

## **Chapter 4**

# **MATERIAL BALANCES AND APPLICATIONS**

# MATERIAL BALANCES AND APPLICATIONS

## 4.1. Introduction

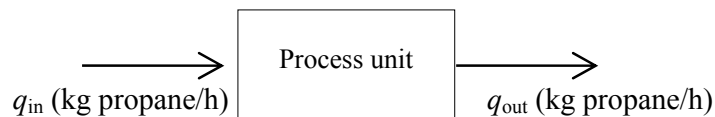
Material balances are important first step when designing a new process or analyzing an existing one. They are almost always prerequisite to all other calculations in the solution of process engineering problems.

Material balances are nothing more than the application of the law of conservation of mass, which states that mass can neither be created nor destroyed. Thus, you cannot, for example, specify an input to a reactor of one ton of naphtha and an output of two tons of gasoline or gases or anything else. One ton of total material input will only give one ton of total output, i.e. total mass of input = total mass of output.

A material balance is an accounting for material. Thus, material balances are often compared to the balancing of current accounts. They are used in industry to calculate mass flow rates of different streams entering or leaving chemical or physical processes.

## 4.2. The General Balance Equation

Suppose propane is a component of both the input and output streams of a continuous process unit shown below, these flow rates of the input and output are measured and found to be different.



If there are no leaks and the measurements are correct, then the other possibilities that can account for this difference are that propane is either being generated, consumed, or accumulated within the unit.

A balance (or inventory) on a material in a system (a single process unit, a collection of units, or an entire process) may be written in the following general way:

<b><i>Input</i></b>	+	<b><i>generation</i></b>	-	<b><i>output</i></b>	-	<b><i>consumption</i></b>	=	<b><i>accumulation</i></b>
(enters through system boundaries)		(produced within system boundaries)		(leaves through system boundaries)		(consumed within system)		(buildup within system)

This **general balance equation** may be written for any material that enters or leaves any process system; it can be applied to the total mass of this material or to any molecular or atomic species involved in the process.

The general balance equation may be simplified according to the process at hand. For example, by definition, the accumulation term for **steady-state continuous process** is zero. Thus the above equation becomes:

$$Input + generation = output + consumption$$

For physical process, since there is no chemical reaction, the generation and consumption terms will become zero, and the balance equation for steady-state physical process will be simply reduced to:

$$Input = Output$$

### 4.3. Balances on Single and Multiple Physical Systems

#### 4.3.1. Procedure for Material Balance Calculations

In material balance problems, you will usually be given a description of a process, the values of several process variables, and a list of quantities to be determined. In order to be trained on using a systematic procedure to solve material balance problems, you are advised to follow the steps summarized below:

1. Draw and label the process flow chart (block diagram). When labeling, write the values of known streams and assign symbols to unknown stream variables. Use the minimum number possible of symbols.
2. Select a basis of calculation. This is usually the given stream amounts or flow rates, if no given then assume an amount of a stream with known composition.

3. Write material balance equations. Note in here the maximum number of independent equations you can write for each system is equal the number of species in the input and output streams of this system. Also note to first write balances that involve the fewest unknown variables.
4. Solve the equations derived in step 3 for the unknown quantities to be determined.

### Notes

- i. Minimize the symbols assigned to unknown quantities by utilizing all the given process specifications and using laws of physics.
- ii. After doing calculations on certain basis, you may scale up or scale down (convert to new basis) while keeping the process balanced. This is done by multiplying all streams (except mass or mole fractions) by the scale factor which is equal to the ratio of the new stream amount or flow rate to the old one. You can only scale between mass amount or flow rates regardless of units used but not from mass to molar quantity or flow rate.

The examples below will illustrate the procedure of balances on physical processes:

### **EXAMPLE: Balance on a mixing unit**

An aqueous solution of sodium hydroxide contains 20% NaOH by mass. It is desired to produce an 8% NaOH solution by diluting a stream of the 20% solution with a stream of pure water.

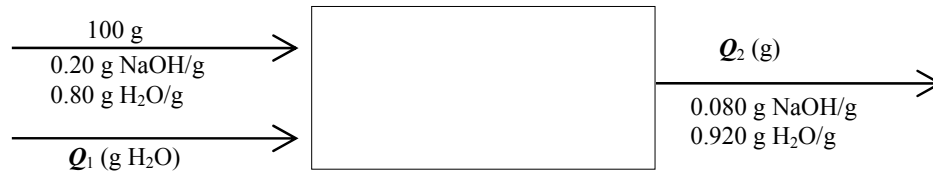
1. Calculate the ratios (g H<sub>2</sub>O/g feed solution) and (g product solution/g feed solution).
2. Determine the feed rates of 20% solution and diluting water needed to produce 2310 lb<sub>m</sub>/min of the 8% solution.

### **Solution**

We could take a basis of 2310 lb<sub>m</sub> product/min, but for illustrative purposes and to have neater numbers to work with let us choose a different basis and scale the final results.

*Basis: 100 g Feed Solution*

Draw and label the flowchart, remembering that the amount of the product stream is now unknown.



(Since the known stream amount is given in grams, it is convenient to label all unknown amounts with this unit.)

There are two unknowns -  $Q_1$  and  $Q_2$  - and since there are two substances - NaOH and  $H_2O$  - in the input and output streams, two balances may be written to solve for them. The total mass balance and the water balance involve both unknowns, but the NaOH balance involves only one.

*NaOH Balance*

$$\begin{aligned}
 (\text{g NaOH})_{\text{in}} &= (\text{g NaOH})_{\text{out}} \\
 \Downarrow \\
 (0.20)(100 \text{ g}) &= 0.080 Q_2 \Rightarrow Q_2 = 250 \text{ g}
 \end{aligned}$$

It is a good practice to write calculated variable values on the flowchart as soon as they are known for ease of use in later calculations; at this point, 250 would therefore be written in place of  $Q_2$  on the chart.

*Total Mass Balance*

$$\begin{aligned}
 100 \text{ g} + Q_1 &= Q_2 \\
 \Downarrow Q_2 = 250 \text{ g} \\
 \Downarrow \\
 Q_1 &= 150 \text{ g } H_2O
 \end{aligned}$$

The desired ratios can now be calculated:

$$\frac{Q_1 \text{ (g H}_2\text{O)}}{100 \text{ g feed solution}} \stackrel{Q_1 = 150}{\Rightarrow} \boxed{1.5 \frac{\text{g H}_2\text{O}}{\text{g feed solution}}}$$

$$\frac{Q_2 \text{ (g H}_2\text{O)}}{100 \text{ g feed solution}} \stackrel{Q_2 = 250}{\Rightarrow} \boxed{2.5 \frac{\text{g product}}{\text{g feed solution}}}$$

The scale factor is obtained as the true flow rate of the product stream divided by the rate calculated on the assumed basis.

$$\frac{2310 \text{ lb}_m \text{ product/min}}{250 \text{ g product}} = 9.24 \frac{\text{lb}_m/\text{min}}{\text{g}}$$

*Feed Solution Flow Rate*

$$\frac{100 \text{ g}}{100 \text{ g}} \left| \frac{9.24 \text{ lb}_m/\text{min}}{\text{g}} \right. = \boxed{924 \frac{\text{lb}_m \text{ feed solution}}{\text{min}}}$$

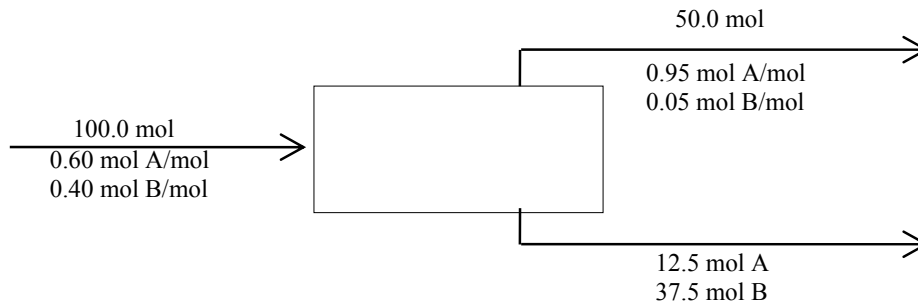
*Dilution Water Flow Rate*

$$\frac{150 \text{ g}}{150 \text{ g}} \left| \frac{9.24 \text{ lb}_m/\text{min}}{\text{g}} \right. = 1386 \frac{\text{lb}_m \text{ H}_2\text{O}}{\text{min}}$$

*Check:*  $(924 + 1386) \text{ lb}_m/\text{min} = 2310 \text{ lb}_m/\text{min}$

### EXAMPLE: Scale up of a separation process flowchart

A 60 - 40 mixture (by moles) of A and B is separated into two fractions. A flowchart of the process is shown here.



It is desired to achieve the same separation with a continuous feed of 1250 lb-moles/h. Scale the flowchart accordingly.

### Solution

The scale factor is

$$\frac{1250 \text{ lbmoles / h}}{100 \text{ mol}} = 12.5 \frac{\text{lbmoles / h}}{\text{mol}}$$

The masses of all streams in the batch process are converted to flow rates as follows:

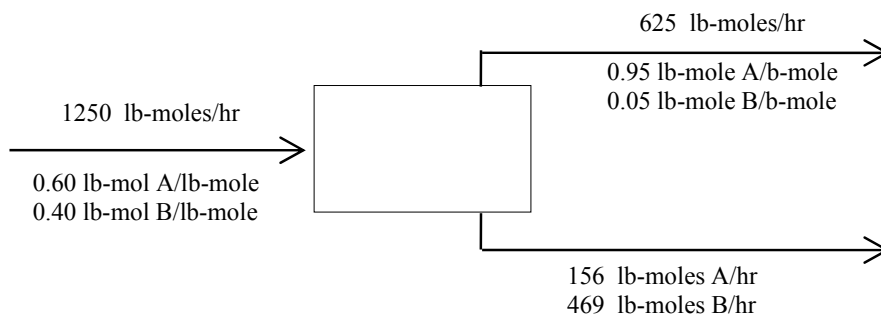
$$\text{Feed: } \frac{100 \text{ mol}}{100 \text{ mol}} \left| \frac{12.5 \text{ lb-moles/h}}{\text{mol}} \right. = 1250 \frac{\text{lb-moles}}{\text{h}} \text{ (as specified)}$$

$$\text{Top product stream: } (50.0)(12.5) = 625 \text{ lb-moles/h}$$

$$\text{Bottom product stream: } (12.5)(12.5) = 156 \text{ lb-moles A/h}$$

$$(37.5)(12.5) = 469 \text{ lb-moles B/h}$$

The units of the mole fractions in the top product stream may be changed from mol/mol to lb-mole/lb-mole, but their values remain the same. The flowchart for the scaled-up process is shown here.



