6.1 The Concept of a Material Balance

A **material balance** is nothing more than the application of the law of the **conservation of mass**:

"Matter is neither created nor destroyed"

6.2 Open and Closed Systems

a. System

By **system** we mean any arbitrary portion of or a whole **process** that you want to consider for analysis. You can define a **system** such as a **reactor**, a **section of a pipe**. Or, you can define the **limits** of the **system** by drawing the **system boundary**, namely a line that encloses the portion of the process that you want to analyze.

b. Closed System

Figure 6.1 shows a two-dimensional view of a three-dimensional vessel holding **1000 kg of H_2O**. **Note that material neither enters nor leaves the vessel**, that is, **no material crosses the system boundary**. Changes can take place **inside the system**, but for a **closed system**, **no mass exchange occurs with the surroundings**.

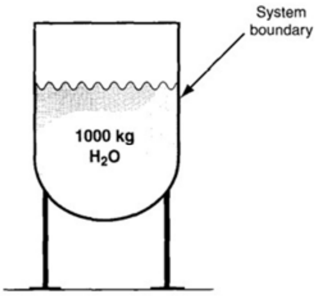


Figure 6.1 A closed system.

c. Open System

Figure 6.2 is an example of an **open system** (also called a **flow system**) because material crosses the system boundary.

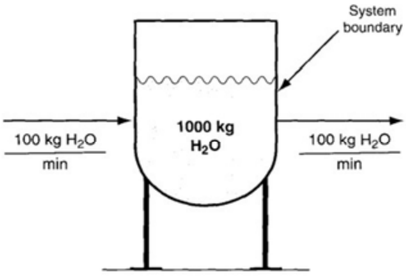


Figure 6.2 An open steady–state system.

6.3 Steady-State and Unsteady-State Systems

a. Steady–State System

Because the rate of addition of water is equal to the rate of removal, the amount of water in the vessel shown in **Figure 6.2** remains constant at its original value (**1000 kg**). We call such a **process** or **system** a **steady–state process** or a **steady–state system** because

1. The **conditions** inside the process (specifically the amount of water in the vessel in Figure 6.2) **remain unchanged with time**, and
2. The **conditions** of the flowing streams **remain constant with time**.

- ✶ Thus, in a **steady-state process**, by definition all of the conditions in the process **(e.g., temperature, pressure, mass of material, flow rate, etc.)** remain constant with time. A **continuous process** is one in which material enters and/or leaves the system without interruption.

b. Unsteady–State System

Because the amount of water in the system **changes with time (Figure 6.3)**, the **process** and **system** are deemed to be an **unsteady–state** (**transient**) **process or system**.

- ✶ For an **unsteady-state process**, not all of the **conditions** in the **process (e.g., temperature, pressure, mass of material, etc.)** remain constant with time, and/or the **flows** in and out of the **system** can **vary with time**.

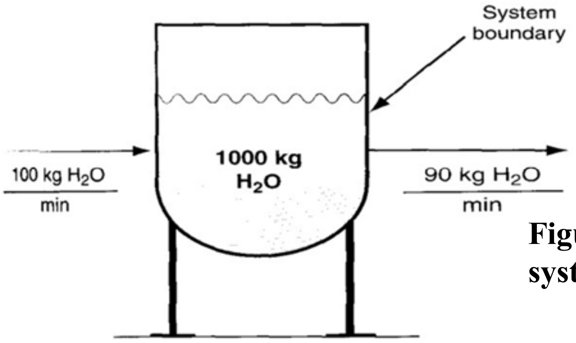


Figure 6.3 Initial conditions for an open unsteady–state system with accumulation.

- Figure 6.4 shows the system after 50 minutes of accumulation (Fifty minutes of accumulation at 10 kg/min amounts to 500 kg of total accumulation).

