Chapter 4

Fundamentals of Material Balances

Material Balance-Part 1
Process Classification

3 type of chemical processes:

1. Batch process
   - Feed is charge to the process and product is removed when the process is completed
   - No mass is fed or removed from the process during the operation
   - Used for small scale production
   - Operate in unsteady state
Process Classification

2. Continuous process
   - Input and output is continuously fed and removed from the process
   - Operate in steady state
   - Used for large scale production

3. Semibatch process
   - Neither batch nor continuous
   - During the process a part of reactant can be fed or a part of product can be removed.
2 type of process operations:

1. Steady state
   - All the variables (i.e. temperatures, pressure, volume, flow rate, etc) do not change with time

2. Unsteady state or transient
   - Process variable change with time
Define type and operation of processes given:

- A balloon is filled with air at steady rate of 2 g/min
  **Semibatch and unsteady state**

- A bottle of milk is taken from the refrigerator and left on the kitchen
  **Batch and unsteady state**

- Water is boiled in open flask
  **Semibatch and unsteady state**
General Balance Equation:

\[ \text{INPUT} + \text{GENERATION} - \text{OUTPUT} - \text{CONSUMPTION} = \text{ACCUMULATION} \]

Balances on Continuous Steady-State Process

- Steady state:
  \[ \text{accumulation} = 0 \]
  \[ \text{INPUT} + \text{GENERATION} = \text{OUTPUT} + \text{CONSUMPTION} \]

- If balance on steady-state non-reactive processes;
  \[ \text{generation} = 0, \text{consumption} = 0 \]
  \[ \text{INPUT} = \text{OUTPUT} \]
Steps for Material Balance Calculations:

1. Learn how to organize information about process variables
   - Flow Chart drawing and Labeling
2. Choose a Basis
3. Set up material balance equations
4. solve the equations for unknown variables.
Flowcharts

• When you are given process information and asked to determine something about the process, it is essential to organize the information in a way that is convenient for subsequent calculations.

• The best way to do this is to draw a flowchart
  – using boxes or other symbols to represent process units (reactors, mixers, separation units, etc.)
  – lines with arrows to represent inputs and outputs.
Flowcharts......

- The flowchart of a process can help get material balance calculations started and keep them moving.
- Flowchart must be fully labeled when it is first drawn, with values of known process variables and symbols for unknown variables being written for each input and output stream.
- Flowchart will functions as a scoreboard for the problem solution: as each unknown variable is determined its value is filled in, so that the flowchart provides a continuous record of where the solution stands and what must still be done.
Step 1.2: Labeling a flowchart

2 suggestions for labeling flowchart:

1. Write the values and units of all known stream variables at the locations of the streams on the flowchart.

   For example, a stream containing 21 mole% O₂ and 79% N₂ at 320°C and 1.4 atm flowing at a rate of 400 mol/h might be labeled as:

   400 mol/h
   
   \[
   \begin{align*}
   &0.21 \text{ mol } O₂/\text{mol} \\
   &0.79 \text{ mol } N₂/\text{mol} \\
   &T = 320°C, \ P = 1.4 \text{ atm}
   \end{align*}
   \]
Labeling a flowchart-continue

Process stream can be given in two ways:

a) As the **total amount** or flow rate of the stream and **the fractions** of each component

b) Or **directly as the amount or flow rate** of each component.

\[
\begin{align*}
\text{3.0 lbm CH}_4 \\
\text{4.0 lbm C}_2\text{H}_4 \\
\text{3.0 lbm C}_2\text{H}_6
\end{align*}
\]

\[
\begin{align*}
\text{60 kmol N}_2/\text{min} \\
\text{40 kmol O}_2/\text{min}
\end{align*}
\]

\[
\begin{align*}
\text{10 lbm} \\
0.3 \text{ lbm CH}_4/\text{lbm} \\
0.4 \text{ lbm C}_2\text{H}_4/\text{lbm} \\
0.3 \text{ lbm C}_2\text{H}_6/\text{lbm}
\end{align*}
\]

\[
\begin{align*}
\text{100 kmol/min} \\
0.6 \text{ kmol N}_2/\text{kmol} \\
0.4 \text{ kmol O}_2/\text{kmol}
\end{align*}
\]
2. Assign algebraic symbols to unknown stream variables

