

Chapter- III: MASS TRANSFER

3.1 Mass transfer

Everything has to go somewhere is a simple way to express one of the most fundamental engineering principles. The *law of conservation of mass* says that mass can never be created nor destroyed. What this concept allows us to do is track materials, that is, pollutants, from one place to another with mass balance equations.

In environmental systems, be it an aerobic cell participating in oxidation process or a river receiving untreated wastes, the movement of nutrients, substrate or metabolic products plays an important role. Thus physical transport phenomena become predominant in governing the processing rate rather than the chemical or biochemical rate. The extent of processes such as decomposition of wastes by microorganisms or **Lake Eutrophication** is governed by either the supply of natural or artificial oxygen or availability of substrate or nutrients. Thus the transfer of mass from one point to another in a system becomes important.

In the biochemical or physical mass-transfer process, interphase diffusion occurs when a driving force is created by a departure from equilibrium. In the gas phase, the driving force is a partial pressure gradient and in the solid or liquid phase, it is the concentration gradient. There could be different mass transfer processes depending upon the underlying phases, for example:

- Gas-liquid mass transfer : aeration or supply of oxygen for decomposing waste
- Liquid –gas transfer : release of methane from anaerobic waste treatment
- Liquid-liquid mass transfer : extraction of organic solvents, liquid phase oxygen transfer
- Liquid-solid mass transfer : adsorption of pollutants on activated carbon
- solid-gas mass transfer : release of gases from solid wastes in a landfill

Intensive properties and extensive properties are types of physical properties of matter. The terms intensive and extensive were first described by physical chemist and physicist Richard C. Tolman in 1917. Intensive properties are bulk properties, which mean they do not depend on the amount of matter that is present. Examples of intensive properties include density, color, temperature, odor, hardness etc.

Extensive properties do depend on the amount of matter that is present. An extensive property is considered additive for subsystems. Examples of extensive properties include volume, mass, size, weight, length etc.

The ratio between two extensive properties is an intensive property. For example, mass and volume are extensive properties, but their ratio (density) is an intensive property of matter.

While extensive properties are great for describing a sample, they aren't very helpful in identifying it because they can change according to sample size or conditions.

3.2 Energy transfer

The law of conservation of energy states that, with the exception of nuclear reactions, energy can neither be created nor destroyed. This energy law serves as an accounting tool in various environmental implications. Be it a metabolic reaction taking inside a cell or dispersion of air pollutants in the atmosphere or the different aspects of climate change processes, a knowledge of transfer of energy is essential to understand the process dynamics. The flow of energy can be analyzed through energy balance equations using *the first law of thermodynamics*. The first law of thermodynamics states that energy can never be created nor be destroyed.

$$\text{Change in energy of system} - \text{change in energy of surroundings} = 0$$

Therefore, when energy disappears in one form, it appears in another. The total energy stored in a system is composed of internal, kinetic, and potential energies.

A simple interpretation of the *second law of thermodynamics* suggests that when work is done there will always be some inefficiency; that is, some portion of the energy put into the process will end up as waste heat. How the waste heat affects the environment is an important consideration in the study of environmental engineering.

Knowledge of mass and energy transfer in pollution control and remediation is essential to:

- Understand the process
- Design the preventive measures
- Design the treatment units
- Design the remediation activities

3.3 Mass balance

It is well understood that matter can neither be created nor destroyed but it can be changed from one form to other. This concept serves as a basis for describing and analyzing environmental engineering problems. The concept is called a *materials balance*, or a *mass balance*. What this concept allows us to do is track materials, for example the pollutants, from one place to another with mass balance equations. The first step a mass balance analysis is to define the particular region in the space that is to be analyzed. This is carried out by drawing a flow chart of the process or a conceptual diagram of the environmental subsystem termed as 'Mass Balance Diagram'. All of the known inputs, outputs, and accumulation are converted to the same mass units and placed on the diagram. This helps us define the problems. 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. We then write material- balance equations to solve for unknown inputs, outputs, or accumulations or to demonstrate that we have accounted for all of the components by demonstrating that the materials balance "closes," that is, the accounting balances. The diagram may include anything from a simple chemical mixing tank, to an entire coal-fired power plant, a lake, a stretch of a stream, an air basin above a city, or the globe itself. By picturing an imaginary boundary around the region, we can then begin to identify the flow of materials across the boundary as well as the accumulation of materials within the region.

