Fundamental
of
Environmental Engineering

Chapter 2: Physical Process and Properties

Physical Processes

- Mass Balance
- Energy Balance
- Mass-Transport Process

Mass Balance

"The law of conservation of mass states that mass can neither be produced nor destroyed".

- General Expression:

$$\text{Accumulation} = \text{in} - \text{out} - \text{loss} + \text{generation}$$

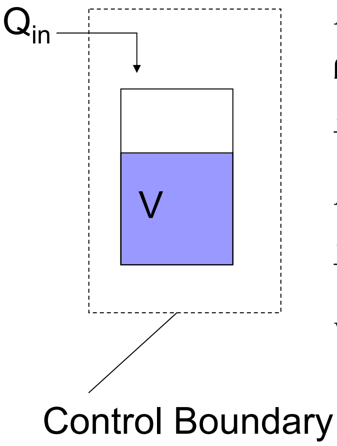
- The Control Boundary: a mass balance is only meaningful in terms of a specific region of space, which has boundaries across which the terms mass-in and mass-out are determined.

Mass Balance (cont.)

Steady State: meaning that a condition of interest no longer changes with time

Non-Steady State: meaning that a condition of interest still changes with time

For example, the mass balance of a water-volume change (ΔV) in a function of time (t) when a water flow rate (Q_{in}) is fed in a tank.



$$\text{Accumulation} = \text{in} - \text{out} - \text{loss} + \text{generation}$$

$$\rho_w \cdot \Delta V = \rho_w \cdot Q_{in} \cdot \Delta t - 0 - 0 - 0$$

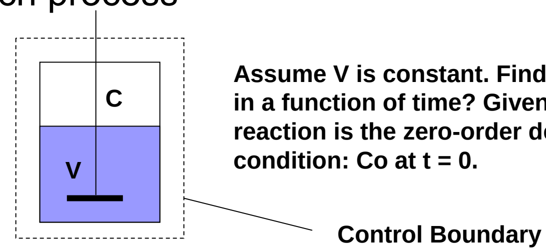
$$\frac{\Delta V}{\Delta t} = Q_{in}$$

As $\Delta t \rightarrow 0$, we can get

$$\frac{dV}{dt} = Q_{in}$$

where ρ_w is the water density

For example, mass balance for a change of concentration with time for a species of interest in a batch process



Assume V is constant. Find the concentration C in a function of time? Given the rate of the reaction is the zero-order decay and the initial condition: Co at t = 0.

Mass Balance:

In – out + generation - loss = Accumulation

0 – 0 + 0 –rV = VdC/dt

0 – 0 + 0 –k = dC/dt

C - Co = -kt

Type of Reactor Units

- Batch Reactors: mostly used to determine the kinetic rate of a reaction.

- Completely Mixed Flow Reactors (CMFRs): used to model well-mixed environmental situations.

- Plug Flow Reactors (PFRs): used to model pipe-liked behavior environmental situations such as downstream transport in a river, in which fluid is not mixed in the upstream-downstream direction.

- Real Reactors: used to model real environmental situations.

See More Details in Unit Operation

Retention Time (θ)

A number of terms, including retention time, detention time, and residence time, are used to refer to the average period spent in a given control volume.

$$\theta = \frac{V}{Q}$$

where V is the volume of the reactor, and

Q is the flow rate

Table 4-3. Typical Retention Times in Unit Processes Used for Treating Drinking Water and Wastewater

Unit Operation	Used for	Approximate Retention Time
Wastewater Treatment		
Grit removal	Removal of large particles (grit)	30 min
Primary settling	Removal of large solids	≤ 1 h
Secondary Settling	Removal of smaller solids	≤ 2 h
Activated sludge	Removal of organic matter using microorganisms and oxygen	4–8 h
Anaerobic digester	Stabilization of organic matter in sludge in absence of oxygen	15–30 days
Drinking-water Treatment		
Rapid-mix tank	Blending of chemical coagulants with water prior to treatment	< 1 min
Flocculator	Gentle mixing to promote flocculation of small particles	30 min
Disinfection	Destruction of pathogens	< 15 min

Overflow Rate (OFR)

The upward velocity of a fluid media.

$$OFR = \frac{Q}{A_{top}}$$

where Q is the fluid - media flow rate and

A_{top} is the surface area of the top of the chamber

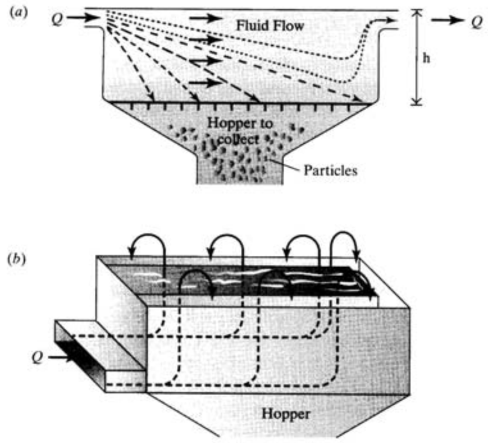


Figure 4-17. Two approaches to determining minimum particle size removed in a nonturbulent chamber. (*a*) The fluid (water or air) travels smoothly from left to right across the settling chamber. Large particles fall rapidly while traveling through the chamber, resulting in a steep trajectory, as indicated by dashed lines; small particles fall slowly, resulting in a shallow trajectory, as indicated by dotted lines. (*b*) The inflow enters near the bottom of the chamber and flows upward, exiting by overflowing out of the open top. Particles that fall faster than the water rises have a net downward velocity and eventually reach the hopper. Particles with settling velocities less than the upward water velocity rise, and are carried out with the effluent flow.