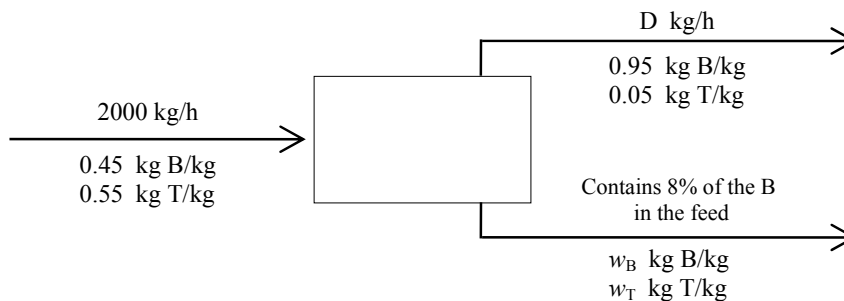
### EXAMPLE: Material balances on a distillation column

A mixture containing 45% benzene (B) and 55% toluene (T) by mass is fed to a distillation column. An overhead stream of 95 wt% B is produced, and 8% of the benzene fed to the column leaves in the bottom stream. The feed rate is 2000 kg/h. Determine the overhead flow rate and the mass flow rates of benzene and toluene in the bottom stream

### Solution

*Basis : Given Feed Rate*

The labeled flowchart is as follows.



There are three unknowns on the chart -  $D$ ,  $w_B$ , and  $w_T$  - and therefore three equations are needed. We are entitled to write only two material balances since two species are involved in the process; the third equation must therefore come from additional given information (the amount of benzene in the bottom stream.) The latter relation is.

$$\text{B in bottom stream} = 0.080 (\text{B in feed})$$

⇓

$$w_B \text{ (kg B/h)} = 0.080[(0.45)(2000) \text{ kg/h}]$$

⇓

$$\boxed{w_B = 72 \text{ kg B/h}} \quad (\text{Write 72 in place of } w_B \text{ on the chart})$$

Toluene and total mass balances each involve two unknowns,  $D$  and  $w_T$ , but a benzene balance involves only one,  $D$ .

*Benzene Balance*

$$(0.45)(2000) \frac{\text{kg B}}{\text{h}} = 0.95 D + w_B$$

$$\Downarrow w_B = 72 \text{ kg B/h}$$

⇓

$$\boxed{D = 870 \text{ kg/h}} \quad (\text{Write it on the chart})$$



Total Mass Balance (A toluene balance could be used equally well)

$$2000 \frac{\text{kg}}{\text{h}} = D + w_B + w_T$$

$$\Downarrow \quad D = 870 \text{ kg/h}$$

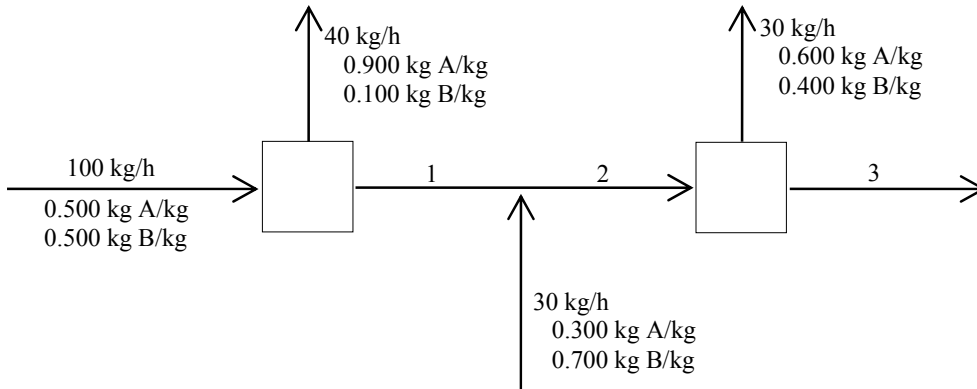
$$\Downarrow \quad w_B = 72 \text{ kg/h}$$

$$\Downarrow$$

$w_T = 1060 \text{ kg T/h}$

**EXAMPLE: Two Unit Distillation Process**

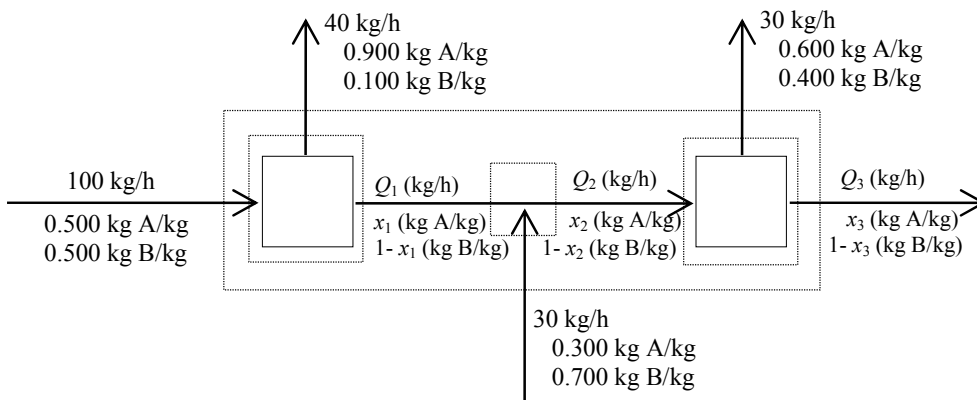
A labeled flowchart of a continuous steady-state two-unit distillation process is shown below. Each stream contains two components, A and B, in different proportions. Three streams whose flow rates and/or compositions are not known are labeled 1, 2 and 3.



Calculate the unknown flow rates and compositions of streams 1, 2, and 3.

**Solution**

The systems about which balances might be taken are shown on the following representation of the flowchart.



The outer boundary encompasses the entire process. Two of the interior boundaries surround the individual process units, and the fourth boundary encloses a stream junction point.

*Basis: Given Flow Rates*

There are two unknowns in the streams that enter and leave the total process,  $Q_3$  and  $x_3$ , and since there are two independent components in these streams (A and B) we may write two balances.

*Overall Mass Balance*

$$(100 + 30) \frac{\text{kg}}{\text{h}} = (40 + 30) \frac{\text{kg}}{\text{h}} + Q_3$$

⇓

$$Q_3 = 60 \text{ kg/h}$$

*Overall Balance On A*

$$(0.500)(100) + (0.300)(30) = (0.900)(40) + (0.600)(30) + (60)(x_3)$$

⇓

$$x_3 = 0.0833 \text{ kg A/kg}$$

To determine the flow rate and composition of a connecting stream, we must write balances on a subsystem whose boundary intersects this stream. Of the three such boundaries shown in the flowchart, the middle one (about the stream junction) would not be a good one to use at this point since its input and output streams contain four unknown quantities ( $Q_1$ ,  $x_1$ ,  $Q_2$ ,  $x_2$ ), while the boundaries about the process units each intersect streams that contain two unknowns.

Let us choose the boundary about unit 1 for the next set of balances. There are two unknowns,  $Q_1$  and  $x_1$ , in the streams that intersect this boundary, and up to two balances may be written.

*Total Mass Balance on Unit 1*

$$100 \text{ kg/h} = 40 \frac{\text{kg}}{\text{h}} + Q_1$$

⇓

$$Q_1 = 60 \text{ kg/h}$$

*Balance on A in Unit 1*

$$(0.500)(100) = (0.900)(40) + 60x_1$$

$$x_1 = 0.233 \text{ kg A/kg}$$

To find  $Q_2$  and  $x_2$ , we could write balances about either the stream mixing point or Unit 2. Let us choose the first alternative.

*Mass Balance About Mixing Point*

$$Q_1 + 30 \text{ kg/h} = Q_2$$

$$\Downarrow Q_1 = 60 \text{ kg/h}$$

$\Downarrow$

$$Q_2 = 90 \text{ kg/h}$$

*Balance on A About Mixing Point*

$$Q_1 x_1 + (0.300)(30) \text{ kg A/h} = Q_2 x_2$$

$$Q_1 = 60 \text{ kg/h}$$

$$\Downarrow x_1 = 0.233 \text{ kg A/kg}$$

$$Q_2 = 90 \text{ kg/h}$$

$\Downarrow$

$$x_2 = 0.255 \text{ kg A/kg}$$

## 4.4. Balances on Reactive Systems

### 4.4.1. Stoichiometry, Limiting and Excess Reactants

For reactive systems, in addition to input and output of materials, generation and consumption terms should be considered in the general mole balance equation. Theory of proportions in which chemical compounds react is called **stoichiometry**. A statement of the **relative** number of moles or molecules reacting to produce products is given by a chemical equation known as **stoichiometric equation**. For example, 2 moles of  $\text{SO}_2$  and one mole of  $\text{O}_2$  react to produce 2 moles of  $\text{SO}_3$ . Then the stoichiometric equation will be  $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$ . Numbers that precede the formulas are known as **stoichiometric coefficients**.

**EXAMPLE:**  $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$ . What is the stoichiometric coefficient of  $\text{SO}_2$ ?

**Solution** The number that precede  $\text{SO}_2$  is 2. Therefore, stoichiometric coefficient of  $\text{SO}_2$  is 2.

In a stoichiometric equation, the number of atoms in both sides of the equation must be balanced. In this example, the number of atoms of S and O are 2 and 6, respectively, in both sides of equation.

Ratio of stoichiometric coefficients of two species is known as **stoichiometric ratio**.

**EXAMPLE:**  $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$ . What is the stoichiometric ratio of  $\text{SO}_2$  to  $\text{SO}_3$ ?

**Solution** stoichiometric ratio of  $\text{SO}_2$  to  $\text{SO}_3 = \frac{2 \text{ mole of } \text{SO}_2 \text{ reacted}}{2 \text{ mole of } \text{SO}_3 \text{ produced}} = 1$

If proportion of chemical species fed to a reactor is same as the stoichiometric ratio, then chemical species combine in **stoichiometric proportion**, otherwise one or more species will be in excess of the other. The chemical compound which is present less than its stoichiometric amount, will disappear first. This reactant will be the **limiting** reactant and all the others will be **excess** reactants. **Fractional** and **percentage excess** are given by the following formulas.

$$\text{fractional excess} = \frac{n - n_s}{n_s}$$

$$\text{percentage excess} = \frac{n - n_s}{n_s} \times 100$$

where

$n$  = number of moles fed

$n_s$  = number of moles corresponding to stoichiometric amount

**EXAMPLE:** 100 moles of  $\text{SO}_2$  and 100 moles  $\text{O}_2$  are fed to a reactor and they react according to  $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$ . Find the limiting reactant, excess reactant, fractional excess and percentage excess?

**Solution**

ratio of  $\text{SO}_2$  to  $\text{O}_2$  fed =  $100/100 = 1$

stoichiometric ratio of  $\text{SO}_2/\text{O}_2 = 2/1=2$

Therefore,  $\text{SO}_2$  is fed less than the stoichiometric proportion (or stoichiometric ratio).  $\text{SO}_2$  is the *limiting* reactant. The other reactant ( $\text{O}_2$ ) will be the *excess reactant*.