In its simplest form it may be viewed as an accounting procedure. For example, a mass balance is performed each time a check book is balanced.

$$\text{Balance} = \text{Deposit} - \text{Withdrawal} \pm \text{Interest} \quad (3.1)$$

In an environmental system or subsystem, the equation would be written as:

$$\text{Accumulation} = \text{Input} - \text{Output} \pm \text{Transformation rate} \quad (3.2)$$

Where, Accumulation, Input, and Output refer to the mass quantities accumulating in the system or flowing into or out of the system. However, a situation may arise when there is a ZERO balance, that is the rates of deposit and withdrawals are equal. In actual case, a bank would not permit one to make the balance a zero. With an analogy to the environmental system, we note that this situation would mean the rate of incoming material is equal to the rate of outgoing material.

3.3.1 Material balance with single material

Material flows can be most readily understood and analyzed by using the concept of a black box. These boxes are schematic representations of real processes or flow junctions, and it is not necessary to specify just what this process is to be able to develop general principles about the analysis of flows.

Fig. 3.1 shows a black box into which some material is flowing. All flows into the box are called influents and represented by the letter X. If the flow is described as mass per unit time, X_0 is the mass per unit time of material X flowing in to the box. Similarly, X_1 is the outflow or effluent. If no processes are going inside the box that will either make of more material or destroy some of it

and if the flow is assumed not vary with time (that is to be at steady state), then it is possible to write a material balance around the box as:



Fig. 3.1 A black box with one inflow and one outflow

$$\begin{array}{|c|} \hline \text{Mass per unit} \\ \text{time X} \\ \hline \text{IN} \\ \hline \end{array} = \begin{array}{|c|} \hline \text{Mass per unit} \\ \text{time X} \\ \hline \text{OUT} \\ \hline \end{array} \quad (3.3)$$

$$\text{or, } [X_0] = [X_1] \quad (3.4)$$

Eq. 3.4 is analogous to Eq. 3.1 in the sense that when there is no balance or minimum balance kept just to maintain the status of the account and no interests are earned.

The black box can be used to establish a volume balance and a mass balance if the density does not change in the process. Because the definition of density is mass per unit volume, the conversion from a mass balance to a volume balance is achieved by dividing each term by the density (a constant). It is generally convenient to use the volume balance for liquids and the mass balance for solids.

3.3.2 Splitting Single-Material Flow Streams

A black box shown in Fig. 3.2 receives flow from one feed source and separates this into two or more flow streams. The flow into the box is labeled X_0 and the two flows out of the box are X_1 and X_2 . If again it is assumed that steady state conditions exist and that no material is being destroyed or produced, then the material balance is

$$\begin{array}{|c|} \hline \text{Mass per unit} \\ \text{time X} \\ \hline \text{IN} \\ \hline \end{array} = \begin{array}{|c|} \hline \text{Mass per unit} \\ \text{time X} \\ \hline \text{OUT} \\ \hline \end{array}$$

$$\text{or, } [X_0] = [X_1 + X_2] \quad (3.5)$$



Fig. 3.2 A separator with one inflow and two outflows

The material X can be separated into more than two fractions, so the material balance can be

$$[X_0] = \left[\sum_{i=1}^n X_i \right] \quad (3.6)$$

Where, there are n exit streams, of effluents.

3.3.3 Combining Single-Material Flow Streams

A black box can also receive numerous influents and discharge one effluent, as shown in Fig. 3.3. If the influents are labeled as X_1, X_2, \dots, X_m the material balance would yield.

$$\left[\sum_{i=1}^m X_i \right] = [X_e] \quad (3.7)$$

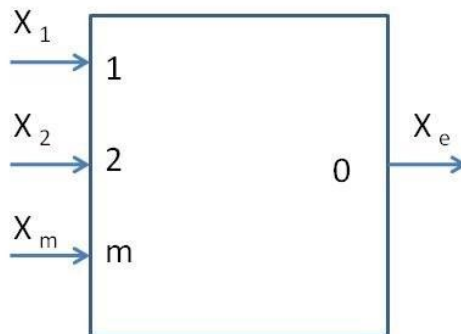


Fig. 3.2 A blender with several inflows and one outflow

Conservative and non-conservative substance

Conservative substances are not physically or chemically transformed to other substances in normal situation. Examples are salt and metals. Non-conservative substances are transformed to other substances through physical, chemical or biological processes in the environment. These include biological oxygen demand (indicator of the quantity of biologically degrading chemicals), ammonia and certain organic compounds.