[such as \( m \) (kg solution/min), \( x \) (lbm N\(_2\)/lbm), and \( n \) (kmol C\(_3\)H\(_8\))], and write these variable names and their units on the flowchart.

\[ \dot{n} \text{ mol/h} \quad 400 \text{ mol/h} \]

\[ 0.21 \text{ mol O}_2/\text{mol} \quad y \text{ mol O}_2/\text{mol} \]
\[ 0.79 \text{ mol N}_2/\text{mol} \quad (1-y) \text{ mol N}_2/\text{mol} \]
\[ T = 320^\circ\text{C}, P = 1.4 \text{ atm} \quad T = 320^\circ\text{C}, P = 1.4 \text{ atm} \]
Labeling a flowchart-continue

• If the mass of stream 1 is half that of stream 2, label the masses of these streams as \( m \) and \( 2m \) rather than \( m_1 \) and \( m_2 \).

• If you know that mass fraction of nitrogen is 3 times than oxygen, label mass fractions as \( y \ g \ O_2/g \) and \( 3y \ g \ N_2/g \) rather than \( y_1 \) and \( y_2 \).

• When labeling component mass fraction or mole fraction, the last one must be 1 minus the sum of the others.

• If volumetric flow rate of a stream is given, it is generally useful to label the mass or molar flow rate of this stream or to calculate it directly, since balance are not written on volumetric qualities.
Consistent on Notation

\( m = \text{mass} \)
\( \dot{m} = \text{mass flow rate} \)
\( n = \text{moles} \)
\( \dot{n} = \text{molar flow rate} \)
\( V = \text{volume} \)
\( \dot{V} = \text{volume flow rate} \)
\( x = \text{component fraction (mass or moles) in liquid} \)
\( y = \text{moles fraction in gas} \)
Try This..

Example 4.2.3

Two methanol-water mixture are contained in separate flasks. The first mixture contains 40wt% methanol and the second flask contains 70wt% methanol. If 20 Kg of the first mixture are going to be mixed with 15000 g of the second in a mixing unit, what are the mass and composition of the product of the mixing unit?
Try This..

Example 4.3.1
An experiment on the growth rate of certain organism requires an environment of humid air enriched in oxygen. Three input streams are fed into an evaporation chamber to produce an output stream with the desired composition.

A: Liquid water fed at rate of 20 cm$^3$/min

B: Air (21% $O_2$ and 79% $N_2$)

C: Pure $O_2$ with a molar flow rate one-fifth of the molar flow rate of stream B

The output gas is analyzed and is found to contain 1.5 mole% water. Draw and label the flowchart of the process, and calculate all unknown stream variables.
Solution

- Convert water flow-rate to mol/min
- Water balance
- Total mol
- Nitrogen / oxygen balance

Evaporation

- $0.200 \dot{n}_1 \text{ mol O}_2/\text{min}$
- $\dot{n}_1 \text{ mol air/min}$
- $0.21 \text{ mol O}_2/\text{mol}$
- $0.79 \text{ mol N}_2/\text{mol}$
- $0.015 \text{ mol H}_2\text{O/mol}$
- $y \text{ mol O}_2/\text{mol}$
- $(0.985-y) \text{ mol N}_2/\text{mol}$
- $20 \text{ cm}^3 \text{ H}_2\text{O (l)/min}$
- $\dot{n}_2 \text{ mol H}_2\text{O/min}$
- $\dot{n}_3 \text{ mol/min}$
Flowchart Scaling & Basis of Calculation

- **Flowchart scaling** – procedure of changing the values of all stream amounts or flow rates by a proportional amount while leaving the stream compositions unchanged. The process would still be balance.

- **Scaling-up** – if final stream quantities are larger than the original quantities.

