

## Chapter 3 Introduction to Environmental Processes

Materials and energy balances are key tools in achieving a quantitative understanding of the behavior of environmental systems. They serve as a method of accounting for the flow of energy and materials into and out of the environmental systems. Mass balances provide us with a tool for modeling the production, transport, and fate of pollutants in the environment. Energy balances likewise provide us with a tool for modeling the production, transport, and fate of energy in the environment.

### 3.1. Unifying Theories

#### Conservation of Matter

The *law of conservation of matter* states that (without nuclear reaction) matter can neither be created nor destroyed. It simply says we ought to be able to account for the “matter” at any point in time. The mathematical representation of this accounting system is called a *materials balance* or *mass balance*.

#### Conservation of Energy

The *law of conservation of energy* states that energy cannot be created or destroyed. Like the law of conservation of matter, this theory means that we should be able to account for the “energy” at any point in time. The mathematical representation of this accounting system we use to trace energy is called an *energy balance*.

### 3.2 Material Balances

The simplest form of a materials balance or mass balance for an environmental process, the equation would be written:

$$\text{Accumulation} = \text{input} - \text{output} \quad (3-1)$$

where accumulation, input, and output refer to the mass quantities accumulating in the system or flowing into or out of the system. The system may be, for example, a pond, a river, or a pollution control device.

**The control volume.** Using the mass balance approach, we begin solving the problem by drawing a flowchart of the process or a conceptual diagram of the environmental subsystem. All of the known inputs, outputs, and accumulation are converted to the same mass units and placed on the diagram. Unknown inputs, outputs, and accumulation are also marked on the diagram. This helps us define the problem. System boundaries (imaginary blocks around the process or part of the process) are drawn in such a way that calculations are made as simple as possible. The system within the boundaries is called the *control volume*.

#### Time as a factor

For many environmental problems time is an important factor in establishing the degree of severity of the problem or in designing a solution. In these instances, Equation 3-1 is modified to the following from:

$$\text{Mass rate of accumulation} = \text{mass rate of input} - \text{mass rate of output} \quad (3-2)$$

where *rate* is used to mean “per unit time.” In the calculus this may be written as

$$\frac{dM}{dt} = \frac{d(in)}{dt} - \frac{d(out)}{dt} \quad (3 - 3)$$

where M refers to the mass accumulated and (in) and (out) refer to the mass flowing in or out. As the part of the description of the problem, a convenient time interval that is meaningful for the system must be chosen.

**Example 3-1** Selam is filling her bathtub but she forgot to put the plug in. If the volume of water for a bath is 0.350 m<sup>3</sup> and the tap is flowing at 1.32 L/min and the drain is running at 0.32 L/min, how long will it take to fill the tub to bath level? Assuming Selam shuts off the water when the tub is full and does not flood the house, how much water will be wasted? Assume the density of water is 1,000 kg/m<sup>3</sup>

### Efficiency

The effectiveness of an environmental process in removing a contaminant can be determined using the mass balance technique. Starting with Equation 3-3, the mass of contaminant per unit of time [d(in)/dt and d(out)/dt] may be calculated as:

$$\frac{Mass}{Time} = (concentration)(flow\ rate)$$

For example,

$$\frac{Mass}{Time} = \left(\frac{mg}{m^3}\right) \left(\frac{m^3}{s}\right) = mg/s$$

This is called a mass flow rate. In concentration and flow rate terms, the mass balance equation is

$$\frac{dM}{dt} = C_{in}Q_{in} - C_{out}Q_{out} \quad (3 - 4)$$

Where dM/dt = rate of accumulation of contaminant in the process

C<sub>in</sub>, C<sub>out</sub> = concentrations of contaminant into and out of the process

Q<sub>in</sub>, Q<sub>out</sub> = flow rates into and out of the process

The ratio of the mass that is accumulated in the process to the incoming mass is a measure of how effective the process is in removing the contaminant

$$\frac{dM/dt}{C_{in}Q_{in}} = \frac{C_{in}Q_{in} - C_{out}Q_{out}}{C_{in}Q_{in}} \quad (3 - 5)$$

The left-hand side of the equation is given the notation η. Efficiency (η) is then defined as

$$\eta = \frac{\text{mass in} - \text{mass out}}{\text{mass in}} (100\%) \quad (3 - 6)$$

### Example 3.2 Baghouse mass balance

### 3.3. Reaction Order and Reactors

#### Reaction kinetics

Not all chemical reactions reach equilibrium quickly. Reactions that are time dependent are called **kinetic reactions**.

