and Zr after 1 day?
b. What is the equilibrium concentration of Sr and Y in the tank?

The rate of decay of such isotopes is $dN/dt = -\lambda N$, where $\lambda = 0.693/t_{1/2}$ and the half-life is $t_{1/2}$. N = moles.

17.16 A tank contains 3 m^3 of pure oxygen at atmospheric pressure. Air is slowly pumped into the tank and mixes uniformly with the contents, an equal volume of which is forced out of the tank. What is the concentration of oxygen in the tank after 9 m^3 of air has been admitted?

17.17 Suppose that an organic compound decomposes as follows:

$$C_6H_{12} \rightarrow C_4H_8 + C_2H_4$$

If 1 mol of C_6H_{12} exists at $t = 0$, but no C_4H_8 and C_2H_4, set up equations showing the moles of C_4H_8 and C_2H_4 as a function of time. The rates of formation of C_4H_8 and C_2H_4 are proportional to the number of moles of C_6H_{12} present.

17.18 A large tank is connected to a smaller tank by means of a valve. The large tank contains N_2 at 690 kPa while the small tank is evacuated. If the valve leaks between the two tanks and the rate of leakage of gas is proportional to the pressure difference between the two tanks ($p_1 - p_2$), how long does it take for the pressure in the small tank to be one-half its final value? The instantaneous initial flow rate with the small tank evacuated is 0.091 kg mol/hr.

	Tank 1	**Tank 2**
Initial pressure (kPa)	700	0
Volume (m^3)	30	15

Assume that the temperature in both tanks is held constant and is 20°C.

17.19 The following chain reactions take place in a constant-volume batch tank:

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

Each reaction is first order and irreversible. If the initial concentration of A is C_{A_0} and if only A is present initially, find an expression for C_B as a function of time. Under what conditions will the concentration of B be dependent primarily on the rate of reaction of A?

17.20 Consider the following chemical reactions in a constant-volume batch tank:

$$\begin{array}{ccc} A & \underset{k_2}{\overset{k_1}{\rightleftharpoons}} & B \\ k_3 \downarrow & & \\ C & & \end{array}$$

All of the indicated reactions are first order. The initial concentration of A is C_{A_0}, and nothing else is present at that time. Determine the concentrations of A, B, and C as functions of time.

17.21 Tanks A, B, and C are each filled with 1000 gal of water. See Figure P17.21. Workers have instructions to dissolve 2000 lb of salt in each tank. By mistake, 3000 lb are dissolved in each of tanks A and C and none in B. You wish to

bring all of the compositions to within 5% of the specified 2 lb/gal. If the units are connected *A*—*B*—*C*—*A* by three 50 gal/min (gpm) pumps:

a. Express the concentrations C_A, C_B, and C_C in terms of t (time).
b. Find the shortest time at which all concentrations are within the specified range. Assume the tanks are all well mixed.

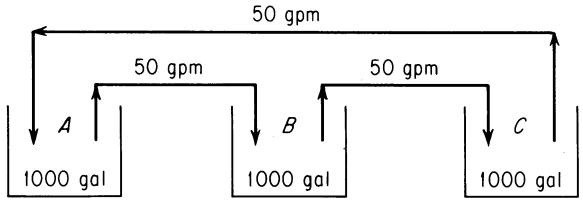


Figure P17.21

17.22 Determine the time required to heat a 10,000 lb batch of liquid from 60°F to 120°F using an external, counterflow heat exchanger having an area of 300 ft^2. Water at 180°F is used as the heating medium and flows at a rate of 6000 lb/hr. An overall heat transfer coefficient of 40 Btu/(hr)(ft^2)(°F) may be assumed; use Newton's law of heating. The liquid is circulated at a rate of 6000 lb/hr, and the specific heat of the liquid is the same as that of water (1.0). Assume that the residence time of the liquid in the external heat exchanger is very small and that there is essentially no holdup of liquid in this circuit.

