2.1 Introduction to Material Balances

A material balance is nothing more than the application of the law of the conservation of mass: “Matter is neither created nor destroyed”.

Process classification

1. **Batch process**: The feed is charged (fed) into a vessel at the beginning of the process and the vessel contents are removed sometime later.

2. **Continuous process:** the inputs and outputs flow continuously throughout the duration of the process.

3. **Semi-batch process:** Any process that is neither batch nor continuous.

Steady-State and Unsteady-State Systems

If the values of all the variables in a process (i.e., all temperatures, pressures, volumes, flow rates) do not change with time, the process is said to be operating at steady state.

If any of the process variables change with time, unsteady state operation is said to exist. By their nature, batch and semi-batch processes are unsteady-state operations whereas continuous processes may be either steady-state or transient.

Material balance for a component without reaction

$$\text{Input} - \text{output} = \text{Accumulation} \qquad (1)$$

If the system is at steady state (Accumulation = 0)

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$$\text{Input} = \text{output} \qquad (2)$$

Material balance for Multiple Component Systems

Suppose the input to a vessel contains more than one component, such as

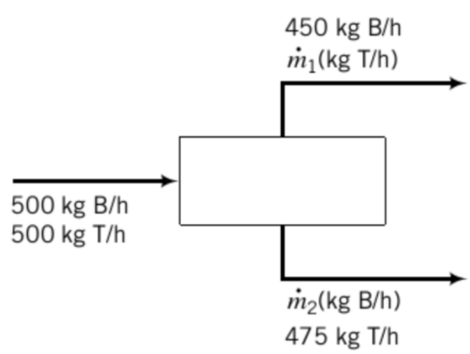
100 kg/min of a 50% water and 50% sugar (sucrose, $C_{12}H_{22}O_{11}$, MW =

342.3) mixture. The mass balances with respect to the sugar and water, balances that we call component balances.

Example 1:

1000 kg/h of a mixture of **benzene (B) and toluene (T)** containing **50%** benzene by mass is separated by distillation into two fractions. The mass flow rate of benzene in the top stream is **450 kg B/h** and that of toluene in the bottom stream is **475 kg T/h.** The operation is at steady state. Write balances on benzene and toluene to calculate the unknown component flow rates in the output streams.

Solution



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Basis : 1 hour

In general : input = output

Benzen balance 500 kg B = 450kg B + m_2

m_2 = 50 kg B

Toluene balance 500 kg T = m_1 + 475 kg T

m_1 = 25 kg T

Check the calculation:

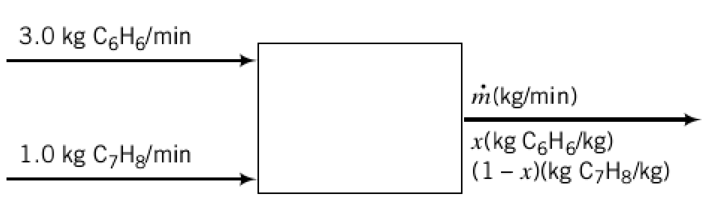
Total mass balance : 1000 kg = 450 + m_1 + m_2 + 475 (all in kg)

1000 kg = 450 + 25 + 50 + 475

1000 kg = 1000 kg

Example 2:

Suppose 3.0 kg/min of benzene and 1.0 kg/min of toluene are mixed. Find the composition and mass rate of the product.



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Solution

There are two unknown quantities, m and x, so two equations are needed to calculate them.

Basis : 1 minute

Total mass balance: 3 kg + 1 kg = m

m = 4 kg

$$\text{benzen balance:}\;\; 3\text{ kg B} = \text{m(kg)} * \frac{\text{x(kg B)}}{\text{kg}}$$

x = 0.75 kg B/ kg.