**Reaction kinetics** can be defined as the study of the effects of temperature, pressure, and concentration on the rate of a chemical reaction.

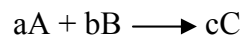
The **rate of reaction**,  $r_i$ , is a term used to describe the rate of formation or disappearance of a substance (or chemical species). Reactions such as biological oxidation and disinfection, which occur within a single phase (i.e., liquid, solid, or gaseous), are called *homogenous reactions*. Those like ion exchange and adsorption, which occur at surfaces between phases (the solid-water or air-water interface) are referred to as *heterogeneous reactions*.

The rate at which these reactions occur is a function (f) of temperature (T) and pressure and also of the concentration of the reactant(s). the rate relation is therefore,

$$r_i = kf_1(T,P);f_2([A],[B], \dots) \quad (3-7)$$

where  $k$  is the rate constant, normally a function of temperature only, and  $f_1$  and  $f_2$  mean “function of (.).”

Assuming that the pressure and temperature are kept constant, we can examine how the concentration of one or more of the reactants affects the reaction rate. For the stoichiometric equation



where  $a$ ,  $b$ , and  $c$  are the stoichiometric equation coefficients for the reactants A and B and the product C, the rate equation is

$$r_A = -k[A]^\alpha [b]^\beta = k[C]^\gamma$$

where  $[A]$ ,  $[B]$ , and  $[C]$  are the respective concentrations and  $\alpha$ ,  $\beta$ , and  $\gamma$  are empirically found exponents. The negative sign indicates that A and B are disappearing while C is increasing.

The order of reaction is defined as the sum of the empirically found exponents  $\alpha + \beta$ , and the order with respect to reactant A is  $\alpha$ , to B is  $\beta$ , and to product C is  $\gamma$ . In many cases, reactions will be zero, first, or second order. Expressed mathematically,

$r_A = -k$	zero-order reaction
$r_A = -k[A]$	first-order reaction
$r_A = -k[A^2]$	second-order reaction
$r_A = -k[A][B]$	second-order reaction

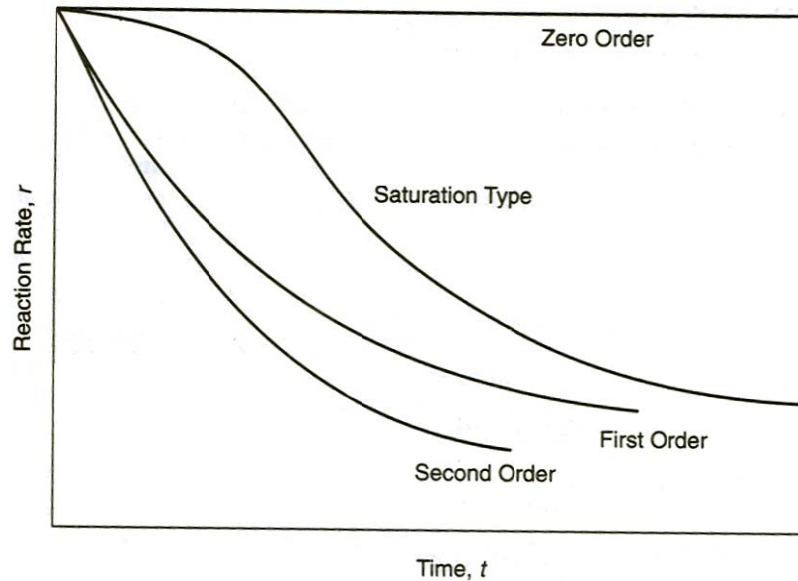
A more complex example is

$$r_A = \frac{-k[A]}{1 + k'[A]} \quad (3 - 8)$$

- At a low concentration of A (at the end of the reaction),  $k'[A] \ll 1$ ; therefore, the reaction reduces to first order.
- At a high concentration of A (at the beginning of the reaction),  $k'[A] \gg 1$ ; therefore, the reaction reduces to zero order.

Equation (3-8) is an example of a saturation reaction, which is quite common on environmental problems.

Figure 3-1 is a graphical representation showing how the reaction rate  $r(d[A]/dt)$  varies with time for different orders of reaction.