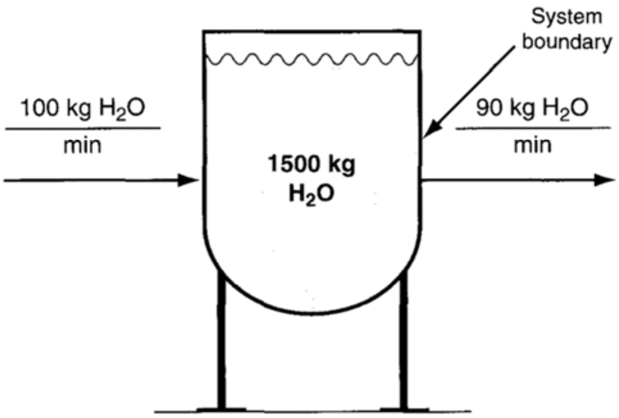


Figure 6.4 The condition of the open unsteady–state system with accumulation after 50 minutes.

- **Figures 6.5** and **6.6** demonstrate **<u>negative accumulation</u>**.

  Note that the amount of water in the system decreases with time at the rate of **10 kg/min**. Figure 6.6 shows the system after **50 minutes** of operation.

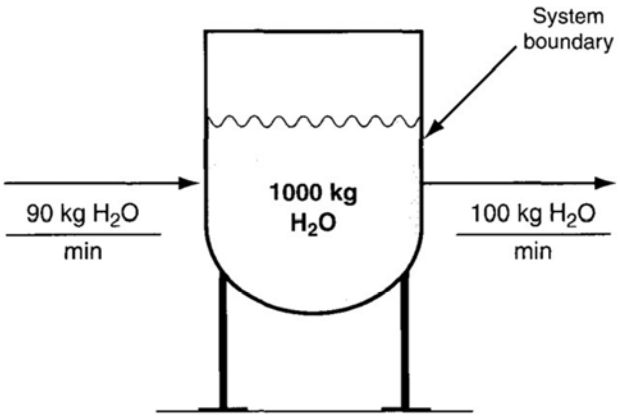


Figure 6.5 Initial conditions for an unsteady–state process with negative accumulation.

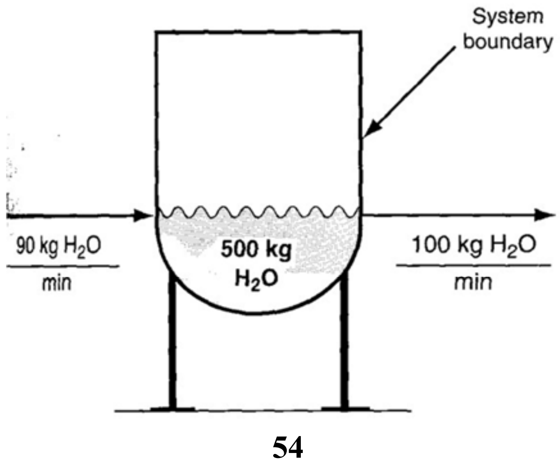


Figure 6.6 Condition of the open unsteady–state system with negative accumulation after 50 minutes.

- **The material balance for a single component process is**

$$\begin{Bmatrix}\text{Accumulation of material}\\ \text{within the system}\end{Bmatrix} = \begin{Bmatrix}\text{Total flow into}\\ \text{the system}\end{Bmatrix} - \begin{Bmatrix}\text{Total flow out}\\ \text{of the system}\end{Bmatrix} \quad \ldots 6.1$$

Equation 6.1 can apply to **moles** or any **quantity** that is **conserved**. As an example, look at **Figure 6.7** in which we have converted all of the mass quantities in **Figure 6.2** to their equivalent values in moles.

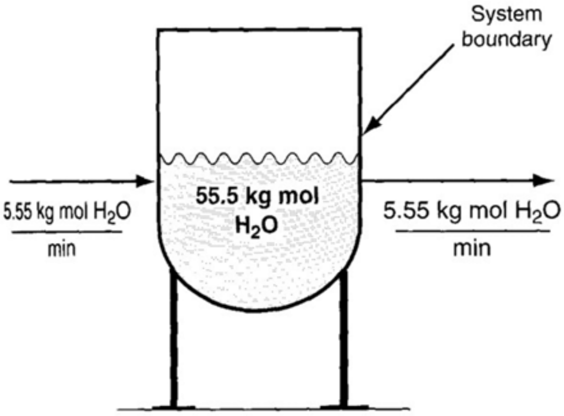


Figure 6.7 The system in Figure 6.2 with the flow rates shown in kg mol.