2.2 General Strategy for Solving Material Balance Problems:

1. Read and understand the problem statement.

2. Draw a sketch of the process and specify the system boundary.

3. Place labels for unknown variables and values for known variables on the sketch.

4. Obtain any data you need to solve the problem, but are missing.

5. Choose a basis.

6. Determine the number of variables whose values are unknowns.

7. Determine the number of independent equations, and carry out a degree of freedom analysis.

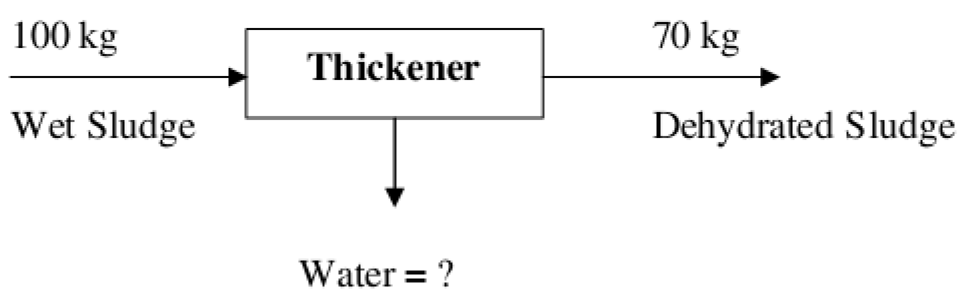
8. Write down the equations to be solved in terms of the knowns and unknowns.

9. Solve the equations and calculate the quantities asked for in the problem.

10. Check your answer(s).

Example 3:

A thickener in a waste disposal unit of a plant removes water from wet sewage sludge as shown in Figure. How many kilograms of water leave the thickener per 100 kg of wet sludge that enter the thickener? The process is in the steady state.



Solution

Basis: 100 kg wet sludge

The total mass balance is In= Out

100 kg = 70 kg + kg of water

Consequently, the water amounts to **30 kg.**

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2.3 The Chemical Reaction Equation and Stoichiometry

The stoichiometric equation of a chemical reaction is a statement of the relative number of molecules or moles of reactants and products that participate in the reaction. For example, the stoichiometric equation:

$$2SO_2 + O_2 \rightarrow 2SO_3$$

Indicates that for every two molecules (g-moles, lb-moles) of SO_2 that react, one molecule (g-mole, lb-mole) of O_2 reacts to produce two molecules (g-moles, lb-moles) of SO_3

The numbers that precede the formulas for each species are the stoichiometric coefficients of the reaction components.

The stoichiometric ratio of two molecular species participating in a reaction is the ratio of their stoichiometric coefficients in the balanced reaction equation. For the reaction:

$$2SO_2 + O_2 \rightarrow 2SO_3$$

you can write the stoichiometric ratios:

$$\frac{2 \text{ moles } SO_3 \text{ generated}}{1 \text{ mol } O_2 \text{ consumed}}, \quad \frac{2 \text{ lb moles } SO_2 \text{ consumed}}{2 \text{ lb moles } SO_3 \text{ generated}}$$

For example, if 1600 kg/h of SO_3 is to be produced, you can calculate the amount of oxygen required as:

$$\frac{1600\ SO_3\ generated}{h} \left| \frac{1\ kmol\ \ SO_3}{80\ kg\ SO_3} \right| \frac{1\ kmol\ \ O_2 consumed}{2\ kmol\ \ SO_3\ generated} = 10\frac{kmol\ \ O_2}{h}$$

$$\longrightarrow \quad 10\frac{kmol\ \ O_2}{h} \left| \frac{32\ kg\ O_2}{1\ kmol\ \ O_2} = 320\ kg\ O_2/h \right.$$

Extent of Reaction

The extent of reaction, ξ, denotes how much reaction occurs.

The extent of reaction is defined as follows:

$$\xi = \frac{n_i - n_{io}}{\nu_i} \qquad (1)$$

n_i= moles of species i present in the system after the reaction occurs,

n_{io} = moles of species i present in the system when the reaction starts,

ν_i = coefficient for species i in the particular chemical reaction equation.

ξ = extent of reaction (moles reacting)

- The coefficients of the products in a chemical reaction are assigned positive values and the reactants assigned negative values. Note that (n_i-n_{io}) is equal to the generation or consumption of component i by reaction.