**Figure 3-1.** Graphical representation of rate equations

**Including reactions.** Equation 3-2 is applicable only if the system is *conserved*, which is a system where no chemical or biological reaction takes place and no radioactive decay occurs for the substance in the mass balance. For *nonconservative* substances (i.e., those that react or settle out) Equation 3-2 may be written to account time-dependent transformation (reaction) as follows:

$$\text{Accumulation rate} = \text{input rate} - \text{output rate} \pm \text{transformation rate} \quad (3-9)$$

With reactions, Equation 3-3 may become

$$\frac{dM}{dt} = \frac{d(in)}{dt} - \frac{d(out)}{dt} + r \quad (3-10)$$

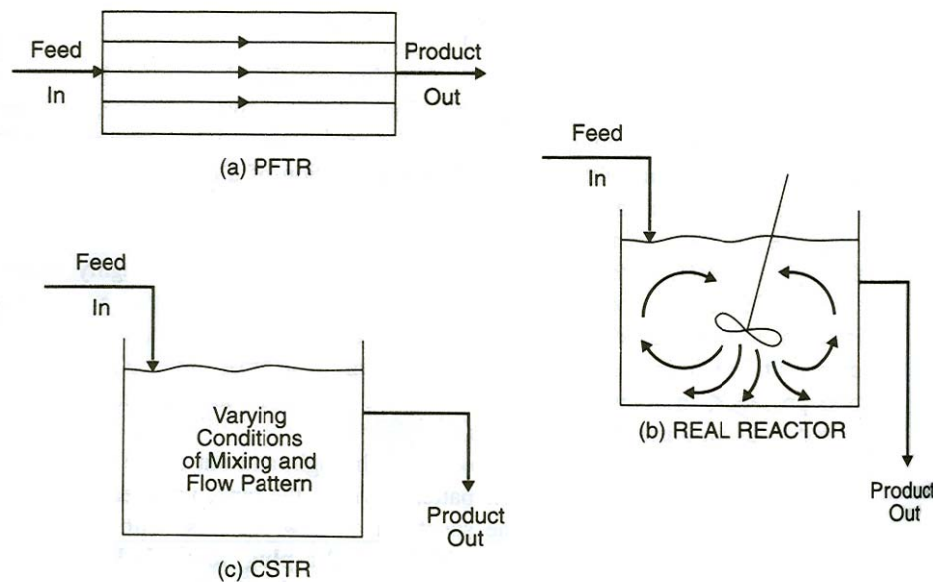
### Types of Reactors

When a reaction of a chemical or biochemical nature occurs within a tank, the tank is usually referred to as *reactor*.

Reactors can generally be divided into two types: **batch reactors** and **flow reactors**. In a *batch reactor* are fill-and-draw type, the materials are added to the tank, thoroughly mixed, left for a

sufficient time for the reaction to occur, and then drained. Because the material in the tank is normally well mixed, the composition within the reactor is uniform at any instant of time. However, as the reaction proceeds, the composition changes with time. A **batch reaction** is therefore referred to as an *unsteady-state operation*.

In a flow reactor, material flows into, through, and out of the reactor. Depending on the mixing conditions and flow patterns within the tank, we speak of *ideal* and *real reactors*. Figure 3-2 shows the spectrum of flow reactors, with an ideal reactor at each end. The ideal reactor of part (a) is called a **plug flow tubular reactor** (PFTR), or sometimes just a *plug flow reactor*. The flow pattern within the tank is characterized as uniform. That is, the fluid particles pass through the tank and are discharged in the same sequence that they entered the tank. The particles remain in the tank for a period equal to the theoretical detention time. There is no mixing of the fluid in a longitudinal direction, although there may or may not be some lateral mixing. The operation can be steady, if the rate of flow is constant with time, or unsteady, if it changes with time. In part (c) is the other ideal flow reactor, called a **completely stirred tank reactor** (CSTR). In this case the contents of the tank are so completely mixed that the composition is uniform throughout. Therefore, the composition of the effluent is the same as that of liquid in the tank. Real flow reactors have mixing conditions which fall between the PFTR (no mixing) and CSTR (complete mixing).