If the process is in the **steady state**, the **accumulation** term by definition is **zero**, and **Equation 6.1** simplifies to a famous truism

What goes in must come out (In = Out) …6.2

If you are analyzing an unsteady-state process, the accumulation term over a time interval can be calculated as

$$\{\text{Accumulation}\} = \begin{Bmatrix}\text{Final material}\\ \text{in the system}\end{Bmatrix} - \begin{Bmatrix}\text{Initial material}\\ \text{in the system}\end{Bmatrix} \quad (6.3)$$

The **times** you select for the final and initial conditions can be anything, but you usually select an **interval** such as **1 minute** or **1 hour** rather than specific times.

- When you combine **Equations 6.1 and 6.3** you get the **general material balance** for a component in the system in the **absence of reaction**

$$\begin{Bmatrix}\text{Final material}\\ \text{in the system}\\ \text{at } t_2\end{Bmatrix} - \begin{Bmatrix}\text{Initial material}\\ \text{in the system}\\ \text{at } t_1\end{Bmatrix} = \begin{Bmatrix}\text{Flow into}\\ \text{the system}\\ \text{from } t_1 \text{ to } t_2\end{Bmatrix} - \begin{Bmatrix}\text{Flow out of}\\ \text{the system}\\ \text{from } t_1 \text{ to } t_2\end{Bmatrix} \quad \ldots 6.4$$

Example 6.1

Will you save money if instead of buying premium 89 octane gasoline at \$1.269 per gallon that has the octane you want, you blend sufficient 93 octane supreme gasoline at \$l.349 per gallon with 87 octane regular gasoline at \$1.149 per gallon?

Solution

Choose a **basis** of **1 gallon of 89 octane gasoline**, the desired product. The system is the gasoline tank.

- For simplicity, assume that **no gasoline exists** in the tank at the start of the blending, and **one gallon exists** in the tank at the end of the blending.
- This arrangement corresponds to an **unsteady-state process**. Clearly it is an **open system**.

The **initial number of gallons** in the system is **zero** and the **final number of gallons** is **one**.

Let **x** = the number of gallons of **87** octane gasoline added, and
y = the number of gallons of **93** octane added to
the blend. Since **x + y = 1** is the total flow into the
tank,
∴ y = 1 – x
According to Equation (6.4) the balance on the octane number is

$$\overset{\textit{Accumulation}}{\left|\frac{89\text{ octane}}{1\text{ gal}}\right|\frac{1\text{ gal}}{} - 0} = \overset{\textit{Inputs}}{\left|\frac{87\text{ octane}}{1\text{ gal}}\right|\frac{x\text{ gal}}{} + \left|\frac{93\text{ octane}}{1\text{ gal}}\right|\frac{(1-x)\text{ gal}}{}}$$

The solution is x = 2/3 gal and thus y = 1 – x = 1/3 gal.
The cost of the blended gasoline is (2/3) (\$l.l49) + (1/3) (\$l.349) = \$
1.216 A value less than the cost of the 89 octane gasoline (\$l.269).

6.4 Multiple Component Systems

Suppose the input to a vessel contains **more than one component**, such as 100 kg/min of a 50% water and 50% sugar (sucrose, $C_{12}H_{22}O_{11}$, MW = 342.3) mixture (see Figure 6.8). The mass balances with respect to the **sugar and water**, balances that we call **component balances**.

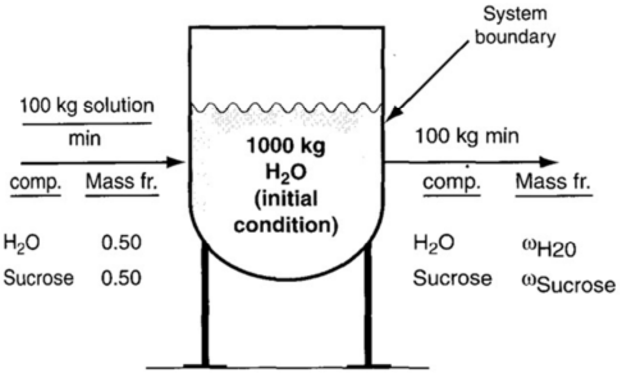


Figure 6.8 An open system involving two components.