Conservative substances tend to be stable, long-lived compounds that persist within environment. Non-conservative substances can transform or degrade into other compounds, but

the rate of transformation depends on the physical, chemical and biological conditions occurring in the environment.

3.3.4 Complex process with a single material

The preceding two sections illustrate the basic principle of material balances. The two assumptions used to approach the analysis above are the flows are in steady state (they do not change with time) and that no material is being destroyed (consumed) or created (produced). If these possibilities are included in the full material balance, the equation reads.

$$\begin{array}{ccccccc} \text{Material per unit} & & \text{Material per} & & \text{Material per} & & \text{Material per} \\ \text{time} & & \text{unit time} & & \text{unit time} & & \text{unit time} \\ \text{ACCUMULATED} & = & \text{IN} & - & \text{OUT} & + & \text{PRODUCED} & - & \text{CONSUMED} \end{array}$$

If the material in question is labeled A, the mass balance equation reads,

$$\begin{array}{ccccccc} \text{Mass of A} & & \text{Mass of A} & & \text{Mass of A} & & \text{Mass of A} & & \text{Mass of A} \\ \text{per unit time} & = & \text{per unit} & - & \text{per unit} & + & \text{per unit time} & - & \text{per unit time} \\ \text{ACCUMULATED} & & \text{time} & & \text{time} & & \text{PRODUCED} & & \text{CONSUMED} \\ & & \text{IN} & & \text{OUT} & & & & \end{array}$$

Or, provided the density does not change, in volume terms as

$$\begin{array}{ccccccc} \text{Volume of A} & & \text{Volume of A} & & \text{Volume of A} & & \text{Volume of A} & & \text{Volume of A} \\ \text{per unit time} & = & \text{per unit} & - & \text{per unit} & + & \text{per unit time} & - & \text{per unit time} \\ \text{ACCUMULATED} & & \text{time} & & \text{time} & & \text{PRODUCED} & & \text{CONSUMED} \\ & & \text{IN} & & \text{OUT} & & & & \end{array}$$

Mass or volume per unit time can be simplified to rate, where rate simply means the flow of mass or volume. Thus, the material balance or mass balance equation for either mass or volume reads

$$\begin{array}{ccccccc} \text{Rate of A} & & \text{Rate of A} & & \text{Rate of A} & & \text{Rate of A} & & \text{Rate of A} \\ \text{ACCUMULATED} & = & \text{IN} & - & \text{OUT} & + & \text{PRODUCED} & - & \text{CONSUMED} \end{array}$$

(3.8)

General rules in solving mass balance problems

1. Draw the system diagram, including all flows (inputs and outputs) as arrows.
2. Add the available information such as flow rates and concentrations. Assign symbols to unknown variables.
3. Draw the continuous dashed line around the component or components that are to be balanced. This could be a unit operation, a junction or a combination of these. Everything inside the dashed line becomes the black box.
4. Decide what material is to be balanced. This could be a volumetric or mass flow rate.
5. Write the material balance equation by starting with the basic equation:

$$\begin{array}{ccccccc} \text{Rate of A} & & \text{Rate of A} & & \text{Rate of A} & & \text{Rate of A} & & \text{Rate of A} \\ \text{ACCUMULATED} & = & \text{IN} & - & \text{OUT} & + & \text{PRODUCED} & - & \text{CONSUMED} \end{array}$$

6. If only one variable is unknown, solve for that variable.
7. If more than one variable is unknown, repeat the procedure using a different black box or a different material for the same black box.

3.3.5 Material balance with multiple materials

Mass and volume balances can be developed with multiple materials flowing in a single system. In some cases the process is one of mixing, where several inflow streams are combined to produce a single outflow stream, while in other cases a single inflow stream is split into several outflow streams according to some material characteristics. Because the mass balance and volume balance equations are actually the same equations for a black box, unless there is more than one material involved in the flow.

3.4 Recycle, Bypass and Purge stream

Recycle stream is a term denoting a process stream that returns material from downstream of a process unit back to the process unit. There are several reasons one might employ a recycle stream.

- Increase in conversion of a reactant to product.
- Recovery of catalyst
- Reuse of working fluid.

Bypass stream: A stream that skips one or more stages of the process and goes directly to another downstream stage. This arrangement is used when it is desired to control the composition of the final exit stream (product) at desired value.

Purge stream: A stream bled off from the process to remove an accumulation of inerts or unwanted material that might otherwise build up in the recycle stream. This is common with multi-phase systems where only one phase is either removed or recycled.