Equation (1) can be rearranged to calculate the number of moles of component i from the value of the extent of reaction:

$$n_i = n_{i0} + \xi \nu_i \tag{2}$$

Example 4:

Determine the extent of reaction for the following chemical reaction

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

given the following analysis of feed and product:

	N_2 (g)	**H_2 (g)**	**NH_3 (g)**
Feed	100	50	5
Product	---	---	90

Also, determine the g and g mol of N_2 and H_2 in the product.

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Solution:

The extent of reaction can be calculated by applying Equation 1 based on NH_3:

$$n_i = 90\ g\ NH_3 \left|\ \frac{1\ mol\ NH_3}{17\ g\ NH_3} = 5.294\ mol\ NH_3\right.$$

$$n_{io} = 5\ g\ NH_3 \left|\ \frac{1\ mol\ NH_3}{17\ g\ NH_3} = 0.294\ mol\ NH_3\right.$$

$$\xi = \frac{n_i - n_{io}}{\nu_i} = \frac{(5.294 - 0.294) mol\ NH_3}{2} = 2.5\ moles\ reacting$$

Equation 2 can be used to determine the mol of N_2 and H_2 in the products of the reaction:

N_2:

$$n_{i0} = 100\ g\ N_2 \left|\ \frac{1\ mol\ N_2}{28\ g\ N_2} = 3.57\ mol\ N_2\right.$$

$$n_{N2} = 3.57 + (-1)(2.5) = 1.07\ mol\ N_2$$

$$m_{N2} = 1.07\ mol\ N_2 \left|\ \frac{28\ g\ N_2}{1\ mol\ N_2} = 30\ g\ N_2\right.$$

H_2:

$$n_{i0} = 50\ g\ H_2 \left|\ \frac{1\ mol\ H_2}{2\ g\ H_2} = 25\ mol\ H_2\right.$$

$$n_{H2} = 25 + (-3)(2.5) = 17.5\ mol\ H_2$$

$$m_{N2} = 17.5\ mol\ H_2 \left|\ \frac{2\ g\ H_2}{1\ mol\ H_2} = 35\ g\ H_2\right.$$

Note: If several independent reactions occur in the reactor, say k of them, ξ can be defined for each reaction, with **νki** being the stoichiometric coefficient of species **i** in the kth reaction, the total number of moles of species **i** is:

$$n_i = n_{i0} + \sum_{k=1}^{R} \nu_{ki}\,\xi_k \qquad (3)$$

Where **R** is the total number of independent reactions.

Limiting and Excess Reactants

The reactant that would run out if a reaction proceeded to completion is called the limiting reactant, and the other reactants are termed excess reactants.

A reactant is limiting if it is present in less than its stoichiometric proportion relative to every other reactant.

If all reactants are present in stoichiometric proportion, then no reactant is limiting.

Suppose $\mathbf{n_{(A)}feed}$ is the number of moles of an excess reactant, A, and $\mathbf{n_{(A)stoich}}$ is the stoichiometric requirement of A, or the amount needed to react completely with the limiting reactant. Then:

$$\text{fractional excess of A} = \frac{n_{(A)\text{feed}} - n_{(A)\text{stoich}}}{n_{(A)\text{stoich}}}$$

As a straightforward way of determining the limiting reactant, you can determine the maximum extent of reaction, ξ^{max}, for each reactant based on the complete reaction of the reactant. The reactant with the smallest maximum extent of reaction is the limiting reactant.

For example, for the chemical reaction equation:

$$C_7H_{16} + 11O_2 \longrightarrow 7CO_2 + 8H_2O$$

If 1 mol of C_7H_{16} and 12 mol of O_2 are mixed, then:

$$\xi^{max}\ (based\ on\ O_2) = \frac{0\ mol\ \ O_2 - 12\ mol\ \ O_2}{-11} = 1.09\ mol\ reacting$$

$$\xi^{max}\ (based\ on\ C_7H_{16}) = \frac{0\ mol\ \ C_7H_{16} - 1 mol\ \ C_7H_{16}}{-1} = 1\ mol\ reacting$$

Therefore, heptane is the limiting reactant and oxygen is the excess reactant.