For Example, look at the mixer shown in Figure 6.9, an apparatus that mixes two streams to increase the concentration of NaOH in a dilute solution. **The mixer is a steady–state open system**. Initially the mixer is empty, and after 1 hour it is empty again.

Basis = 1 hour for convenience. As an alternate to the **basis** we selected, you could select **F_1 = 9000 kg/hr as the basis, or F_2 = 1000 kg/hr as the basis;** the **numbers** for this example would not change – just the **units** would change. Here are the components and total balances in **kg**:

	Flow in			
Balances	F_1	F_2	Flow out	Accum.
NaOH	450	500	950	= 0
H_2O	8,550	500	9,050	= 0
Total	9,000	1,000	10,000	= 0

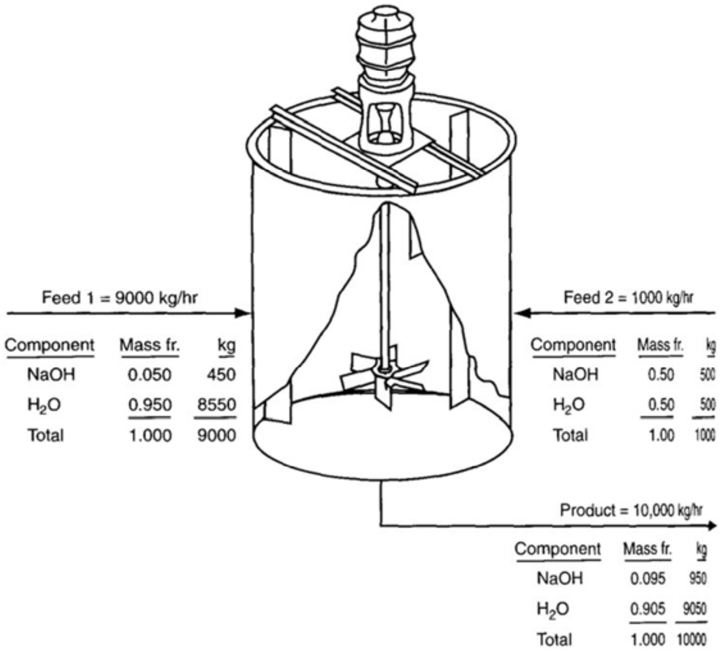
We can convert the kg shown in Figure 6.9 to kg moles by dividing each compound by its respective molecular weight (NaOH = 40 and H_2O = 18).

$$\text{NaOH:}\quad \frac{450}{40} = 11.25 \qquad \frac{500}{40} = 12.50 \qquad \frac{950}{40} = 23.75$$

$$H_2O:\quad \frac{8550}{18} = 475 \qquad \frac{500}{18} = 27.78 \qquad \frac{9050}{18} = 502.78$$

Then the component and total balances in **kg mol** are:

	Flow in			
Balances	F_1	F_2	Flow out	Accum.
NaOH	11.25	12.50	23.75	= 0
H_2O	475	27.78	502.78	= 0
Total	486.25	40.28	536.53	= 0



Component	Mass fr.	kg
NaOH	0.050	450
H_2O	0.950	8550
Total	1.000	9000

Component	Mass fr.	kg
NaOH	0.50	500
H_2O	0.50	500
Total	1.00	1000

Component	Mass fr.	kg
NaOH	0.095	950
H_2O	0.905	9050
Total	1.000	10000

Figure 6.9 Mixing of a dilute stream of NaOH with a concentrated stream of NaOH. Values below the stream arrows are based on 1 hour of operation.

Example 6.2

Centrifuges are used to separate particles in the range of 0.1 to 100 µm in diameter from a liquid using centrifugal force. Yeast cells are recovered from a broth (a liquid mixture containing cells) using a tubular centrifuge (a cylindrical system rotating about a cylindrical axis). Determine the amount of the cell-free discharge per hour if 1000 L/hr is fed to the centrifuge, the feed contains 500 mg cells/L, and the product stream contains 50 wt.% cells. Assume that the feed has a density of 1 g/cm^3.