$n$  = number of moles of excess reactant ( $O_2$ ) fed = 100

$n_s$  = stoichiometric amount of  $O_2$  to react with 100 moles of the limiting reactant  $SO_2 = 50$

Therefore, fractional excess =  $\frac{n - n_s}{n_s} = \frac{100 - 50}{50} = 1.0$

percentage excess =  $\frac{n - n_s}{n_s} \times 100 = 100\%$

#### 4.4.2. Fractional Conversions, Extent of Reaction, Chemical Equilibrium

In many cases, chemical reactions do not go to completion and only a fraction will be converted. Therefore, **fractional** and **percentage conversions** are used. They are defined as follows,

fractional conversion ( $f$ ) =  $\frac{\text{mole reacted}}{\text{mole fed to the reactor}}$

percentage conversion =  $f \times 100$

fraction unreacted =  $(1-f)$

**EXAMPLE:** 200 moles of  $SO_2$  and 100 moles  $O_2$  are fed to a reactor. Only 100 moles of  $SO_2$  react according to  $2SO_2 + O_2 \rightarrow 2SO_3$ . Find fractional conversion, percentage conversion and fraction unreacted?

#### **Solution**

fractional conversion of  $SO_2$  ( $f$ ) =  $\frac{\text{mole reacted}}{\text{mole fed to the reactor}} = 100/200 = 0.5$

percentage conversion =  $f \times 100 = 0.5 \times 100 = 50\%$

fraction unreacted =  $(1-f) = 1 - 0.5 = 0.5$

When a reaction is not complete, remaining amount in the reactor will be given by

$$n_i = n_{i0} + \beta_i \zeta$$

where,  $\xi$  = **extent of reaction** (mole reacted or produced/ $v_i$ )  
 $i$  = compound  $i$ ,  $n_i$  = remaining amount  
 $n_{i0}$  = amount initially put in the reactor  
 $\beta_i = +v_i$ , stoichiometric coefficient of a product  
 $= -v_i$ , stoichiometric coefficient of a reactant  
 $= 0$ , inert

The same equation is true if quantities (i.e., moles) are replaced by flow rates (mole/hr).

**EXAMPLE:** 200 moles of  $\text{SO}_2$  and 100 moles  $\text{O}_2$  are fed to a reactor. Only 50 moles of  $\text{O}_2$  react according to  $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$ . Find the moles remaining for all species?

**Solution**

For  $\text{O}_2$ ,  $\xi = 50$ ,  $n_{i0} = 100$ ,  $\beta_i = -v_i = -1$ ,  $n_i = n_{i0} + \beta_i \xi = 100 - 1 \times 50 = 50$  moles

For  $\text{SO}_2$ ,  $\xi = 50$ ,  $n_{i0} = 200$ ,  $\beta_i = -v_i = -2$ ,  $n_i = 200 - 2 \times 50 = 100$  moles

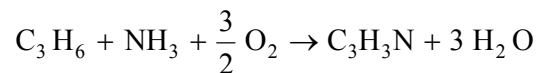
For  $\text{SO}_3$ ,  $\xi = 50$ ,  $n_{i0} = 0$ ,  $\beta_i = +v_i = +2$ ,  $n_i = 0 + 2 \times 50 = 100$  moles

When the chemical reaction proceeds in one direction only, we call it **irreversible**. If the reaction proceeds in forward and backward directions then it is **reversible**. When forward reaction rate and reverse reaction rate becomes equal, reaction is said to be in **equilibrium**. Equilibrium constant (K) for a gas phase reaction,  $\text{A}(\text{gas}) + \text{B}(\text{gas}) \rightleftharpoons \text{C}(\text{gas}) + \text{D}(\text{gas})$ , is given by

$$K = \frac{y_C y_D}{y_A y_B}, \quad \text{where } y \text{ is the mole fraction of the components in the gas phase.}$$

**EXAMPLE: Reaction Stoichiometry**

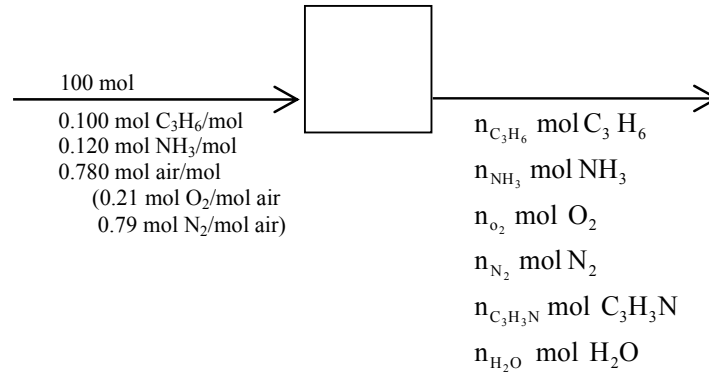
Acrylonitrile is produced by the reaction of propylene, ammonia, and oxygen.



The feed contains 10 mole% propylene, 12% ammonia, and 78% air. A fractional conversion of 30% of the limiting reactant is achieved. Determine which reactant is limiting, the percentage by which each of the other reactants is in excess, and the molar flow rates of all product gas constituents for a 30% conversion of the limiting reactant, taking 100 mol of feed as a basis.

## Solution

Basis : 100 mol Feed



The feed to the reactor contains

$$\begin{aligned} (C_3H_6)_{in} &= 10.0 \text{ mol} \\ (NH_3)_{in} &= 12.0 \text{ mol} \\ (O_2)_{in} &= \frac{78.0 \text{ mol air}}{\text{mol air}} \left| \frac{0.210 \text{ mol } O_2}{\text{mol air}} \right. = 16.4 \text{ mol} \end{aligned}$$

⇓

$$\left. \begin{aligned} (NH_3/C_3H_6)_{in} &= 12.0/10.0 = 1.20 \\ (NH_3/C_3H_6)_{stoich} &= 1/1 = 1 \end{aligned} \right\} \Rightarrow NH_3 \text{ is in excess}$$

$$\left. \begin{aligned} (O_2/C_3H_6)_{in} &= 16.4/10.0 = 1.64 \\ (O_2/C_3H_6)_{stoich} &= 1.5/1 = 1.5 \end{aligned} \right\} \Rightarrow O_2 \text{ is in excess}$$

Since propylene is fed in less than the stoichiometric proportion relative to the two other reactants, propylene is the limiting reactant.

To determine the percentages by which ammonia and oxygen are in excess, we must first determine the stoichiometric amounts of these reactants corresponding to the amount of propylene in the feed (10 mol).

$$(NH_3)_{stoich} = \frac{10.0 \text{ mol } C_3H_6}{1 \text{ mol } C_3H_6} \left| \frac{1 \text{ mol } NH_3}{1 \text{ mol } C_3H_6} \right. = 10.0 \text{ mol } NH_3$$

$$(O_2)_{stoich} = \frac{10.0 \text{ mol } C_3H_6}{1 \text{ mol } C_3H_6} \left| \frac{1.5 \text{ mol } O_2}{1 \text{ mol } C_3H_6} \right. = 15.0 \text{ mol } O_2$$

$$\begin{aligned} (\% \text{ excess})_{NH_3} &= \frac{(NH_3)_0 - (NH_3)_{stoich}}{(NH_3)_{stoich}} \times 100\% \\ &= [(12 - 10)/10] \times 100\% = 20\% \text{ excess } NH_3 \end{aligned}$$

$$(\% \text{ excess})_{\text{O}_2} = [(16.4 - 15.0)/15.0] \times 100\% = \boxed{9.3\% \text{ excess O}_2}$$

If the fractional conversion of C<sub>3</sub>H<sub>6</sub> is 30%

$$(\text{C}_3\text{H}_6)_{\text{out}} = 0.700(\text{C}_3\text{H}_6)_{\text{in}} = \boxed{7.0 \text{ mol C}_3\text{H}_6}$$

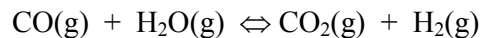
But  $n_{\text{C}_3\text{H}_6} = 10.0 - \xi$ . The extent of reactions is therefore:  $\xi = 3.0$ .

Then,

$$\begin{array}{rcl} n_{\text{NH}_3} & = 12.0 - \xi & = 9.0 \text{ mol NH}_3 \\ n_{\text{O}_2} & = 16.4 - 1.5\xi & = 11.9 \text{ mol O}_2 \\ n_{\text{C}_3\text{H}_6\text{N}} & = \xi & = 3.00 \text{ mol C}_3\text{H}_3\text{N} \\ n_{\text{N}_2} & = (\text{N}_2)_0 & = 61.6 \text{ mol N}_2 \\ n_{\text{H}_2\text{O}} & = 3\xi & = 9.0 \text{ mol H}_2\text{O} \end{array}$$

### EXAMPLE: Calculation of an Equilibrium Composition

If the water-gas shift reaction,



proceeds to equilibrium at a temperature T(K), the mole fractions of the four reactive species satisfy the relation

$$\frac{y_{\text{CO}_2} y_{\text{H}_2}}{y_{\text{CO}} y_{\text{H}_2\text{O}}} = K(T)$$

where K (T) is the reaction **equilibrium constant**. At T = 1105 K (832°C), K = 1.00. Suppose the feed to a reactor contains 1.00 mol CO, 2.00 mol of H<sub>2</sub>O, and no CO<sub>2</sub> or H<sub>2</sub>, and the reaction mixture comes to equilibrium at 1105 K. Calculate the equilibrium composition and the fractional conversion of the limiting reactant.

### Solution

The strategy is to express all mole fractions in terms of a single variable ( $\xi_e$ , the extent of reaction at equilibrium), substitute in the equilibrium relation, solve for  $\xi_e$ , and back-substitute to calculate the mole fractions and any other desired quantity.



$$\begin{aligned}
n_{\text{CO}} &= 1.00 - \xi_e \quad (\text{number of mols of CO present at equilibrium}) \\
n_{\text{H}_2\text{O}} &= 2.00 - \xi_e \\
n_{\text{CO}_2} &= \xi_e \\
n_{\text{H}_2} &= 1\xi_e \\
n_{\text{total}} &= 3.00
\end{aligned}$$

from which

$$\begin{aligned}
y_{\text{CO}} &= (1.00 - \xi_e)/3.00 \\
y_{\text{H}_2\text{O}} &= (2.00 - \xi_e)/3.00 \\
y_{\text{CO}_2} &= \xi_e/3.00 \\
y_{\text{H}_2} &= \xi_e/3.00
\end{aligned}$$

Substitution of these expressions in the equilibrium relation (with  $K = 1.00$ ) yields

$$\frac{\xi_e^2}{(1.00 - \xi_e)(2.00 - \xi_e)} = 1.00$$

This may be rewritten as a standard quadratic equation and solve to yield  $\xi_e = 0.667$ . This quantity may in turn be substituted back into the expressions for  $y_i(\xi_e)$  to yield

$$y_{\text{CO}} = 0.111, \quad y_{\text{H}_2\text{O}} = 0.444, \quad y_{\text{CO}_2} = 0.222, \quad y_{\text{H}_2} = 0.222$$

The limiting reactant in this case is CO (verify). At equilibrium,

$$n_{\text{CO}} = 1.00 - 0.667 = 0.333$$

The fractional conversion of CO at equilibrium is therefore

$$f_{\text{CO}} = (1.00 - 0.333) \text{ mol reacted} / (1.00 \text{ mol fed}) = 0.667$$

#### 4.4.3. Multiple Reactions, Yield and Selectivity

In a chemical process, our objective is to produce a certain product (desired product), but there may be several unwanted reactions which will produce undesirable by products. Therefore, we must maximize the production of a desired product in the process. Two quantities, **yield** and **selectivity**, are used for this purpose and they are defined as follows,

$$\text{yield} = \frac{\text{moles of desired product formed}}{\text{moles of desired product formed if there were no side reactions and the limiting reactant reacts completely}}$$

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

When we have multiple reactions, the remaining amount or flow rate will be given by

$$n_i = n_{i0} + \sum_j \beta_{ij} \xi_j$$

where

i = compound i

j = reaction j

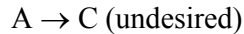
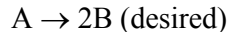
$\xi_j$  = extent of reaction for the j<sup>th</sup> reaction

$\beta_{ij} = +v_i$ , stoichiometric coefficient of a product i in the j<sup>th</sup> reaction

=  $-v_i$ , stoichiometric coefficient of a reactant i in the j<sup>th</sup> reaction

= 0, inert

**EXAMPLE:** Consider the following pair of reactions.



100 moles of A are fed to a batch reactor and the final product contains 10 mol of A, 160 mol of B and 10 mol of C. Calculate (1) percentage yield of B, (2) the selectivity of B relative to C and (3) the extents of the reactions.