Conversion and degree of completion

The fractional conversion of a reactant is the ratio:

$$f = \frac{\text{moles reacted}}{\text{moles fed}}$$

Example 5:

for the chemical reaction equation:

$$C_7H_{16} + 11O_2 \longrightarrow 7CO_2 + 8H_2O$$

If 14.4 kg of CO_2 are formed in the reaction of 10 kg of C_7H_{16}, what is the fractional conversion of heptan?

Solution

1. moles of C_7H_{16} in the feed:

$$\text{moles of } C_7H_{16} \text{ fed} = \frac{10\ kg\ C7H16}{101.1 \frac{kg\ C7H16}{k\ mol\ \ C7H16}} = 0.099\ kmol\ C_7H_{16}$$

2. moles of C_7H_{16} reacted:

$$\text{moles of } CO_2 = \frac{14.4\ kg\ CO2}{44 \frac{kg\ CO2}{k\ mol\ \ CO2}} = 0.327\ kmol\ CO_2$$

then from reaction equation: 1 mol of C_7H_{16} equivalent to 7 moles of CO_2:

moles of C_7H_{16} reacted $= 0.327 \text{ k mol } CO_2 * \frac{1 \text{ kmol } C_7H_{16}}{7 \text{ kmol } CO2} = 0.0467 \text{ k mol } C_7H_{16}$

$$f = \frac{0.0468 \text{ kmol reacted}}{0.0999 \text{ kmol fed}} = 0.468$$

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Selectivity

Selectivity is the ratio of the moles of the desired product produced to the moles of undesired product produced in a set of reactions.

$$\text{selectivity} = \frac{\text{moles of desired product}}{\text{moles of undesired product}}$$

For example, methanol (CH_3OH) can be converted into ethylene (C_2H_4) or propylene (C_3H_6 $2CH_3OH \rightarrow C_2H_4 + 2H_2O$) by the reactions**:**

$$\mathbf{2CH_3OH \rightarrow C_2H_4 + 2H_2O}$$

$$\mathbf{3CH_3OH \rightarrow C_3H_6 + 3H_2O}$$

What is the selectivity of C_2H_4 relative to the C_3H_6 at 80% conversion of the CH_3OH? Given that At 80% conversion: C_2H_4 19 mole % and for C_3H_6 8 mole %

Because the basis for both values is the same,

$$\text{selectivity} = \frac{19 \text{ moles}}{8 \text{ moles}} = 2.4 \text{ mol}C_2H_4/\text{mol}C_3H_6$$

Yield

Yield (based on feed)—the amount (mass or moles) of desired product obtained divided by the amount of the key (frequently the limiting) reactant fed.

Example 6:

The two reactions of interest for this example are:

$$Cl_2(g) + C_3H_6(g) \rightarrow C_3H_5Cl(g) + HCl(g) \qquad (a)$$

$$Cl_2(g) + C_3H_6(g) \rightarrow C_3H_6Cl_2(g) \qquad (b)$$

C_3H_6 is propylene (propene) (MW = 42.08)

C_3H_5 C1 is allyl chloride (3-chloropropene) (MW = 76.53) $C_3H_6Cl_2$ is propylene chloride (1,2—dichloropropane) (MW = 112.99)

The species recovered after the reaction takes place for some time are listed in Table:

species	Cl_2	C_3H_6	C_3H_5Cl	$C_3H_6Cl_2$	HCl
mol	141	651	4.6	24.5	4.6

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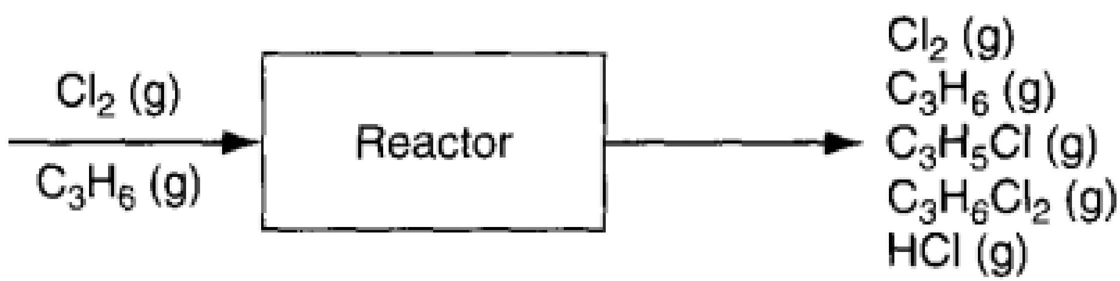
Based on the product distribution assuming that no allyl chlorides were present in the feed, calculate the following:

a. How much Cl_2 and C_3H_6
b. What was the limiting reactant?
c. What was the excess reactant?
d. What was the fraction conversion of C_3H_6 to C_3H_5C1?
e. What was the selectivity of C_3H_5C1 relative to $C_3H_6Cl_2$?
f. What was the yield of C_3H_5C1 expressed in g of C_3H_5C1 to the g of C_3H_6 g. fed to the reactor?
g. What was the extent of reaction of the first and second reactions?

Solution



A convenient basis is what is given in the product list in Table.

Reaction (a): 1 mol of Cl_2 equivalent to 1 mole of C_3H_7Cl

moles of Cl_2 reacts = $4.6 \; mol \; C_3H_7Cl * \frac{1 \; mol \; Cl2}{1 \; mol \; C_3H_7Cl} = 4.6 \; mol \; Cl_2$

Reaction (b): 1 mol of Cl_2 equivalent to 1 mole of $C_3H_6Cl_2$

moles of Cl_2 reacts = $24.5 \; mol \; C_3H_6Cl_2 * \frac{1 \; mol \; Cl2}{1 \; mol \; C_3H_6Cl_2} = 24.5 \; mol \; Cl_2$

Total = 4.6 + 24.5 = 29.1 mol Cl_2 reacts

Cl_2 in product = 141.0 mol from Table

(a) Total Cl_2 fed = 141.0 + 29.1 = 170.1 mol Cl_2

Total C_3H_6 fed = 651.0 + 29.1 = 680.1 mol of C_3H_6

(b) and (c) Since both reactions involve the same value of respective reaction stoichiometric coefficients, both reactions will h the same limiting and excess reactants**:**

$$\xi^{max} \text{ (based on } C_3H_6) = \frac{-680.1 \text{ mol } C_3H_6}{-1} = 680.1 \text{ mol reacting}$$

$$\xi^{max} \text{ (based on } Cl_2) = \frac{-170.1 \text{ mol } Cl_2}{-1} = 170.1 \text{ mol reacting}$$

Thus, C_3H_6 was the excess reactantand Cl_2 the limiting reactant.

(d) The fraction conversion of C_3H_6 to C_3H_5C1 was

$$f = \frac{4.6 \text{ mol } C_3H_6 \text{ reacted}}{680.1 \text{ mol } C_3H_6 \text{ fed}} = 0.0067$$

(e) The selectivity was**:**

$$\text{selectivity} = \frac{4.6 \text{ mol } C_3H_5Cl}{24.5 \text{ mol } C_3H_6Cl_2} = 0.19 \frac{\text{mol } C_3H_5Cl}{\text{mol } C_3H_6Cl_2}$$

(f) The yield was:

$$\text{Yield} = \frac{(76.53)(4.6) \text{ g } C_3H_5Cl}{(42.08)(680.1) \text{ g } C_3H_6} = 0.012 \frac{\text{g } C_3H_5Cl}{\text{g } C_3H_6}$$

(g) Because $C_3H_5C1$is produced only by the first reaction, the extent of reactionof the first reaction is:

$$\xi_1 = \frac{n_i - n_{io}}{\nu_i} = \frac{4.6-0}{1} = 4.6 \text{ mol reacting}$$

Because $C_3H_6C1_2$ is produced only by the second reaction, the extent of reaction of the second reaction is

$$\xi_2 = \frac{n_i - n_{io}}{\nu_i} = \frac{24.5-0}{1} = 24.5 \text{ mol reacting}$$

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