Solution

This problem involves a **steady state**, **open (flow)** system **without reaction**.

Basis = 1 hour

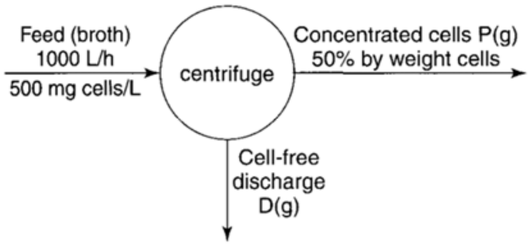


Figure E6.2

M.B. on cells

In (mass) = Out (mass)

$$\frac{1000\text{ L feed}}{}\Bigg|\frac{500\text{ mg cells}}{1\text{ L feed}}\Bigg|\frac{1\text{ g}}{1000\text{ mg}}=\frac{0.5\text{ g cells}}{1\text{ g }P}\Bigg|\frac{P\text{ g}}{}$$

P = 1000 g

M.B. on fluid

In (mass) = Out (mass)

$$\frac{1000\text{ L}}{}\Bigg|\frac{1000\text{ cm}^3}{1\text{ L}}\Bigg|\frac{1\text{ g fluid}}{1\text{ cm}^3}=\frac{1000\text{ g }P}{}\Bigg|\frac{0.50\text{ g fluid}}{1\text{ g }P}+D\text{ g fluid}$$

$D = (10^6 - 500)$ g

6.5 Accounting for Chemical Reactions in Material Balances

Chemical reaction in a system requires the augmentation of **Equation 6.4** to take into account the **effects of the reaction**. To illustrate this point, look at **Figure 6.10**, which shows a steady–state system in which **HCl** reacts with **NaOH** by the following reaction:

$$\mathbf{NaOH + HCl \longrightarrow NaCl + H_2O}$$

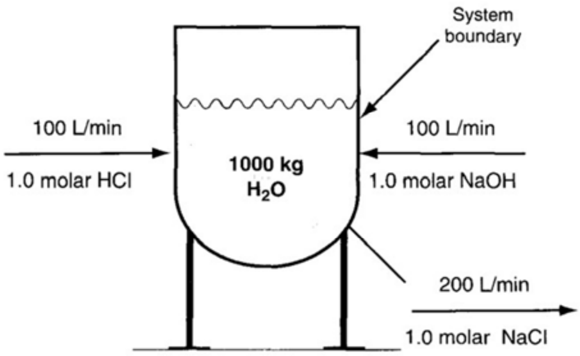


Figure 6.10 Reactor for neutralizing HCl with NaOH.

Equation 6.4 must be augmented to include terms for the **generation** and **consumption** of components by the **chemical reaction** in the system as follows

$$\left\{\begin{array}{c}\text{Accumulation}\\ \text{within the}\\ \text{system}\end{array}\right\}=\left\{\begin{array}{c}\text{Input}\\ \text{through}\\ \text{the system}\\ \text{boundaries}\end{array}\right\}-\left\{\begin{array}{c}\text{Output}\\ \text{through}\\ \text{the system}\\ \text{boundaries}\end{array}\right\}+\left\{\begin{array}{c}\text{Generation}\\ \text{within the}\\ \text{system}\end{array}\right\}-\left\{\begin{array}{c}\text{Consumption}\\ \text{within the}\\ \text{system}\end{array}\right\} \quad ...6.5$$

6.6 Material Balances for Batch and Semi-Batch Processes

- A **batch process** is used to process a **fixed amount** of material each time it is operated. **Initially**, the material to be processed is charged into the system. After processing of the material is complete, the products are **removed**.
- **Batch processes** are used **industrially** for specialty processing applications (e.g., producing **pharmaceutical** products), which typically operate at relatively **low production rates**.
- Look at Figure 6.11a that illustrates what occurs at the start of a batch process, and after thorough mixing, the final solution remains in the system (Figure 6.11b).