### **Solution**

#### *Percentage Yield*

moles of desired product (B) formed = 160

moles of desired product formed if there were no side reactions and the limiting reactant reacts completely = 100 moles of A  $\times$   $\frac{2 \text{ moles of B produced}}{1 \text{ mole of A reacted}}$  = 200 moles

yield (%) = 160/200\*100 = 80%

#### *Selectivity*

moles of desired product (B) formed = 160

moles of undesired product (C) formed = 10

$$\text{selectivity} = \frac{\text{moles of desired product formed}}{\text{moles of undesired product formed}} = 160/10 = 16.$$

*Extent of Reactions*

$$n_i = n_{i0} + \sum_j \beta_{ij} \xi_j$$

for two reaction system as above,  $n_i = n_{i0} + \beta_{i1} \xi_1 + \beta_{i2} \xi_2$

applying this equation for B,  $160 = 0 + 2\xi_1$ , this gives  $\xi_1 = 80$

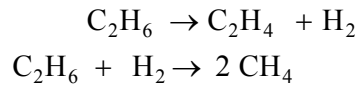
for C,  $10 = 0 + \xi_2$  this gives  $\xi_2 = 10$ .

check: for A,

$$10 = 100 - \xi_1 - \xi_2, \quad 10 = 100 - 80 - 10 = 10$$

**EXAMPLE: Yield and Selectivity in a Dehydrogenation Reactor**

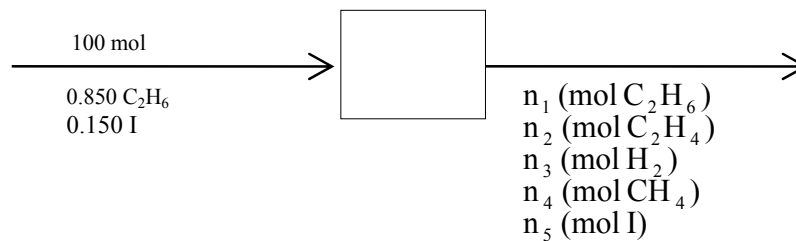
The reactions



take place in a continuous reactor at steady state. The feed contains 85.0 mole% ethane (C<sub>2</sub>H<sub>6</sub>) and the balance inerts (I). The fractional conversion of ethane is 0.501, and the fractional yield of ethylene is 0.471. Calculate the molar composition of the product gas and the selectivity of ethylene to methane production.

**Solution**

*Basis: 100 mol Feed*



The outlet component amounts in terms of extents of reaction are as follows:

$$\begin{aligned}
 n_1 \text{ (mol C}_2\text{H}_6) &= 85.0 - \xi_1 - \xi_2 \\
 n_2 \text{ (mol C}_2\text{H}_4) &= \xi_1 \\
 n_3 \text{ (mol H}_2) &= \xi_1 - \xi_2 \\
 n_4 \text{ (mol CH}_4) &= 2\xi_2 \\
 n_5 \text{ (mol I)} &= 15.0
 \end{aligned}$$

#### *Ethane Conversion*

$$\begin{aligned}
 n_1 &= \frac{(1.000 - 0.501) \text{ mol C}_2\text{H}_6 \text{ unreacted}}{\text{mol C}_2\text{H}_6 \text{ fed}} \bigg| \frac{85.0 \text{ mol C}_2\text{H}_6 \text{ fed}}{1} \\
 &= 42.4 \text{ mol C}_2\text{H}_6 = 85.0 - \xi_1 - \xi_2
 \end{aligned}$$

#### *Ethylene Yield*

$$\begin{aligned}
 \text{Maximum possible ethylene} &= \frac{85.0 \text{ mol C}_2\text{H}_6 \text{ fed}}{1 \text{ mol C}_2\text{H}_6} \bigg| \frac{1 \text{ mol C}_2\text{H}_4}{1 \text{ mol C}_2\text{H}_6} = 85.0 \text{ mol} \\
 n_2 &= 0.471 (85.0 \text{ mol C}_2\text{H}_4) \downarrow = 40.0 \text{ mol C}_2\text{H}_4 = \xi_1
 \end{aligned}$$

Substituting 40.0 for  $\xi_1$  in (1) yield  $\xi_2 = 2.6$  mol. Then

$$\begin{aligned}
 n_3 &= \xi_1 - \xi_2 = 37.4 \text{ mol H}_2 \\
 n_4 &= 2 \xi_2 = 5.2 \text{ mol CH}_4 \\
 n_5 &= 15.0 \text{ mol I} \\
 n_{\text{tot}} &= (42.4 + 40.0 + 37.4 + 5.2 + 15.0) = 140.0 \text{ mol}
 \end{aligned}$$

↓

30.3% C <sub>2</sub> H <sub>6</sub> , 28.6% C <sub>2</sub> H <sub>4</sub> , 26.7% H <sub>2</sub> , 3.7% CH <sub>4</sub> , 10.7% I
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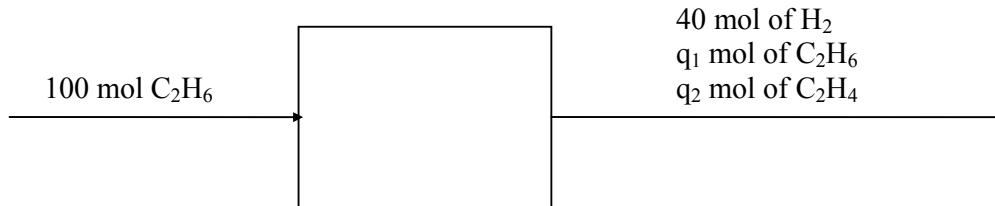
$$\text{Selectivity} = (40.0 \text{ mol C}_2\text{H}_4)/(5.2 \text{ mol CH}_4) = \boxed{7.7 \frac{\text{mol C}_2\text{H}_4}{\text{mol CH}_4}}$$

#### **4.4.4. Atomic and Molecular Balances**

In a chemical process, molecules are either generated (produced) or consumed. Therefore, one should take into account the amounts (moles) generated, consumed, fed and remaining in **molecular balances**.

**EXAMPLE:** In a steady state process, 100 moles ethane ( $C_2H_6$ ) react to produce ethylene ( $C_2H_4$ ) and hydrogen ( $H_2$ ) according to  $C_2H_6 \rightarrow C_2H_4 + H_2$ . Product gas shows 40 moles of hydrogen remaining. Perform molecular balances for all species.

**Solution:**



Then, the molecular balance of  $H_2$  is as follows,

$$\text{input} + \text{generated (produced)} = \text{output} + \text{consumed (reacted)}$$

$$\text{input} = 0.0$$

$$\text{output} = 40$$

$$\text{consumed} = 0$$

$$0 + \text{generated (produced)} = 40 + 0 \Rightarrow H_2 \text{ (generated)} = \underline{40 \text{ moles}}$$

Molecular balance of  $C_2H_6$  is as follows,

$$\text{input} + \text{generated (produced)} = \text{output} + \text{consumed (reacted)}$$

$$\text{input} = 100$$

$$\text{generated} = 0$$

$$\text{output} = q_1$$

$$100 + 0 = q_1 + \text{consumed} \Rightarrow C_2H_6 \text{ (consumed)} = 100 - q_1$$

$$H_2 \text{ (generated)} = 40 \text{ moles} = C_2H_6 \text{ (consumed)} = 100 - q_1 \Rightarrow q_1 = \underline{60 \text{ moles}}$$

Molecular balance of  $C_2H_4$  is as follows,

$$\text{input} + \text{generated (produced)} = \text{output} + \text{consumed (reacted)}$$

$$\text{input} = 0$$

$$\text{output} = q_2$$

$$\text{consumed} = 0$$

$$0 + \text{generated} = q_2 + 0 \Rightarrow C_2H_4 \text{ (generated)} = q_2$$

$$C_2H_4 \text{ (generated)} = q_2 = H_2 \text{ (generated)} = 40 \text{ moles} \Rightarrow q_2 = \underline{40 \text{ moles}}$$

According to conservation principle, atoms can neither be created (produced) nor destroyed (consumed). Therefore, in **atomic balances** there is no generation or consumption terms. Simply, input = output.

**EXAMPLE:** For the same problem as above, do atomic balances?

**Solution**

Atomic carbon balance:  $100 \times 2 = q_1 \times 2 + q_2 \times 2$

Atomic hydrogen balance  $100 \times 6 = 40 \times 2 + q_1 \times 6 + q_2 \times 4$

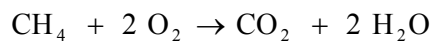
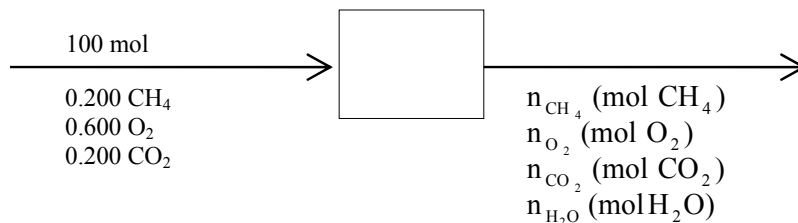
Solving these two atomic balance equations, you will get the same answer as above.

**EXAMPLE: Combustion of Methane**

Methane is burned with oxygen to yield carbon dioxide and water. The feed contains 20 mole% CH<sub>4</sub>, 60% O<sub>2</sub>, and 20% CO<sub>2</sub>, and a 90% conversion of the limiting reactant is achieved. Calculate the molar composition of the product stream using (1) balances on molecular species, (2) atomic balances, (3) the extent of reaction.

**Solution**

*Basis : 100 mol Feed*



Since a 2:1 ratio of O<sub>2</sub> to CH<sub>4</sub> would be stoichiometric and the actual ratio is 3:1, CH<sub>4</sub> is the limiting reactant and O<sub>2</sub> is in excess.

Before the balances are written, the given process information should be used to determine the unknown variables or relations between them. In this case, the methane conversion of 90% tells us that 10% of the methane fed to the reactor emerges in the product, or

$$n_{\text{CH}_4} = 0.100 \times (20.0 \text{ mol CH}_4 \text{ fed}) = 2.0 \text{ mol CH}_4$$

Now all that remains are the balances. We will proceed by each of the indicated methods.