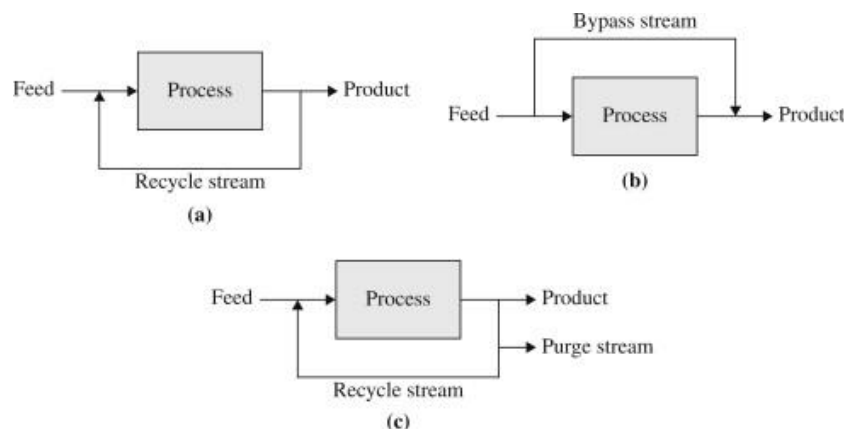


Figure 3.4 Recycle, Bypass and Purge Stream

3.5 Steady state condition

For many environmental problems, time is an important factor in establishing the degree of severity of the problem or in the designing a solution. In these instances, Equation (3.8) is modified to the following form:

$$\text{Rate of accumulation} = \text{Rate of input} - \text{Rate of output} \quad (3.9)$$

Where, rate is used to mean per unit of time. In the calculus this may be written as:

$$\frac{dM}{dt} = \frac{d(In)}{dt} - \frac{d(Out)}{dt} \quad (3.10)$$

In most systems of environmental interest, transformation occurs within the system: byproducts are formed (e.g. sludge, CO may be oxidized to CO₂) or compounds are destroyed (e.g. ozone). Because many environmental reactions do not occur instantaneously, the time dependence of the reaction must be taken into account.

Thus the mass balance equation may be written as follows:

$$\text{Accumulation rate} = \text{Input rate} - \text{Output rate} \pm \text{Transformation rate} \quad (3.11)$$

Time-dependent reactions are called *kinetic reactions*.

The rate of transformation, or reaction rate (r), is used to describe the rate of formation (ex. growth of microorganisms) or disappearance (utilization of substrate) of a substance or chemical species.

In the calculus:

The reaction rate is often some complex function of temperature, pressure, the reacting components, and/or product of reaction.

Frequently, Eq. (2.11) can be simplified. The most common simplification results when *steady state* or *equilibrium* conditions can be assumed. This implies that there is no accumulation in the system.

$$\text{Or, } dM / dt = 0 \quad (3.12)$$

Steady-State with Conservative Systems

A conservative system implies that there would be no transformation inside the system (no growth, no decomposition and no conversion). In this case, if steady state condition is assumed then Eq. 2.11 is reduced to:

$$\text{Input rate} = \text{Output rate} \quad (3.13)$$

Steady-State System with Non-conservative Pollutants

Many environmental pollutants undergo chemical, biological, or nuclear reactions at a rate sufficient to require us to treat them as non-conservative substances. Thus an assumption of steady state condition would reduce Eq. 2.11 to:

$$\text{Input rate} - \text{Output rate} \pm \text{transformation rate} = 0 \quad (3.14)$$

If the transformation rate is simply the decomposition or decay of the substance (various pollutants are decomposed in the environment) then Eq. 2.14 is further reduced to:

$$\text{Input rate} = \text{Output rate} + \text{decay rate} \quad (3.15)$$

The decay of non-conservative substances is frequently modeled as a first-order reaction; that is, it is assumed that the rate of loss of the substance is proportional to the amount of substance that is present at any given time. That is,

$$\frac{dC}{dt} = -kC \quad (3.16)$$

Where, k is the reaction rate coefficient with dimension of (1/ time), the negative sign implies a loss of substance with time, and C is the pollutant concentration (mass per unit volume). The differential equation may be integrated to yield either,

$$\ln \frac{C}{C_o} = -kt \quad (3.17)$$

$$\text{or,} \quad C = C_o e^{-k t} \quad (3.18)$$

Eq. 3.16 indicates the rate of change of concentration of the substance. If we assume the substance is uniformly distributed throughout the volume V . Thus the total mass (M) of the substance is equal to the product of the concentration and volume (V). The total rate of decay of the amount of a nonconservative substance is thus $d(CV) / dt = V dC / dt$ decay rate = kCV