Energy Balance

"The first law of thermodynamics states that energy can neither be produced nor destroyed". The movement of energy and changes in its form can be tracked using energy balances, which are analogous to mass balances. However, all energy balances are treated as conservative; as long as all the possible forms of energy are considered, there is on term in energy balances that is analogous to the chemical-reaction term in mass balances.

General Expression:

$$\begin{pmatrix} \text{Change in internal} \\ \text{plus external energy} \\ \text{per unit time} \end{pmatrix} = (\text{Energy flux in}) - (\text{Energy flux out})$$

or

$$\frac{dE}{dt} = \dot{E}_{in} - \dot{E}_{out}$$

Forms of Energy

- Internal energy: energy that is a part of the molecular structure or organization of a given substance.

- External energy: energy that results from the location or motion of a given substance.

Internal Energy

- Heat internal energy: results from the random motions of atoms.

$$\begin{pmatrix}\text{Change in} \\ \text{internal} \\ \text{energy } (\Delta E)\end{pmatrix} = (\text{mass of } H_2O) \cdot c \cdot \Delta T$$

where c is the heat capacity or specific heat of the water $(4{,}184\ \mathrm{J\ kg^{-1}\ {}^{o}C^{-1}}$

Internal Energy (cont.)

- Chemical internal energy: results from the chemical bonds and interaction within a given substance.
  - The energy of the atomic bonds in the substance.
  - The energy in the interactions between molecules.
    - The latent heat of condensation: the heat released when a unit mass of the substance condenses to form a liquid (an equal amount of energy is required for evaporation).
    - The latent heat of fusion: the heat released when a unit of mass solidifies (an equal amount of energy is required to melt the substance).

External Energy

- Gravitational potential energy
- Kinetic energy

Table 4-5. Some Common Forms of Energy Encountered in Environmental Engineering and Science

	Representation for Energy or Change in Energy
Heat internal energy	$\Delta E = (\text{mass})c\Delta T$
Chemical internal energy	$\Delta E = \Delta H_{rxn}$ at constant volume
Gravitational potential	$\Delta E = (\text{mass})(\Delta\text{height})$
Kinetic	$E = (\text{mass})(\text{velocity})^2/2$
Electromagnetic	$E = (\text{Planck's constant})(\text{photon frequency})$

Mass-Transport Process

- Advection: refers to transport with the mean fluid flow such as wind is blowing toward the east, advection will carry any pollutants present in the atmosphere toward the east.
- Dispersion: refers to the transport of compounds through the action of random motions.
  - Molecular diffusion: the random motion of molecules.
  - Turbulent dispersion or eddy dispersion: the random eddies that arise in turbulent flow.

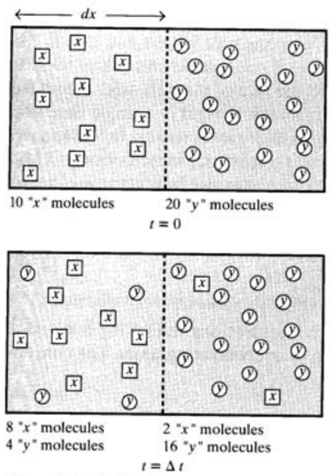


Figure 4-13. Diffusion of gas molecules in a box. A box is divided into two regions of equal size. Ten gas molecules of one type (x) are added to the left side, while 20 gas molecules of another type (y) are added to the right side. Although they are distinguishable, the two types of molecules are identical in every physical respect. At time $t = 0$, the divider separating the two regions is removed. As a result of random motion, each molecule within the box has a 20% probability of moving to the opposite side of the box during each time interval of duration Δt. The result after one time interval is shown in the bottom figure. (From Fischer et al., 1979. Reprinted by permission of Academic Press, Inc.)

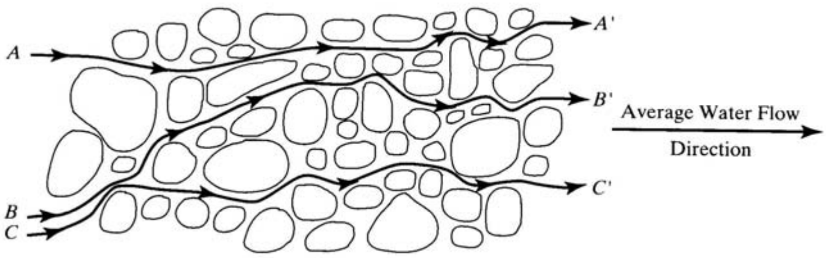


Figure 4-15. The process of mechanical dispersion in groundwater flow. Two fluid parcels starting near each other at locations B and C are dispersed to locations farther apart (B' and C') during transport through the soil pores, while parcels from A and B are brought closer together, resulting in mixing of water from the two regions. (From Hemond, H. F., and E. J. Fechner, 1994. Reprinted by permission of Academic Press, Inc.)