17.23 A ground material is to be suspended in water and heated in preparation for a chemical reaction. It is desired to carry out the mixing and heating simultaneously in a tank equipped with an agitator and a steam coil. The cold liquid and solid are to be added continuously, and the heated suspension will be withdrawn at the same rate. One method of operation for starting up is to (1) fill the tank initially with water and solid in the proper proportions, (2) start the agitator, (3) introduce freshwater and solid in the proper proportions and simultaneously begin to withdraw the suspension for reaction, and (4) turn on the steam. An estimate is needed of the time required, after the steam is turned on, for the temperature of the effluent suspension to reach a certain elevated temperature.

a. Using the nomenclature given below, formulate a differential equation for this process. Integrate the equation to obtain n as a function of B and ϕ (see nomenclature).
b. Calculate the time required for the effluent temperature to reach 180°F if the initial contents of the tank and the inflow are both at 120°F and the steam temperature is 220°F. The surface area for heat transfer is 23.9 ft^2, and the heat transfer coefficient is 100 Btu/(hr)(ft^2)(°F). The tank contains 6000 lb, and the rate of flow of both streams is 1200 lb/hr. In the proportions used, the specific heat of the suspension may be assumed to be 1.00.

If the area available for heat transfer is doubled, how will the time required be affected? Why is the time with the larger area less than half that obtained previously? The heat transferred is $Q = UA(T_{\text{tank}} - T_{\text{steam}})$.

Nomenclature

W = weight of tank contents, lb
G = rate of flow of suspension, lb/hr
T_S = temperature of steam, °F
T = temperature in tank at any instant, perfect mixing assumed, °F
T_0 = temperature of suspension introduced into tank; also initial temperature of tank contents, °F
U = heat transfer coefficient, Btu/(hr)(ft^2)(°F)
A = area of heat transfer surface, ft^2
C_p = specific heat of suspension, Btu/(lb)(°F)
t = time elapsed from the instant the steam is turned on, hr
n = dimensionless time, Gt/W
B = dimensionless ratio, UA/GC_p
ϕ = dimensionless temperature (relative approach to the steam temperature) $(T - T_0)/(T_S - T_0)$

17.24 Consider a well-agitated cylindrical tank in which the heat transfer surface is in the form of a coil that is distributed uniformly from the bottom of the tank to the top of the tank. The tank itself is completely insulated. Liquid is introduced into the tank at a uniform rate, starting with no liquid in the tank, and the steam is turned on at the instant that liquid flows into the tank.

a. Using the nomenclature of problem 17.23, formulate a differential equation for this process. Integrate the differential equation to obtain an equation for ϕ as a function of B and f, where f = fraction filled = W/W_{filled}.
b. If the heat transfer surface consists of a coil of 10 turns of 1-in.-OD tubing 4 ft in diameter, the feed rate is 1200 lb/hr, the heat capacity of the liquid is 1.0 Btu/(lb)(°F), the heat transfer coefficient is 100 Btu/(hr)(°F)(ft^2) of covered area, the steam temperature is 200°F, and the temperature of the liquid introduced into the tank is 70°F, what is the temperature in the tank when it is completely full? What is the temperature when the tank is half full? The heat transfer is given by $Q = UA(T_{\text{tank}} - T_{\text{steam}})$.

17.25 A cylindrical tank 5 ft in diameter and 5 ft high is full of water at 70°F. The water is to be heated by means of a steam jacket around the sides only. The steam temperature is 230°F, and the overall coefficient of heat transfer is constant at 40 Btu/(hr)(ft^2)(°F). Use Newton's law of cooling (heating) to estimate the heat transfer. Neglecting the heat losses from the top and the bottom, calculate the time necessary to raise the temperature of the tank contents to 170°F. Repeat, taking the heat losses from the top and the bottom into account. The air temperature around the tank is 70°F, and the overall coefficient of heat transfer for both the top and the bottom is constant at 10 Btu/(hr)(ft^2)(°F).