Eq. 3.15 can be re-written as

$$\text{Input rate} = \text{Output rate} + k C V \quad (3.19)$$

Implicit in Eq. 2.15 is the assumption that the concentration C is uniform throughout the volume V . This complete mixing assumption is common in the analysis of chemical tanks, called *reactors*, and in such cases the idealization is referred to as a *continuously stirred tank reactor (CSTR)* model. In other contexts, such as modeling air pollution, the assumption is referred to as a *complete mix box model*.

Idealized models involving non-conservative pollutants in completely mixed, steady-state systems are used to analyze a variety of commonly encountered water pollution problems such as mixing of sewage in receiving waters. The same simple models can be applied to certain problems involving air quality.

References

Bailey, J. E. and Ollis, D. F. (1986) Biochemical Engineering Fundamentals, McGraw-Hill International, New York

Examples:

1. **Mixing:** An Industry discharges wastewater into a river that has a flow rate of $10 \text{ m}^3/\text{s}$. The waste discharge stream has flow rate of $0.1 \text{ m}^3/\text{s}$ and the concentration is 3000 mg/L . The concentration of river before mixing is 20 mg/L . The state regulation allows upto 100 mg/L for the pollutants in river. Will the industry be able to discharge the water to river under state regulation? Assume complete mixing, non-reactive organic material and steady state conditions.
2. **Generation:** Estimate the concentration of SO_2 in the urban air the above Kathmandu University premises at Dhulikhel. The mixing height above Kathmandu Valley and Banepa urban areas is 1 km . The length and width of the box representing the mixing zone (as shown in Fig) is 50 km by 30 km . The average annual wind speed is $10,000 \text{ m/hr}$. There are 200 brick kilns in the area. SO_2 release rate is 0.2 kg/brick produced and the annual brick production rate is 10 million bricks /year. **(Ans: 0.77 kg/km^3)**

First, construct the box above Kathmandu Valley and Banepa area, as shown in Fig below. The volume of the air moving into the box is calculated as the velocity times the area through which the flow occurs, or $Q = Av$, where v = wind velocity and A = area of the side of the box (mixing depth times width).

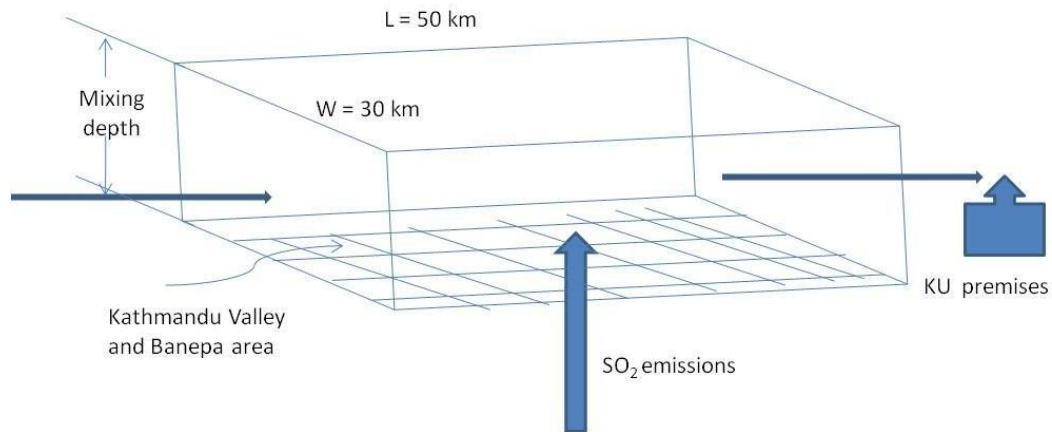


Fig. 3.5 Air quality box model

3. **Non conservative system:** A kitchen with volume 500 m^3 operating for an hour is using 10 wood burning stoves, each using 3 kg of wood. 1 kg of wood emits 1.4 mg of harmful chemical (CO). The CO is converted to CO_2 with reaction rate coefficient of 0.35 /hr . Fresh air enters in the air with the rate of $1500 \text{ m}^3/\text{hr}$ and state air leaves at the same rate. For a completely mixed system, calculate the steady state concentration of harmful chemical in the air using mass balance method. **(Ans : 0.025 mg/m^3)**