**Figure 3-2.** Flow reactors: (a) plug flow tubular reactor (ideal reactor); (b) real reactor; (c) completely stirred tank reactor (ideal reactor)

For simple completely mixed systems with first-order reactions, the total mass of substance ( $M$ ) is equal to the product of the concentration ( $C$ ) and volume ( $V$ ) and, when  $V$  is a constant, the mass rate of decay of the substance is

$$\frac{dM}{dt} = \frac{d(CV)}{dt} = V \frac{d(C)}{dt} \quad (3 - 11)$$

Because first-order reactions can be described by  $r = -kC = dC/dt$ , we can rewrite Equation 3-10 as

$$\frac{dM}{dt} = \frac{d(in)}{dt} - \frac{d(out)}{dt} - kCV \quad (3 - 12)$$

**Example 3.3.** A storm sewer is carrying snow melt containing 1,200 g/L of sodium chloride into a small stream. The stream has a naturally occurring sodium chloride concentration of 20 mg/L. If the storm sewer flow rate is 2,000 L/min and the stream flow rate is 2.0 m<sup>3</sup>/s, what is the concentration of salt in the stream after the discharge point? Assume that the sewer flow and the stream flow are completely mixed, that the salt is a conservative substance (it does not react), and that the system is at steady state.

### Example 3.4 A well-mixed sewage lagoon

For batch reactors because there is no flow into or out of a batch reactor

$$\frac{d(in)}{dt} = \frac{d(out)}{dt} = 0$$

For batch reactor Equation 3-12 reduces to

$$\frac{dM}{dt} = -kCV \quad (3 - 13)$$

Noting Equation 3-11 for first-order reaction in a batch reactor, Equation 3-13 may be simplified to

$$\frac{dC}{dt} = -kC \quad (3 - 14)$$

For plug-flow reactors, even at steady state, the contents within the “plug” element of fluid can change with time as the plug moves downstream. The control volume for the mass balance is the plug or differential element of fluid. The mass balance for this moving plug may be written as

$$\frac{dM}{dt} = \frac{d(in)}{dt} - \frac{d(out)}{dt} + V \frac{d(C)}{dt} \quad (3 - 15)$$

Because no mass exchange occurs across the plug boundaries,  $d(in)$  and  $d(out) = 0$ . Equation 3-15 may be rewritten as

$$\frac{dM}{dt} = 0 - 0 + V \frac{d(C)}{dt} \quad (3 - 16)$$

As noted earlier, for a first-order decay reaction, the right-hand term may be expressed as

$$V \frac{dC}{dt} = -kCV \quad (3 - 17)$$

With similar analogy of Equation 3-13, the mass rate of decay of the substance ( $dM/dt$ ) in Equation 3-16 may be expressed as

$$V \frac{dC}{dt} = -kCV \quad (3 - 18)$$

The steady-state solution to the mass-balance equation for the plug-flow system with first-order kinetics is

$$\ln \frac{C_{out}}{C_{in}} = -k\theta \quad (3 - 19)$$

Or

$$C_{out} = (C_{in})e^{-k\theta} \quad (3 - 20)$$

where  $k$  = reaction rate constant,  $s^{-1}$ ,  $min^{-1}$ , or  $d^{-1}$

$\theta$  = residence time in plug-flow system, s, min, or d

in a plug-flow system of length  $L$ , each plug travels for a period  $=L/u$ , where  $u$  = the speed of flow. Alternatively, for a cross-sectional area  $A$ , the residence time is

$$\theta = \frac{(L)(A)}{(u)(A)} = \frac{V}{Q} \quad (3 - 21)$$

where  $V$  = volume of the plug-flow system,  $m^3$

$Q$  = flow rate (in  $m^3/s$ )

Thus, for example, Equation 3-19, may be written as

$$\ln \frac{C_{out}}{C_{in}} = -k \frac{L}{u} = -k \frac{V}{Q} \quad (3 - 22)$$

Although the concentration within a given plug changes over times as the plug moves downstream, the concentration at a fixed point in the plug-flow system remains constant with respect to time. Thus, Equation 3-22 has no time dependence.

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**Example 3.5** A wastewater treatment plant must disinfect its effluent before discharging the wastewater to a near-by stream. The wastewater contains  $4.5 \times 10^5$  fecal coliform colony-forming units (CFU) per liter. The maximum permissible fecal coliform concentration that may be discharged is 2,000 fecal coliform CFU/L. It is proposed that a pipe carrying the wastewater be used for disinfection process. Determine the length of pipe required if the linear velocity of the wastewater in the pipe is 0.75 m/s. Assume that the pipe behaves as a steady-state pug-flow system and that the reaction rate constant for destruction of the fecal coliforms is  $0.23 \text{ min}^{-1}$ .

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