- **Scaling down** – if final stream quantities are smaller than the original quantities.
Flowchart Scaling & Basis of Calculation

1 kg $\text{C}_6\text{H}_6$  
1 kg $\text{C}_7\text{H}_8$  
300 kg $\text{C}_6\text{H}_6$  
300 kg $\text{C}_7\text{H}_8$  
300 lbm/h  
300 lbm/h  

2 kg  
0.5 kg $\text{C}_6\text{H}_6$/kg  
0.5 kg $\text{C}_7\text{H}_8$/kg  
600 kg  
0.5 kg $\text{C}_6\text{H}_6$/kg  
0.5 kg $\text{C}_7\text{H}_8$/kg  
600 lbm/h  
0.5 lbm $\text{C}_6\text{H}_6$/lbm  
0.5 lbm $\text{C}_7\text{H}_8$/lbm

$\times 300$

Replace kg with lbm

March 31, 2009  ChE 201/shoukat@buet.ac.bd
Flowchart Scaling & Basis of Calculation

• Suppose you have balanced a process and the amount or flow rate of one of the process streams is \( n_1 \). You can scale the flow chart to make the amount or flow rate of this stream \( n_2 \) by multiplying all stream amounts or flow rate by the ratio \( n_2/n_1 \).

• You cannot, however, scale masses or mass flow rates to molar quantities or vice versa by simple multiplication; conversions of this type must be carried out using the methods as discussed in mass fraction and mol fraction section.
Basis of Calculation

• A basis of calculation is an amount (mass or moles) of flow rate (mass or molar) of one stream or stream component in a process. All unknown variables are determined to be consistent with the basis.

• If a stream amount or flow rate is given in problem, choose this quantity as a basis

• If no stream amount or flow rate are known, assume one stream with known composition. If mass fraction is known, choose total mass or mass flow rate as basis. If mole fraction is known, choose a total moles or molar flow rate as basis.
Recycle and Bypass

- Reuse of reactants/feed
- Recovery of catalyst
- Dilution of process streams (improve filter operation)
- Control of a process variable (Reduce reactant concentration)
- Circulation of a working fluid (Refrigeration)

What is wrong here?
Product Separation

Reactants → Reactor → Product Separation Unit → Products
K-salt Recovery

• In a steady state process crystalline potassium chromate (K₂CrO₄) is recovered from an aqueous solution of this salt.

• 10 ton per hour of a solution that is 30% K₂CrO₄ by mass is fed into an evaporator. The concentrated stream leaving the evaporator contains 50% K₂CrO₄; this stream is fed into a crystallizer in which it is cooled (causing crystals of K₂CrO₄ to come out of solution) and then filtered. The filter cake consists of K₂CrO₄ crystals and a solution that contain 35% K₂CrO₄ by mass; the crystals account for 95% of the total mass of the filter cake. The filtrate drains out of the system also contains 35% K₂CrO₄.
Product Separation

- $m_1 = 4000 \text{ kg W/h}$
- $m_2 = 6000 \text{ kg K-soln/h}$
- $m_3 = 1385 \text{ kg K(S)/h}$
- $m_4 = 73 \text{ kg K-soln/h}$
- $m_5 = 4542 \text{ kg K-soln/h}$

Fresh Feed

- 10,000 kg/h
- 0.30 kg K/kg
- 0.70 kg W/kg

Evaporator

Crystallizer & Filter

- $m_2$ kg/h
- 0.50 kg K/kg
- 0.50 kg W/kg

Filter Cake

- $m_3$ kg/h
- 0.35 kg K/kg
- 0.65 kg W/kg

Filtrate

- $m_5$ kg/h
- 0.35 kg K/kg
- 0.65 kg W/kg
K-salt Recovery (similar to example 4.5.2 except data are different)

- In a steady state process crystalline potassium chromate ($\text{K}_2\text{CrO}_4$) is recovered from an aqueous solution of this salt.
- 10 ton per hour of a solution that is 30% $\text{K}_2\text{CrO}_4$ by mass is joined by a recycle stream containing 35% $\text{K}_2\text{CrO}_4$, and combined stream is fed into an evaporator.
- The concentrated stream leaving the evaporator contains 50% $\text{K}_2\text{CrO}_4$; this stream is fed into a crystallizer in which it is cooled (causing crystals of $\text{K}_2\text{CrO}_4$ to come out of solution) and then filtered.
- The filter cake consists of $\text{K}_2\text{CrO}_4$ crystals and a solution that contain 35% $\text{K}_2\text{CrO}_4$ by mass; the crystals account for 95% of the total mass of the filter cake. The solution that passes through the filter also 35% $\text{K}_2\text{CrO}_4$, is the recycle stream.
- Calculate the rate of evaporation, the rate of production of crystalline $\text{K}_2\text{CrO}_4$, the feed rates that the evaporator and the crystallizer must be designed to handle, and the recycle ratio (mass of recycle/mass of fresh feed).
Product Separation & Recycling