Chemical properties needed to perform environmental hazard screenings

Environmental Process	Relevant Properties
Estimates of releases and environmental dispersion	Volatility, density, melting point, water solubility
Persistence in the environment	Atmospheric oxidation rate, aqueous hydrolysis rate, photolysis rate, rate of microbial degradation
Uptake by organisms	Volatility, lipophilicity, molecular size, degradation rate in organism
Human uptake	Transport across dermal layers, transport rates across lung membrane, degradation rates within the human body

Basic physical and chemical properties that describe a chemical's partitioning between solid, liquid, and gas phases.

Melting point

Boiling point

Vapor pressure

Water solubility

Additional molecular properties, related to phase partitioning, that are frequently used in assessing the environmental fate of chemicals include:

Octanol-water partition coefficient

Soil sorption coefficients

Henry's law constants

Bioconcentration factors

Properties

Melting point (T_m)

Definition

Temperature at which solid and liquid coexist at equilibrium

Significance in estimating environmental fate and risks

Sometimes used as a correlating parameter in estimating other properties for compounds that are solids at ambient or near-ambient conditions

Properties

Boiling point (T_b)

Definition

Temperature at which the vapor pressure of a compound equals atmospheric pressure; normal boiling points is the temperature at which pressure equals one atmosphere.

Significance in estimating environmental fate and risks

Characterizes the partitioning between gas and liquid phase

Properties

Vapor pressure (P_{vp})

Definition

Partial pressure exerted by a vapor when the vapor is in equilibrium with its liquid

Significance in estimating environmental fate and risks

Characterizes the partitioning between gas and liquid phases

Properties

Henry's law coefficient (H)

Definition

Equilibrium ratio of the concentration of a compound in gas phase to the concentration of the compound in a dilute aqueous solution

Significance in estimating environmental fate and risks

Characterizes the partitioning between gas and aqueous phases

Properties

Octanol-water partition coefficient (K_{ow})

Definition

Equilibrium ratio of the concentration of a compound in water to the concentration of the compound in octanol.

Significance in estimating environmental fate and risks

Characterizes the partitioning between hydrophilic and hydrophobic phases in the environment and the human body.

Properties

Water solubility (S)

Definition

Equilibrium solubility in mol/L

Significance in estimating environmental fate and risks

Characterizes the partitioning between hydrophobic and hydrophilic phases in the environment.

Properties

Soil-sorption coefficient (K_{oc})

Definition

Equilibrium ratio of the mass of a compound adsorbed per unit weight of organic carbon in a soil (in ug/g organic carbon) to the concentration of the compound in a liquid phase (in ug/ml).

Significance in estimating environmental fate and risks

Characterizes the partitioning between solid and liquid phases in soil which in turn determines mobility in soils.

Properties

Bioconcentration factor (BCF)

Definition

Ratio of a chemical's concentration in the tissue of an aquatic organism to its concentration in water.

Significance in estimating environmental fate and risks

Characterizes the magnification of concentrations through the food chain.

Normal boiling point (T_b)

$$T_b(K) = 198.2 + \sum n_i g_i \qquad (1)$$

T_b = normal boiling point (K)

n_i = number of groups of type i in the molecule

g_i = the contribution of each group to the boiling point

The boiling point predicted by equation 1 is corrected using one of the following equations:

For $T_b \leq 700$ K

$$T_{b(corrected)} = T_b - 94.84 + 0.5577T_b - 0.0007705(T_b)^2$$

For $T_b > 700$ K

$$T_{b(corrected)} = T_b - 282.7 + 0.5209T_b$$

Melting point (T_m)

$$T_m\,(K) = 0.5839T_b(K)$$

Vapor pressure

High vapor pressure materials will generally have higher atmospheric concentrations than lower vapor pressure materials and therefore have the potential to be transported over long distances as gases or inhaled as gases.

Antoine equation:

$$LnP_{vp} = A+B/(T-C)$$

P_{vp} = vapor pressure

A and C = empirical constants

B = parameter that is related to the heat of vaporization

T = absolute temperature

For gas and liquid

$$LnP_{vp} = \frac{\left[A(T_b - C)^2\right]}{\left[0.97RT_b\right]} \times \left[\frac{1}{T_b - C} - \frac{1}{T - C}\right]$$

$C = -18 + 0.19T_b$

$A = K_F(8.75+RLnT_b)$

For solid

$LnP = -(4.4+LnT_b)[1.803(T_b/T-1)-0.803Ln(T_b/T)]-6.8(T_m/(T-1)$

P = the vapor pressure in atmosphere

T_b = normal boiling point (K)

T = the temperature at which the vapor pressure is to be evaluated (K)

T_m = the melting point (K)