### 1. Molecular Balances

$$\text{CH}_4 \text{ reacted} = \frac{20.0 \text{ mol CH}_4 \text{ fed}}{\text{mol fed}} \left| \frac{0.900 \text{ mol react}}{\text{mol fed}} \right. = 18 \text{ mol CH}_4 \text{ react}$$

*CO<sub>2</sub> Balance* (input + generation = output)

$$\frac{100 \text{ mol}}{\text{mol fed}} \left| \frac{0.200 \text{ mol CO}_2}{\text{mol fed}} \right. + \frac{18 \text{ mol CH}_4 \text{ react}}{\text{mol fed}} \left| \frac{1 \text{ mol CO}_2 \text{ produced}}{1 \text{ mol CH}_4} \right. = n_{\text{CO}_2}$$

$$\Downarrow$$

$$n_{\text{CO}_2} = 38 \text{ mol CO}_2$$

*H<sub>2</sub>O Balance* (generation = output)

$$\frac{18 \text{ mol CH}_4 \text{ react}}{\text{mol fed}} \left| \frac{2 \text{ mol H}_2\text{O produced}}{1 \text{ mol CH}_4 \text{ react}} \right. = n_{\text{H}_2\text{O}}$$

$$\Downarrow$$

$$n_{\text{H}_2\text{O}} = 36 \text{ mol H}_2\text{O}$$

*O<sub>2</sub> Balance* (input = output + consumption)

$$\frac{100 \text{ mol}}{\text{mol}} \left| \frac{0.600 \text{ mol O}_2}{\text{mol}} \right. = n_{\text{O}_2} + \frac{18 \text{ mol CH}_4 \text{ react}}{\text{mol fed}} \left| \frac{2 \text{ mol O}_2 \text{ react}}{1 \text{ mol CH}_4 \text{ react}} \right.$$

$$\Downarrow$$

$$n_{\text{O}_2} = (60 - 36) \text{ mol O}_2 = 24 \text{ mol O}_2$$

In summary, the output quantities are 2 mol CH<sub>4</sub>, 24 mol O<sub>2</sub>, 38 mol CO<sub>2</sub>, and 36 mol H<sub>2</sub>O, for a total of 100 mol. (Since 3 moles of products are produced for every 3 moles of reactants consumed, it should come as no surprise that total moles in = total moles out.) The mole fractions of the product gas components are thus:

0.02 mol CH <sub>4</sub> /mol, 0.24 mol O <sub>2</sub> /mol, 0.38 mol CO <sub>2</sub> /mol, 0.36 mol H <sub>2</sub> O/mol
--

## 2. Atomic Balances

Referring to the flowchart, we see that a balance on atomic carbon involves only one unknown ( $n_{\text{CO}_2}$ ), and a balance on atomic hydrogen also involves one unknown ( $n_{\text{H}_2\text{O}}$ ), but a balance on atomic oxygen involves three unknowns. We should therefore write the C and H balances first, and then the O balance to determine the remaining unknown variable. All atomic balances have the form input = output. (We will just determine the component amounts; calculation of the mole fractions then follows as in part 1.)

### C Balance

$$\begin{aligned} & \frac{20.0 \text{ mol CH}_4}{1 \text{ mol CH}_4} \left| \frac{1 \text{ mol C}}{1 \text{ mol CH}_4} \right. + \frac{20.0 \text{ mol CO}_2}{1 \text{ mol CO}_2} \left| \frac{1 \text{ mol C}}{1 \text{ mol CO}_2} \right. \\ &= \frac{2.0 \text{ mol CH}_4}{1 \text{ mol CH}_4} \left| \frac{1 \text{ mol C}}{1 \text{ mol CH}_4} \right. + \frac{n_{\text{CO}_2} \text{ mol CO}_2}{1 \text{ mol CO}_2} \left| \frac{1 \text{ mol C}}{1 \text{ mol CO}_2} \right. \\ &\Downarrow \\ &n_{\text{CO}_2} = 38 \text{ mol CO}_2 \end{aligned}$$

### H Balance

$$\begin{aligned} & \frac{20 \text{ mol CH}_4}{1 \text{ mol CH}_4} \left| \frac{4 \text{ mol H}}{1 \text{ mol CH}_4} \right. = \frac{2 \text{ mol CH}_4}{1 \text{ mol CH}_4} \left| \frac{4 \text{ mol H}}{1 \text{ mol CH}_4} \right. \\ & \quad + \frac{n_{\text{H}_2\text{O}} \text{ mol H}_2\text{O}}{1 \text{ mol H}_2\text{O}} \left| \frac{2 \text{ mol H}}{1 \text{ mol H}_2\text{O}} \right. \\ &\Downarrow \\ &n_{\text{H}_2\text{O}} = 36 \text{ mol H}_2\text{O} \end{aligned}$$

### O Balance

$$\begin{aligned} & \frac{60 \text{ mol O}_2}{1 \text{ mol O}_2} \left| \frac{2 \text{ mol O}}{1 \text{ mol O}_2} \right. + \frac{20 \text{ mol CO}_2}{1 \text{ mol O}_2} \left| \frac{2 \text{ mol O}}{1 \text{ mol O}_2} \right. \\ &= (n_{\text{O}_2} \text{ mol O}_2)(2) + (38 \text{ mol CO}_2)(2) + (36 \text{ mol H}_2\text{O})(1) \\ &\Downarrow \\ &n_{\text{O}_2} = 24 \text{ mol O}_2 \end{aligned}$$

confirming the results obtained using molecular balances.

## 3. Extent of Reaction

As discussed earlier, for all reactive species

$$n_{\text{out}} = n_{\text{in}} + \beta_i \xi$$

For the species in this problem, we may write



$$\begin{aligned}
 n_{\text{CH}_4} &= 20.0 \text{ mol} - \xi \quad \overset{n_{\text{CH}_4} = 2 \text{ mol CH}_4}{\Rightarrow} \quad \xi = 18.0 \text{ mol} \\
 n_{\text{C}_2} &= 60.0 \text{ mol} - 2\xi = 60.0 - (2)(18.0) = 24.0 \text{ mol O}_2 \\
 n_{\text{C}_2} &= 20.0 \text{ mol} + \xi = 20.0 + 18.0 = 38.0 \text{ mol CO}_2 \\
 n_{\text{H}_2\text{O}} &= 0 + 2\xi = (2)(18.0) = 36.0 \text{ mol H}_2\text{O}
 \end{aligned}$$

again, the previous solutions are obtained.

## 4.5. The Case of Recycle and Purge

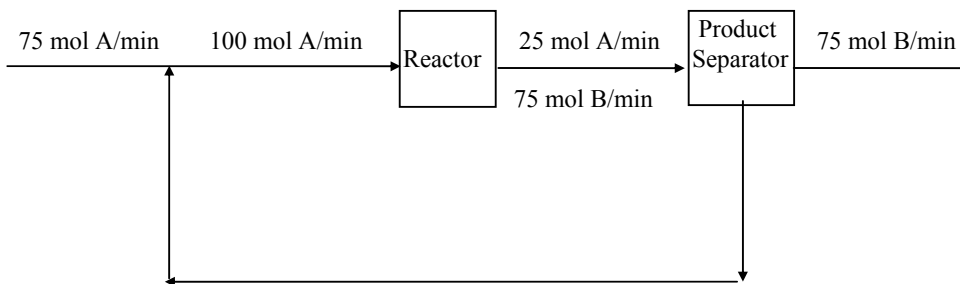
### 4.5.1. Overall and Single Pass Conversion

Two definitions of conversion are used in the analysis of chemical reactors with product separation and recycle of unconsumed reactants:

$$\text{overall conversion} = \frac{\text{reactant input to the process} - \text{reactant output from the process}}{\text{reactant input to the process}}$$

$$\text{single pass conversion} = \frac{\text{reactant input to the reactor} - \text{reactant output from the reactor}}{\text{reactant input to the reactor}}$$

**EXAMPLE :** Find the overall and single pass conversion of A ?



$$\text{overall conversion of A} = \frac{(75 \text{ mol A/min})_{\text{in}} - (0 \text{ mol A/min})_{\text{out}}}{(75 \text{ mol A/min})_{\text{in}}} \times 100 = 100\%$$

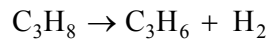
$$\text{single pass conversion of A} = \frac{(100 \text{ mol A/min})_{\text{in}} - (25 \text{ mol A/min})_{\text{out}}}{(100 \text{ mol A/min})_{\text{in}}} \times 100 = 75\%$$

#### 4.5.2. Recycle and Purge

A material such as an inert gas or impurities which enter with the feed will remain in the recycle stream. This material will accumulate and the process will never reach steady state. To prevent this buildup, a portion of the recycle stream must be withdrawn as a **purge stream**.

#### EXAMPLE: Dehydrogenation of Propane

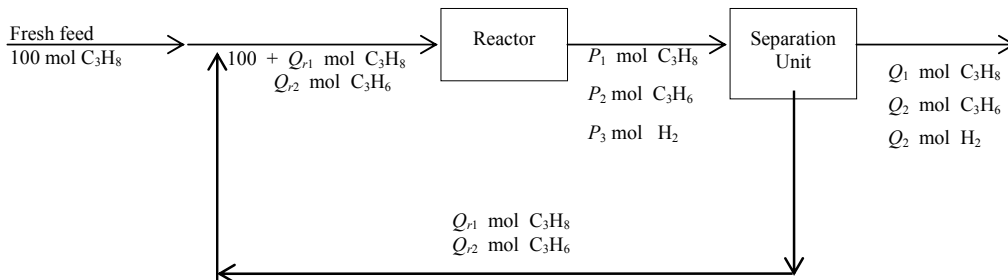
Propane is dehydrogenated to form propylene in a catalytic reactor



The process is to be designed for a 95% overall conversion of propane. The reaction products are separated into two streams: the first, which contains  $\text{H}_2$ ,  $\text{C}_3\text{H}_6$ , and 0.555% of the propane that leaves the reactor, is taken off as product; the second stream, which contains the balance of the unreacted propane and 5% of the propylene in the product stream, is recycled to the reactor. Calculate the composition of the product, the ratio (moles recycled)/(moles fresh feed), and the single-pass conversion.

#### Solution

*Basis : 100 mol Fresh Feed*



**Note:** In labeling the feed stream to the reactor, we have implicitly used balances on propane and propylene about the stream junction.

In terms of the labeled variables, the quantities to be calculated are

Mole Fractions of Product Stream Components:  $\frac{Q_1}{Q_1 + Q_2 + Q_3}, \dots$  etc.

Recycle Ratio:  $\frac{Q_{r1} + Q_{r2}}{100}$

$$\text{Single-Pass Conversion: } \frac{(100 + Q_{r1}) - P_1}{(100 + Q_{r1})} \times 100\%$$

We must therefore calculate the values of  $Q_1$ ,  $Q_2$ ,  $Q_3$ ,  $Q_{r1}$ ,  $Q_{r2}$  and  $P_1$ .