Evaporator

Crystallizer & Filter

Fresh Feed
10,000 kg/h
0.30 kg K/kg
0.70 kg W/kg

Filter Cake

Recycle

m 1 kg/h

m 2 kg W/h

m 3 kg/h

m 4 kg/h

m 5 kg/h

m 6 kg/h

0.35 kg K/kg
0.65 kg W/kg

0.50 kg K/kg
0.50 kg W/kg

0.35 kg K/kg
0.65 kg W/kg
Product Separation & Recycling

\[
\begin{align*}
\text{m1} &= 19662 \text{ kg mixed feed/h} \\
\text{m2} &= 6900 \text{ kg Water evaporated/h} \\
\text{m3} &= 12762 \text{ kg fed to crystallizer/h} \\
\text{m4} &= 2945 \text{ kg crystals/h} \\
\text{m5} &= 155 \text{ kg K-soln/h} \\
\text{m6} &= 9662 \text{ kg recycle/h} \\
\text{Recycle Ratio} &= ??? \\
\text{Comment:} \\
\text{Crystal production increases 113\% due to recycling}
\end{align*}
\]
4.6 Balances on Reactive Systems

• Stoichiometry
  - The theory of proportions in which chemical species combine with one another.
  - Example: $2 \text{SO}_2 + \text{O}_2 \rightarrow 2 \text{SO}_3$

• Stoichiometric Ratio
  - Ratio of stoichiometric coefficients
  - Example

\[
\frac{2 \text{ mol SO}_3 \text{ produced}}{1 \text{ mol O}_2 \text{ reacted}} = \frac{2 \text{ mol SO}_2 \text{ reacted}}{2 \text{ mol SO}_3 \text{ produced}}
\]
Concept of conversions:

• Normally, reactions are not complete
  - Separation and recycle
  - Improved yield, conversion, ...

Reactants \rightarrow \text{Reactor} \rightarrow \text{Product Separation Unit} \rightarrow \text{Products}

Recycle

✓ Overall conversion
✓ Once-through conversion or Single-pass conversion
✓ Process feed
✓ Fresh feed
✓ Gross product
✓ Net product
Terminology

• Fractional conversion
  - Chemical reactions are not always completed.
  - Fractional conversion
    • $f = \frac{\text{moles reacted}}{\text{moles fed}}$
    - When fresh feed consists of more than one material the conversion must be stated for a single component, usually the limiting reactant.
Terminology

Overall Conversions = \( \frac{\text{reactant input to process} - \text{reactant output from process}}{\text{reactant input to process}} \)

Single-Pass Conversions = \( \frac{\text{reactant input to reactor} - \text{reactant output from reactor}}{\text{reactant input to reactor}} \)

• In general, high overall conversions can be achieved in two ways:
  - Design the reactor to yield a high single-pass conversion, or
  - Design the reactor to yield a low single-pass conversion and follow it with a separation unit to recover and recycle unconsumed reactant.
Terminology

• **Limiting reactants**
  - Exist less than stoichiometric proportion

• **Excess reactants**
  - Exist more than stoichiometric proportion

• **Example**

\[ 2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3 \]

(30 mol) (10 mol)
Terminology

• Fractional excess \( \frac{n - n_s}{n_s} \)

• Percent excess \( \frac{n - n_s}{n_s} \times 100 \)

• Example

  - \( \text{H}_2 + \text{Br}_2 \rightarrow \text{HBr} \)
  - \( \text{H}_2 : 25 \text{ mol /hr} \)
  - \( \text{Br}_2 : 20 \text{ mol /hr} \)
  - Fractional Excess \( \text{H}_2 = \frac{25 - 20}{20} = 0.25 \)
  - Percent Excess = 25 %
Problem

• Consider the reaction

$$6 \text{NaClO}_3 + 6 \text{H}_2\text{SO}_4 + \text{CH}_3\text{OH} \rightarrow 6 \text{ClO}_2 + 6 \text{NaHSO}_4 + \text{CO}_2$$

• if the reactor feed has the composition (mol%) of 36% NaClO$_3$, 54% H$_2$SO$_4$, and the rest CH$_3$OH, which is the limiting reactant?

• Calculate the reactant flows required to produce 10 ton per hour of ClO$_2$ assuming 90% conversion is obtained.
Questions