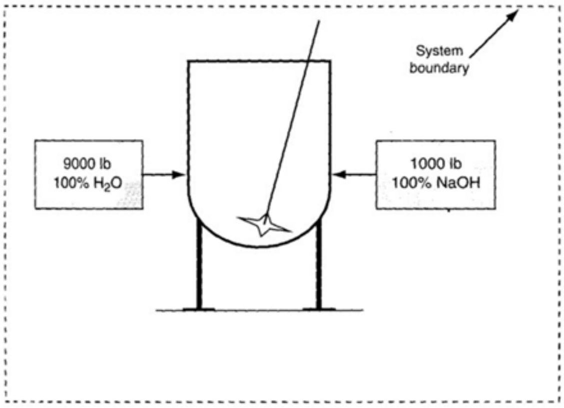


Figure 6.11a The initial state of a batch mixing process.

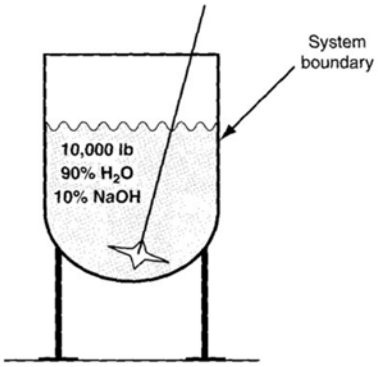


Figure 6.11b The final state of a batch mixing process.

- We can summarize the **hypothetical operation** of the **batch** as a flow system (open system) as follows (**Figure 6.12**):

Final conditions: All values = 0 **Flows out:**

NaOH = 1,000 lb

H_2O = 9,000 lb

Total = 10,000 lb

Initial conditions: All value = 0 **Flows in:**

NaOH = 1,000 lb

H_2O = 9,000 lb

Total 10,000 lb

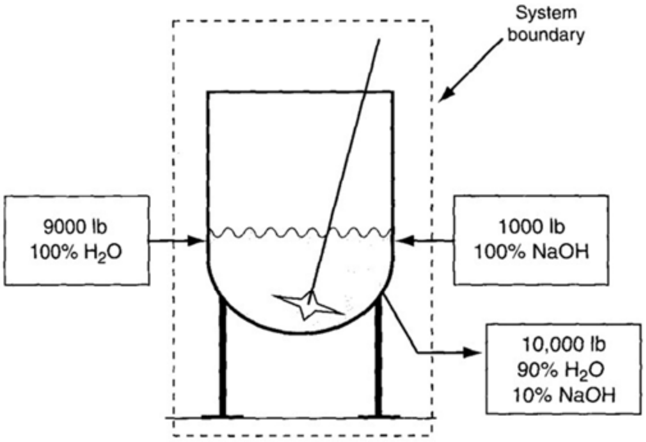


Figure 6.12 The batch process in Figure 6.11 represented as an open system.

☒ In a **semi-batch process** material **enters** the process during its operation, but does **not leave**. Instead, mass is allowed to accumulate in the process vessel. Product is **withdrawn** only after the process is over.

☒ **A Figure 6.13 illustrates** a **semi-batch mixing process**. Initially the vessel is empty (**Figure 6.13a**). **Figure 6.13b** shows the **semi-batch system** after **1 hour** of operation. **Semi-batch processes** are **open** and **unsteady – state**.

☒ Only flows **enter** the systems, and **none leave**, hence the system is an **unsteady state** – one that you can treat as having **continuous flows**, as follows:

Final conditions: **Flows out:** All values = 0

NaOH = 1,000 lb

$\underline{H_2O = 9{,}000\ lb}$
Total = 10,000 lb

Flows in:

NaOH = 1,000 lb
$\underline{H_2O = 9{,}000\ lb}$
Total = 10,000 lb

Initial conditions: All values = 0

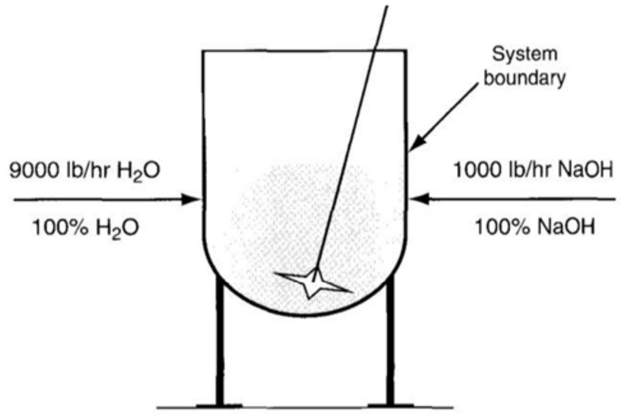


Figure 6.13a Initial condition for the semi-batch mixing process. Vessel is empty.

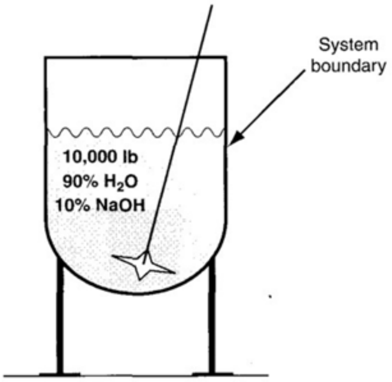


Figure 6.13b Condition of a semi-batch mixing process after 1 hour of operation.

Example 6.3

A measurement for water flushing of a steel tank originally containing motor oil showed that 0.15 percent by weight of the original contents remained on the interior tank surface. What is the fractional loss of oil before flushing with water, and the pounds of discharge of motor oil into the environment during of a 10,000 gal tank truck that carried motor oil? (The density of motor oil is about 0.80 g/cm^3).

Solution

Basis: 10,000 gal motor oil at an assumed 77°F

The initial mass of the motor oil in the tank was

(10000 gal)(3.785 lit/1 gal)(1000 cm^3/1 lit)(0.8 g/cm^3)(1 lb/454 g) = 66700 lb

The mass fractional loss is **0.0015**. The oil material balance is

Initial		unloaded		residual discharged on cleaning
66,700	=	66,700 (0.9985)	+	66,700 (0.0015)

Thus, the discharge on flushing is **66,700 (0.00 15) = 100 lb**.

Questions

1. Is it true that if no material crosses the boundary of a system, the system is a closed system?

2. Is mass conserved within an open process?
3. Can an accumulation be negative? What does a negative accumulation mean?
4. Under what circumstances can the accumulation term in the material balance be zero for a process?
5. Distinguish between a steady-state and an unsteady-state process.
6. What is a transient process? Is it different than an unsteady-state process?

7. Does Equation 6.4 apply to a system involving more than one component?
8. When a chemical plant or refinery uses various feeds and produces various products, does Equation 6.4 apply to each component in the plant?
9. What terms of the general material balance, Equation (6.5), can be deleted if
   a. The process is known to be a steady-state process.
   b. The process is carried out inside a closed vessel.
   c. The process does not involve a chemical reaction.
10. What is the difference between a batch process and a closed process?
11. What is the difference between a semi-batch process and a closed process?
12. What is the difference between a semi-batch process and an open process?

Answers:

1. Yes
2. Not necessarily – accumulation can occur
3. Yes; depletion
4. No reaction (a) closed system, or (b) flow of a component in and out are equal.
5. In an unsteady-state system, the state of the system changes with time, whereas with a steady-state system, it does not.
6. A transient process is an unsteady-state process.
7. Yes
8. Yes
9. (a) Accumulation; (b) flow in and out; (c) generation and consumption
10. None
11. A flow in occurs
12. None, except in a flow process, usually flows occur both in and out

Problems

1. Here is a report from a catalytic polymerization unit:

Charge:	**Pounds per hour**
Propanes and butanes	15,500
Production:	

Propane and lighter	5,680
Butane	2,080
Polymer	missing

What is the production in pounds per hour of the polymer?

2. A plant discharges 4,000 gal/min of treated wastewater that contains 0.25 mg/L of PCB, (polychloronated biphenyls) into a river that contains no measurable PCBs upstream of the discharge. If the river flow rate is 1,500 cubic feet per second, after the discharged water has thoroughly mixed with the river water, what is the concentration of PCBs in the river in mg/L?