Let us first examine the overall process.

$$\text{Overall conversion} = 95\% \Rightarrow \frac{100 \text{ mol C}_3\text{H}_8 - Q_1}{100 \text{ mol C}_3\text{H}_8} = 0.95$$

↓

$$Q_1 = 5 \text{ mol C}_3\text{H}_8$$

*Overall Propane Balance:* input = output + consumption

$$100 \text{ mol C}_3\text{H}_8 = 5 \text{ mol C}_3\text{H}_8 + C \text{ (mol C}_3\text{H}_8 \text{ reacted)}$$

↓

$$C = 95 \text{ mol C}_3\text{H}_8 \text{ reacted}$$

*Overall Propylene Balance:* output = generation

$$Q_2 = \frac{95 \text{ mol C}_3\text{H}_8 \text{ reacted} \left| \frac{1 \text{ mol C}_3\text{H}_6 \text{ formed}}{1 \text{ mol C}_3\text{H}_8 \text{ reacted}} \right.}{1}$$

↓

$$Q_2 = 95 \text{ mol C}_3\text{H}_6$$

Similarly, *overall H<sub>2</sub> balance* yields

$$Q_3 = 95 \text{ mol H}_2$$

The analysis of the product is, therefore,

5 mol C <sub>3</sub> H <sub>8</sub>	⇒	2.6% C <sub>3</sub> H <sub>8</sub>
95 mol C <sub>3</sub> H <sub>6</sub>		48.7% C <sub>3</sub> H <sub>6</sub>
95 mol H <sub>2</sub>		48.7% H <sub>2</sub>
195 mol total		

We may now proceed to the analysis of the interior streams including the recycle stream. First, we summarize the information given in the problem statement.

$$Q_1 = 0.00555 P_1 \quad Q_1 = 5 \text{ mol C}_3\text{H}_8 \quad \Rightarrow \quad \boxed{P_1 = 900 \text{ mol C}_3\text{H}_8}$$

$$Q_{r2} = 0.05 Q_2 \quad Q_2 = 95 \text{ mol C}_3\text{H}_6 \quad \Rightarrow \quad \boxed{Q_{r2} = 4.75 \text{ mol C}_3\text{H}_6}$$

Next, write balances around the separation unit (which is nonreactive, so that input = output for all species.)

*C<sub>3</sub>H<sub>8</sub> Balance About Separation Unit*

$$P_1 = Q_1 + Q_{r1}$$

$$\Downarrow \quad P_1 = 900 \text{ mol C}_3\text{H}_8$$

$$\quad \quad Q_1 = 5 \text{ mol C}_3\text{H}_8$$

$$\boxed{Q_{r1} = 895 \text{ mol C}_3\text{H}_8}$$

We now have all the variable values we need. The desired quantities are

$$\text{Recycle ratio} = \frac{(Q_{r1} + Q_{r2}) \text{ mol recycle}}{100 \text{ mol fresh feed}}$$

$$\Downarrow \quad Q_{r1} = 895 \text{ mol}$$

$$\quad \quad Q_{r2} = 4.75 \text{ mol}$$

$$\boxed{9.00 \frac{\text{mol recycle}}{\text{mol fresh feed}}}$$

$$\text{Single-pass conversion} = \frac{(100 + Q_{r1}) - P_1}{(100 + Q_{r1})} \times 100\%$$

$$\Downarrow \quad Q_{r1} = 895 \text{ mol C}_3\text{H}_8$$

$$\quad \quad P_1 = 900 \text{ mol C}_3\text{H}_8$$

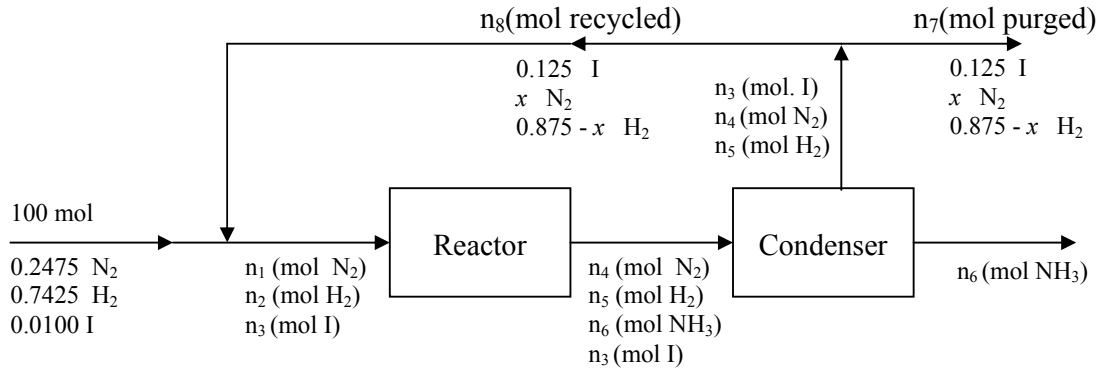
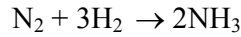
$$\boxed{9.55\%}$$

### **EXAMPLE: Recycle and Purge in the Synthesis of Ammonia**

The fresh feed to an ammonia production process contains 24.75 mole % nitrogen, 74.25 mole% hydrogen, and the balance inerts (I). The feed is combined with a recycle stream containing the same species, and the combined stream is fed to a reactor in which a 25% single-pass conversion of nitrogen is achieved. The products pass through a condenser in which essentially all of the ammonia is removed, and the remaining gases are recycled. However, to prevent buildup of the inerts in the system, a purge stream must be taken off. The recycle stream contains 12.5 mole% inerts. Calculate the overall conversion of nitrogen, the ratio (moles purge gas/mole of gas leaving the condenser), and the ratio (moles fresh feed/mole fed to the reactor).

**Solution**

Basis : 100 mol Fresh Feed.



**Strategy:** Overall N, H, I balances  $\Rightarrow n_6, n_7, x \Rightarrow$  overall conversion of N<sub>2</sub>  
 $n_6$ , 25% single pass conversion  $\Rightarrow n_1, n_4$   
 $n_7, x, n_4, n_2$  balance around purge-recycle split point  $\Rightarrow n_8$   
 $\text{H}_2, \text{I}$  balances around recycle-fresh mixing point  $\Rightarrow n_2, n_3$

Overall I balance:  $(0.0100)(100) = 0.125 n_7 \Rightarrow n_7 = 8.00$  mol purge gas

Overall N balance:  $(100)(0.2475)(2) = 8.00(x)(2) + n_6$   
 Overall H balance:  $(100)(0.7425)(2) = 8.00(0.875 - x)(2) + 3n_6$

$$\left. \begin{array}{l} n_6 = 46.0 \text{ mol NH}_3 \\ x = 0.219 \text{ mol N}_2/\text{mol} \end{array} \right\} \Rightarrow$$

Overall N<sub>2</sub> balance =  $\frac{24.75 \text{ mol fed} - (0.219)(8.00) \text{ mol in effluent}}{24.75 \text{ mol fed}} \times 100\% = \boxed{92.9\%}$

25% Single Pass Conversion:  $\frac{n_1 \text{ mol N}_2 \text{ fed}}{1 \text{ mol fed}} \Big| \frac{0.25 \text{ mol react}}{1 \text{ mol fed}} \Big| \frac{2 \text{ mol NH}_3}{1 \text{ mol N}_2} = 46.0 \text{ mol NH}_3$

$\Downarrow$   
 $n_1 = 92.0$  mol N<sub>2</sub> feed to reactor

$n_4 = (0.75)(92.0) = 69.0$  mol N<sub>2</sub>

$$N_2 \text{ balance around purge-recycle split point: } 69.0 = (0.219)n_8 + (0.219)(8.00)$$

$$\downarrow$$

$$n_8 = 307 \text{ mol recycled}$$

$$H_2 \text{ balance around mixing point: } (100)(0.7425) + (307)(0.875 - 0.219) = n_2$$

$$\downarrow$$

$$n_2 = 276 \text{ mol } H_2$$

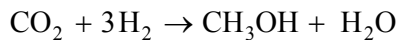
$$I \text{ balance around mixing point: } (100)(0.01) + (307)(0.125) = n_3 \Rightarrow n_3 = 39.4 \text{ mol } I$$

$$\frac{\text{moles purge}}{\text{moles leaving condenser}} = \frac{8}{8 + 307} = 0.025$$

$$\frac{100}{92 + 276 + 39.4} = 0.245 \frac{\text{moles fresh feed}}{\text{mol fed to reactor}}$$

### **EXAMPLE: Recycle and Purge in the Synthesis of Methanol**

Methanol may be produced by the reaction of carbon dioxide and hydrogen.

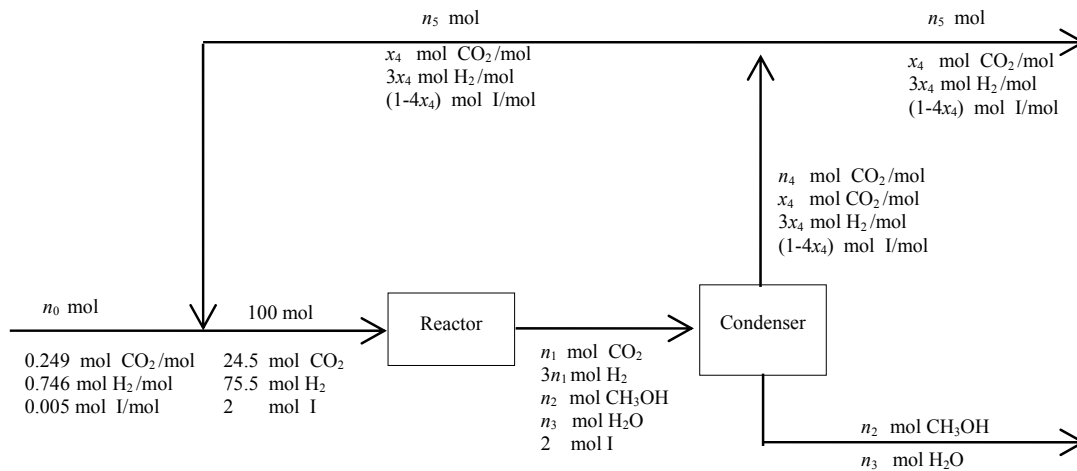


The fresh feed to the process contains hydrogen and carbon dioxide in stoichiometric proportion, and 0.5 mole% inerts (I). The reactor effluent passes to a condenser, which removes essentially all of the methanol and water formed, none of the reactants or inerts. The latter substances are recycled to the reactor. To avoid build-up of the inerts in the system, a purge stream is withdrawn from the recycle. The feed to the reactor contains 2% inerts, and the single-pass conversion is 60%. Calculate the molar flow rates of the fresh feed, the total feed to the reactor, and the purge stream for methanol production rate of 1000 mol/h.

### **Solution**

*Basis: 100 mol Combined Feed to the Reactor*

As a general rule, the combined feed to the reactor is a convenient stream to use as a basis of calculation for recycle problems, provided that its composition is known. Since in this process the reactants are fed in stoichiometric proportion and they are never separated from each other, they must be present in stoichiometric proportion throughout the process; that is,  $(CO_2/H_2) = 1/3$ . The feed thus contains 2 mol I (2% of 100 mol), and 98 mol  $CO_2 + H_2$ , of which 24.5 mol are  $CO_2$  (1/4 of 98) and 73.5 mol are  $H_2$ .



Take a moment to examine the chart labeling. In particular, notice that we have built in the facts that  $\text{CO}_2$  and  $\text{H}_2$  are always present in a 1:3 ratio and that the compositions of the gaseous effluent from the condenser, the purge stream, and the recycle stream are all identical. The more of this sort of information you can incorporate in the chart labeling, the easier the subsequent calculations become. Let us outline the solution, referring to the flowchart.

1. Calculate  $n_1$ ,  $n_2$ , and  $n_3$ , from the feed to the reactor, the single-pass conversion and reactor balances.
2. Calculate  $n_4$ , from a total mole balance about the condenser, and then  $x_4$  from a  $\text{CO}_2$  balance about the condenser.
3. Calculate  $n_0$ , and  $n_6$ , from balances on total moles and I about the recycle-fresh-feed mixing point. (Two equations, two unknowns.) Then calculate  $n_5$ , from a mole balance about the recycle-purge split point.
4. Scale up the calculated flows of fresh feed, combined reactor feed, and purge streams by the factor  $(1000/n_2)$ . The results will be the flow rates in mol/h corresponding to a methanol production of 1000/h.

### 60% Single-Pass Conversion

$$\begin{aligned}
 n_1 &= 0.400(24.5) = 9.80 \text{ mol CO}_2 \\
 3n_1 &= 29.4 \text{ mol H}_2 \\
 0.600(24.5) &= 14.7 \text{ mol CO}_2 \text{ react} \\
 &\Downarrow \text{ Balances on CH}_3\text{OH, H}_2\text{O: output = generation} \\
 n_2 &= 14.7 \text{ mol CH}_3\text{OH} \\
 n_3 &= 14.7 \text{ mol H}_2\text{O}
 \end{aligned}$$

*Mole Balance About Condenser*

$$2.4n_1 + n_2 + n_3 = n_2 + n_3 + n_4$$

↓ substitute for  $n_1$

$$n_4 = 41.2 \text{ mol}$$

*CO<sub>2</sub> Balance About Condenser*

$$n_1 = n_4 x_4$$

↓

$$x_4 = (9.80/41.2) = 0.2379 \text{ mol CO}_2 / \text{mol}$$

*Mole Balance About Mixing Point*

$$n_0 + n_6 = 100$$

*I Balance About Mixing Point*

$$0.00500n_0 + n_6(1 - 4x_4) = 2$$

↓  $x_4 = 0.2379$

$$0.00500n_0 + 0.0484n_6 = 2$$

Solving the above two equations simultaneously yields

$$n_0 = 65.4 \text{ mol fresh feed}$$
$$n_6 = 34.6 \text{ mol recycle}$$

*Mole balance About Purge Takeoff*

$$n_4 = n_5 + n_6$$

↓

$$n_5 = 41.2 - 34.6 = 6.6 \text{ mol purge}$$

The required scale factor is

$$[(1000 \text{ mol/h})/n_2 \text{ mol}]^{n_2 = 14.7} \Rightarrow 68.03 \text{ h}^{-1}$$



The desired flow rates are therefore

$65.4 \times 68.06 =$	4450 mol fresh feed/h
$100.0 \times 68.03 =$	6803 mol/h fed to reactor
$6.6 \times 68.03 =$	449 mol/h purge

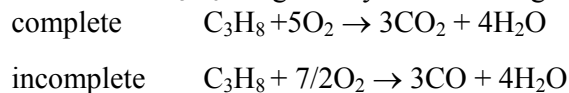
## 4.6. Combustion Reactions and Their Material Balances

### 4.6.1. Complete and Partial Combustion

Combustion is a rapid reaction of fuel with oxygen. Combustion products are CO<sub>2</sub>, NO, CO, H<sub>2</sub>O, and SO<sub>2</sub>. In a combustion reaction if CO is formed, then the reaction is incomplete and referred as **incomplete combustion** or partial combustion. During a complete combustion of a fuel, carbon will be oxidized to CO<sub>2</sub>, hydrogen will be oxidized to H<sub>2</sub>O, and sulfur will be oxidized to SO<sub>2</sub>.



Complete and incomplete combustion of C<sub>3</sub>H<sub>8</sub> are given by the following chemical reactions,



### 4.6.2. Wet and Dry Basis

Product gas that leaves the combustion chamber is called **stack** or **flue gas**. Composition of a flue gas is given on a **wet** (including water ) or **dry basis** (excluding water).

**EXAMPLE:** Suppose a stack gas contains equimolar amounts of CO<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub>O. Find the composition on wet and dry basis?

#### Solution

Suppose we have n moles of each, then

$$\text{composition of CO}_2 \text{ on wet basis} = \frac{\text{moles of CO}_2}{\text{total moles on wet basis}} \times 100 = (n/3n) \times 100 = 33.33\%$$

$$\text{composition of CO}_2 \text{ on dry basis} = \frac{\text{moles of CO}_2}{\text{total moles on dry basis}} \times 100 = (n/2n) \times 100 = 50\%.$$

**EXAMPLE:** A stack gas contains 60 mole% N<sub>2</sub>, 15% CO<sub>2</sub>, 10% O<sub>2</sub>, and the balance H<sub>2</sub>O. Calculate the molar composition of the gas on a dry basis.

**Solution**

*Basis: 100 mol Wet Gas*

$$\begin{array}{r} 60 \text{ mol N}_2 \\ 15 \text{ mol CO}_2 \\ 10 \text{ mol O}_2 \\ \hline 85 \text{ mol dry gas} \\ \Downarrow \\ \frac{60}{85} = 0.706 \frac{\text{mol N}_2}{\text{mol dry gas}} \\ \frac{15}{85} = 0.176 \frac{\text{mol CO}_2}{\text{mol dry gas}} \\ \frac{10}{85} = 0.118 \frac{\text{mol O}_2}{\text{mol dry gas}} \end{array}$$

**EXAMPLE: Dry Basis ⇒ Wet Basis**

An **Orsat analysis** (a technique for stack gas analysis) yields the following dry basis composition:

N <sub>2</sub>	65%
CO <sub>2</sub>	14%
CO	11%
O <sub>2</sub>	10%

A humidity measurement shows that the mole fraction of H<sub>2</sub>O in the stack gas is 0.07. Calculate the stack gas composition on a wet basis.

## Solution

*Basis: 100 lb-moles Dry Gas*

$$\begin{aligned} 0.07 \frac{\text{lb-mole H}_2\text{O}}{\text{lb-mole wet gas}} &\Leftrightarrow 0.93 \frac{\text{lb-mole dry gas}}{\text{lb-mole wet gas}} \\ &\Downarrow \\ \frac{0.07 \text{ lb-mole H}_2\text{O} / \text{lb-mole wet gas}}{0.93 \text{ lb-mole dry gas} / \text{lb-mole wet gas}} &= 0.0753 \frac{\text{lb-mole H}_2\text{O}}{\text{lb-mole dry gas}} \\ \frac{100 \text{ lb-mole dry gas}}{100 \text{ lb-mole dry gas}} \Bigg| \frac{0.0753 \text{ lb-mole H}_2\text{O}}{\text{lb-mole wet gas}} &= 7.53 \text{ lb-moles H}_2\text{O} \\ \frac{100 \text{ lb-mole dry gas}}{100 \text{ lb-mole dry gas}} \Bigg| \frac{0.650 \text{ lb-mole N}_2}{\text{lb-mole dry gas}} &= 65.0 \text{ lb-mole N}_2 \\ &(100)(0.140) = 14.0 \text{ lb-mole CO}_2 \\ &(100)(0.110) = 11.0 \text{ lb-mole CO} \\ &(100)(0.100) = \frac{10.00 \text{ lb-mole O}_2}{107.5 \text{ lb-mole wet gas}} \end{aligned}$$

The mole fractions of each stack gas component may now easily be calculated:

$$y_{\text{H}_2\text{O}} = \frac{7.53 \text{ lb-moles H}_2\text{O}}{107.5 \text{ lb-moles wet gas}} = 0.070 \frac{\text{lb-moles H}_2\text{O}}{\text{lb-moles wet gas}}, \dots \text{etc.}$$

### **4.6.3. Theoretical and Excess Air**

**Theoretical oxygen** is the amount needed for **complete** combustion of reactants to form CO<sub>2</sub> and H<sub>2</sub>O. Air that contains the theoretical amount of oxygen is called **theoretical air**. Theoretical air does not depend on how much of a reactant is converted. The difference between the amount of air initial fed and the theoretical air is known as excess air. Therefore, percentage excess air is defined as,

$$\% \text{ excess air} = \{[\text{Air (fed)} - \text{Air (theoretical)}] / \text{Air (theoretical)}\} \times 100.$$

### **EXAMPLE: Theoretical and Excess Air**

One hundred mol per hour of butane (C<sub>4</sub>H<sub>10</sub>) and 5000 mol per hour of air are fed into a combustion reactor. Calculate the percent excess air.

### **Solution**

First, calculate the theoretical air from the feed rate of fuel and the stoichiometric equation for complete combustion of butane.

$$\begin{aligned} \text{C}_4\text{H}_{10} + \frac{13}{2}\text{O}_2 &\rightarrow 4\text{CO}_2 + 5\text{H}_2\text{O} \\ (\text{O}_2)_{\text{theoretical}} &= \frac{100 \text{ mol C}_4\text{H}_{10}}{\text{h}} \left| \frac{6.5 \text{ mol O}_2 \text{ required}}{\text{mol C}_4\text{H}_{10}} \right. \\ &= 650 \frac{\text{mol O}_2}{\text{h}} \\ (\text{air})_{\text{th}} &= \frac{650 \text{ mol O}_2}{\text{h}} \left| \frac{4.76 \text{ mol air}}{\text{mol O}_2} \right. = 3094 \frac{\text{mol air}}{\text{h}} \end{aligned}$$

Hence

$$\% \text{ excess air} = \frac{(\text{air})_{\text{fed}} - (\text{air})_{\text{th}}}{(\text{air})_{\text{th}}} \times 100\% = \frac{5000 - 3094}{3094} \times 100\% = \boxed{61.6\%}$$

If instead you had been given 61.6% excess air, you could have calculated

$$(\text{air})_{\text{fed}} = 1.616 (\text{air})_{\text{th}} = 1.616 (3094) = 5000 \text{ mol/h.}$$

#### **4.6.4. Combustion Material Balances**

When doing material balances for combustion reactions, one should consider balances of the followings:

- inert  $\text{N}_2$  at both inlet and outlet
- unreacted fuel
- excess oxygen
- combustion products  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{CO}$  etc.