Answers:

1. 7740 lb/hr
2. $1.49 * 10^{-3}$ mg/L

Supplementary Problems (Chapter Six):

Problem 1

b. The input is 1.5 kg in one hour.

c. The output is 1.2 kg in one hour.

d. Assume the process is unsteady state. Then the accumulation in the soil is 0.3 kg in one hour.

e. Assume unsteady state. If not, the accumulation would be zero and perhaps some leak from the closed system occurred (as would likely occur in the field).

Problem 2

Problem 6.2

If 1 L. of ethy alcohol is mixed with 1 L. of water, how many kilograms of solution result? How many liters?

Solution

The densities of alcohol and water at 20°C are 0.789 and 0.998 g/cm³, respectively.

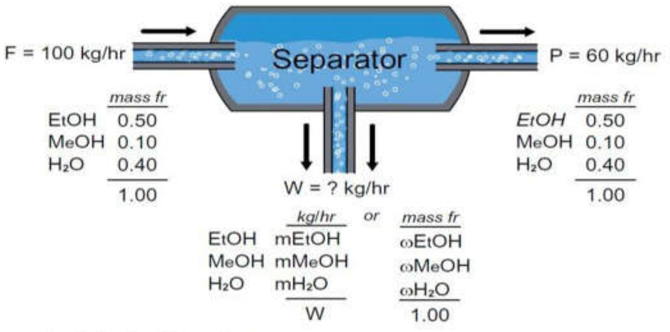
Basis: 1 L. of each compound

$$\frac{1000\ \text{cm}^3}{}\Big|\frac{0.789\ \text{g}}{\text{cm}^3} = 89\ \text{g} \qquad \frac{1000\ \text{cm}^3}{}\Big|\frac{0.998\ \text{g}}{\text{cm}^3} = 998\ \text{g}$$

The total kg are 789 + 998 = 1787 g.

The volumes are not additive. For a 789/1789 = 0.442 mass fraction solution of alcohol in water, the density at 20°C is 0.929 g/cm³.

$$\frac{1787\ \text{g}}{}\Big|\frac{\text{cm}^3}{0.929\ \text{g}} = 1923\ \text{cm}^3$$



An obvious basis is one hour.

Problem 3

The variables whose values are unknown are either (a) m_{EtOH}, m_{MeOH}, and m_{H_2O} plus W, or (b) ω_{EtOH}, ω_{MeOH}, and ω_{H_2O} plus W. Either set of four is acceptable as they are equivalent. We have four unknowns, and need four independent equations.

$$\begin{array}{lccccccccccc}
\text{Total:} & F & = & P & + & W & & F & = & P & + & W \\
\text{EtOH:} & 0.50F & = & 0.80P & + & m_{EtOH} & & 0.50F & = & 0.80P & + & \omega_{EtOH}W \\
\text{MeOH:} & 0.10F & = & 0.15P & + & m_{MeOH} & \text{or} & 0.10F & = & 0.15P & + & \omega_{MeOH}W \\
H_2O\text{:} & 0.40F & = & 0.05P & + & m_{H_2O} & & 0.40F & = & 0.05P & + & \omega_{H_2O}W
\end{array}$$

In addition you know one more independent equation holds for the components in W

$$m_{EtOH} + m_{MeOH} + m_{H2O} = W \qquad \text{or} \qquad \omega_{EtOH} + \omega_{MeOH} + \omega_{H2O} = 1$$

The solution of the equations is (using the total and first two component balances)

	m_i (kg/hr)	*ω_i (mass fr)*
EtOH	2	0.050
MeOH	1	0.025
H_2O	37	0.925
	40	1.00

As a check, we will use the third component balance, the one for H_2O, a redundant equation

$$\begin{array}{rcl}
0.40(100) & \overset{?}{=} & 0.05(60) + 37 \\
40 & = & 3 + 37
\end{array}
\qquad \text{or} \qquad
\begin{array}{rcl}
0.40(100) & = & 0.05(60) + 0.925(40) \\
40 & = & 3 + 37
\end{array}$$