Suppose 15% excess of oxygen is fed,

$$\text{oxygen fed} = 1.15 \times \text{theoretical oxygen}$$

$$\text{nitrogen fed} = (79/21) \times \text{oxygen fed}$$

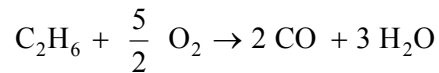
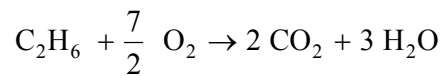
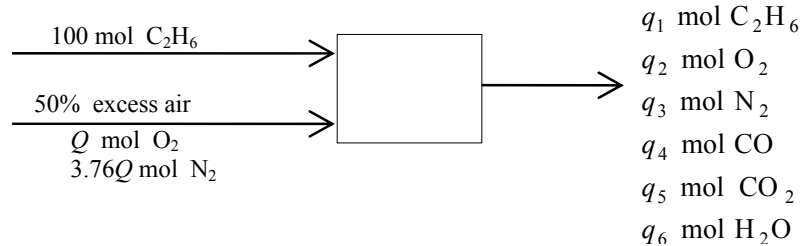
$$\text{air fed} = (100/21) \times \text{oxygen fed}$$

### EXAMPLE: Combustion of Ethane

Ethane ( $C_2H_6$ ) is burned with 50% excess air. The percentage conversion of the ethane is 90%; of the ethane burned, 25% reacts to form CO and the balance to form  $CO_2$ . Calculate the composition of the fuel gas and the ratio of water to dry fuel gas.

### Solution

*Basis: 100 mol Ethane Fed*



### Note:

1. Since no product stream mole fractions are known, subsequent calculations are easier if individual component amounts rather than a total amount and mole fractions are labeled.
2. Known information about the composition of air has been used to label the incoming  $N_2$  stream  $\left(3.76 = \frac{79}{21}\right)$ .
3. If the ethane reacted completely,  $q_1$  would be omitted.
4. Since excess air is supplied,  $O_2$  must appear in the product stream.

*Theoretical  $O_2$*

$$\frac{100 \text{ mol } C_2H_6}{1 \text{ mol } C_2H_6} \left| \frac{3.50 \text{ mol } O_2}{1 \text{ mol } C_2H_6} \right. = 350 \text{ mol}$$

*$O_2$  Fed*

$$Q = (1.5)(350) = \boxed{525 \text{ mol } O_2 \text{ fed}}$$

*$N_2$  Fed*

$$(3.76)(525) = \boxed{1974 \text{ mol } N_2 \text{ fed}}$$

$C_2H_6$  Reacted

$$(0.90)(100) = 90 \text{ mol } C_2H_6 \text{ reacted}$$

$C_2H_6$  Balance

$$\text{Output} = \text{input} - \text{consumption} \implies q_1 = 100 - 90 = 10 \text{ mol}$$

$N_2$  Balance

$$\text{Input} = \text{output} \implies 1974 \text{ mol } N_2 = q_3$$

CO Balance

Output = generation

$$q_4 = \frac{0.25 \times 90 \text{ mol } C_2H_6 \text{ react to form CO}}{1 \text{ mol } C_2H_6 \text{ reacted}} \left| \frac{2 \text{ mol CO formed}}{1 \text{ mol } C_2H_6 \text{ reacted}} \right.$$

↓

$$q_4 = 45 \text{ mol CO}$$

Atomic C Balance

Input = Output

$C_2H_6$       CO       $CO_2$

$$\frac{100 \text{ mol } C_2H_6}{1 \text{ mol } C_2H_6} \left| \frac{2 \text{ mol C}}{1 \text{ mol } C_2H_6} \right. = \overbrace{(q_1)(2)} + \overbrace{(q_4)(1)} + \overbrace{(q_5)(1)}$$

$$\Downarrow \quad q_1 = 10$$

$$q_4 = 45$$

$$q_5 = 135 \text{ mol } CO_2$$

Atomic H Balance

Input = Output

$$\frac{100 \text{ mol } C_2H_6}{1 \text{ mol } C_2H_6} \left| \frac{6 \text{ mol H}}{1 \text{ mol } C_2H_6} \right. = \frac{10 \text{ mol } C_2H_6}{1 \text{ mol } C_2H_6} \left| \frac{6 \text{ mol H}}{1 \text{ mol } C_2H_6} \right. + \frac{q_6 \text{ (mol } H_2O)}{1 \text{ mol } H_2O} \left| \frac{2 \text{ mol H}}{1 \text{ mol } H_2O} \right.$$

↓

$$q_6 = 270 \text{ mol } H_2O$$

Atomic O Balance

$$\begin{array}{r}
 \text{Input} = \text{Output} \\
 \frac{525 \text{ mol O}_2}{1 \text{ mol O}_2} \left| \frac{2 \text{ mol O}}{1 \text{ mol O}_2} \right. = \frac{q_2 (\text{mol O}_2)}{1 \text{ mol O}_2} \left| \frac{2 \text{ mol O}}{1 \text{ mol O}_2} \right. + \frac{45 \text{ mol CO}}{1 \text{ mol CO}} \left| \frac{1 \text{ mol O}}{1 \text{ mol CO}} \right. \\
 \quad + \frac{135 \text{ mol CO}_2}{1 \text{ mol CO}_2} \left| \frac{2 \text{ mol O}}{1 \text{ mol CO}_2} \right. \\
 \quad + \frac{270 \text{ mol H}_2\text{O}}{1 \text{ mol H}_2\text{O}} \left| \frac{1 \text{ mol O}}{1 \text{ mol H}_2\text{O}} \right. \\
 \quad \Downarrow \\
 \boxed{q_2 = 232 \text{ mol O}_2}
 \end{array}$$

The analysis of the stack gas is now complete. Summarizing:

$$\begin{array}{r}
 q_1 = 10 \text{ mol C}_2\text{H}_6 \\
 q_2 = 232 \text{ mol O}_2 \\
 q_3 = 1974 \text{ mol N}_2 \\
 q_4 = 45 \text{ mol CO} \\
 q_5 = 135 \text{ mol CO}_2 \\
 \hline
 2396 \text{ mol dry gas} \\
 + q_6 = 270 \text{ mol H}_2\text{O} \\
 \hline
 2666 \text{ mol total}
 \end{array}$$

Hence the flue gas composition on a dry basis is

$$\begin{aligned}
 y_1 &= \frac{10 \text{ mol C}_2\text{H}_6}{2396 \text{ mol dry gas}} = 0.00417 \frac{\text{mol C}_2\text{H}_6}{\text{mol}} \\
 y_2 &= \frac{232 \text{ mol O}_2}{2396 \text{ mol dry gas}} = 0.0970 \frac{\text{mol O}_2}{\text{mol}} \\
 y_3 &= \frac{1974 \text{ mol N}_2}{2396 \text{ mol dry gas}} = 0.824 \frac{\text{mol N}_2}{\text{mol}} \\
 y_4 &= \frac{45 \text{ mol CO}}{2396 \text{ mol dry gas}} = 0.019 \frac{\text{mol CO}}{\text{mol}} \\
 y_5 &= \frac{135 \text{ mol CO}_2}{2396 \text{ mol dry gas}} = 0.0563 \frac{\text{mol CO}_2}{\text{mol}}
 \end{aligned}$$

and the mole ratio of water to dry flue gas is

$$\frac{270 \text{ mol H}_2\text{O}}{2396 \text{ mol dry flue gas}} = 0.113 \frac{\text{mol H}_2\text{O}}{\text{mol dry flue gas}}$$

**EXAMPLE: Combustion of a Natural Gas**

A natural gas of an unknown composition is burned with air. An analysis of the product gas yields the following results

0.130 mole H<sub>2</sub>O/mole wet gas

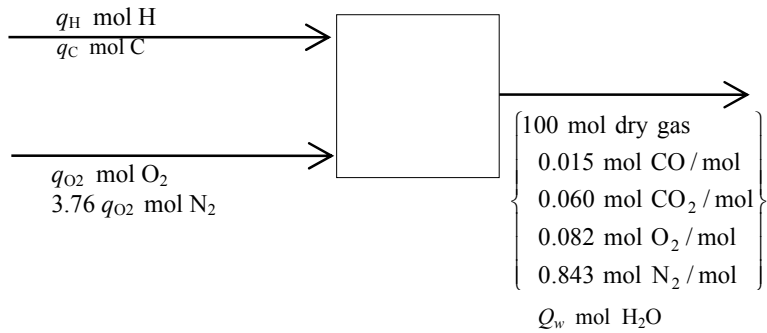
Orsat analysis of flue gas:      1.5% CO  
    6.0% CO<sub>2</sub>  
    8.2% O<sub>2</sub>  
    84.3% N<sub>2</sub>

Calculate the ratio of hydrogen to carbon in the gas, and speculate on what the gas might be.

**Solution**

*Basis: 100 mol Dry Flue Gas*

Since the composition of the fuel is unknown, label it as though carbon and hydrogen were entering separately.



From the given mole fraction of water,

$$Q_w = \frac{100 \text{ mol dry gas}}{0.870 \text{ mol dry gas}} \left| \frac{0.130 \text{ mol H}_2\text{O}}{0.870 \text{ mol dry gas}} \right. = 14.9 \text{ mol H}_2\text{O}$$



*Atomic Carbon Balance*

$$q_c = \frac{100 \text{ mol flue gas}}{\text{mol flue gas}} \left| \frac{0.015 \text{ mol CO}}{\text{mol flue gas}} \right| \frac{1 \text{ mol C}}{1 \text{ mol CO}}$$
$$\text{C in CO}_2$$
$$+ \overbrace{(100)(0.06)(1)} = 7.5 \text{ mol C}$$

*Atomic H Balance*

$$q_H = \frac{Q_w (\text{mol H}_2\text{O})}{\text{mol H}_2\text{O}} \left| \frac{2 \text{ mol H}}{\text{mol H}_2\text{O}} \right| = 2 \times 14.9 = 29.8 \text{ mol H}$$

from which

$$\frac{q_H}{q_C} = \frac{29.8 \text{ mol H}}{7.5 \text{ mol C}} = 3.97 \frac{\text{mol H}}{\text{mol C}}$$

The natural gas may therefore be written with the formula  $(\text{CH}_{3.97})_n$ . Since there is only one hydrocarbon for which the ratio of H to C is close to 3.97 - that is,  $\text{CH}_4$  - we may conclude in this case that the natural gas is essentially pure methane, with perhaps trace amounts of other hydrocarbons. [If we had obtained, say,  $q_H/q_C \approx 2$ , we could have gone no further than to write the fuel as  $(\text{CH}_2)_n$ : from the information given, there would have been no way to distinguish between  $\text{C}_2\text{H}_4$ ,  $\text{C}_3\text{H}_6$ , a mixture of  $\text{CH}_4$  and  $\text{C}_2\text{H}_2$ , etc].

## References

1. Felder, R. and Rousseau, R. W., Elementary Principles of Chemical Processes, 2<sup>nd</sup> ed., John Wiley & Sons, 1986.
2. Himmelblau, D. M., Basic Principles and Calculations in Chemical Engineering, 4<sup>th</sup> ed., Prentice Hall, New Jersey, 1982.
3. Perry, R. H. and Green, D., Perry's Chemical Engineering Handbook, 6<sup>th</sup> ed., McGraw Hill, New York, 1984.
4. Al-Amer, M. J., Session 1 of a Short Course on "Introduction to Chemical Engineering for Non-Chemical Engineers", KFUPM, Dhahran, 1998.