MATERIAL BALANCES FOR PROCESSES INVOLVING REACTION

10.1 Species Material Balances

10.1-1 Processes Involving a Single Reaction

$$\begin{Bmatrix}\text{moles of}\\ i\text{ at }t_2\\ \text{in the}\\ \text{system}\end{Bmatrix} - \begin{Bmatrix}\text{moles of}\\ i\text{ at }t_1\\ \text{in the}\\ \text{system}\end{Bmatrix} = \begin{Bmatrix}\text{moles of }i\\ \text{entering}\\ \text{the system}\\ \text{between }t_2\text{ and }t_1\end{Bmatrix} - \begin{Bmatrix}\text{moles of }i\\ \text{leaving}\\ \text{the system}\\ \text{between }t_2\text{ and }t_1\end{Bmatrix} + \begin{Bmatrix}\text{moles of }i\\ \text{generated}\\ \text{by reaction}\\ \text{between }t_2\text{ and }t_1\end{Bmatrix} - \begin{Bmatrix}\text{moles of }i\\ \text{consumed}\\ \text{by reaction}\\ \text{between }t_2\text{ and }t_1\end{Bmatrix}$$

Example:

$N_2 + 3\,H_2 \leftrightarrow 2NH_3$

The process is open, steady-state system operating for 1 min so that the accumulation terms are zero

MATERIAL BALANCES FOR PROCESSES INVOLVING REACTION

$N_2 + 3\ H_2 \leftrightarrow 2NH_3$

NH_3 (generation): $6 - 0 = 6$ g mol

H_2 (consumption): $9 - 18 = -9$ g mol

N_2 (consumption): $12 - 15 = -3$ g mol

$$\xi = \frac{n_i^{out} - n_i^{in}}{v_i}$$

and the extent of reaction can be calculated via any species:

MATERIAL BALANCES FOR PROCESSES INVOLVING REACTION

For open system:

$$\xi = \frac{n_i^{\text{out}} - n_i^{\text{in}}}{\nu_i} \qquad i = 1, \cdots N$$

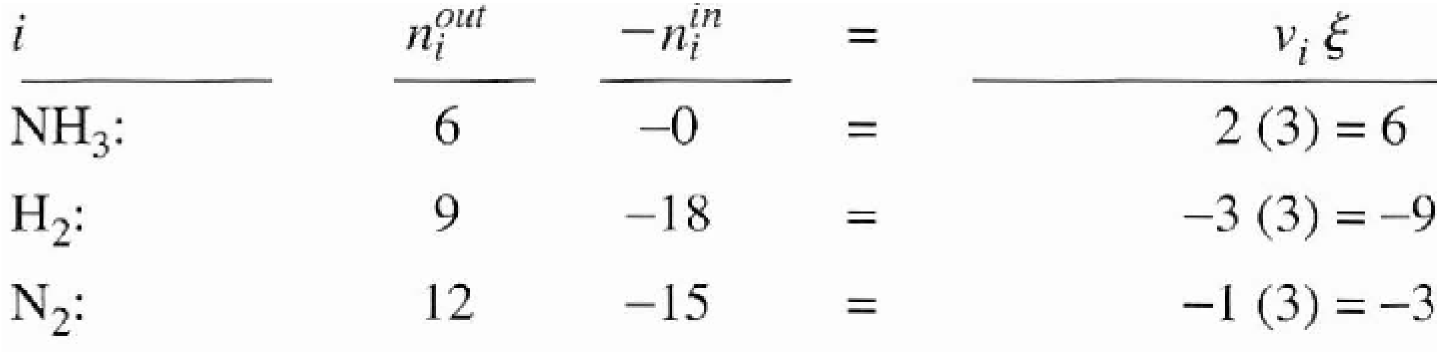
$$\xi = \frac{n_{\text{NH}_3}^{\text{out}} - n_{\text{NH}_3}^{\text{in}}}{\nu_{\text{NH}_3}} = \frac{6 - 0}{2} = 3$$

$$\xi = \frac{n_{\text{H}_2}^{\text{out}} - n_{\text{H}_2}^{\text{in}}}{\nu_{\text{H}_2}} = \frac{9 - 18}{-3} = 3$$

$$\xi = \frac{n_{\text{N}_2}^{\text{out}} - n_{\text{N}_2}^{\text{in}}}{\nu_{\text{N}_2}} = \frac{12 - 15}{-1} = 3$$

MATERIAL BALANCES FOR PROCESSES INVOLVING REACTION

Component	*Out*	*In*	=	*Generation or Consumption*



i	n_i^{out}	$-n_i^{in}$	=	$\nu_i\,\xi$
NH_3:	6	−0	=	2 (3) = 6
H_2:	9	−18	=	−3 (3) = −9
N_2:	12	−15	=	−1 (3) = −3

The term $\nu_i\xi$ corresponds to the moles of *i* generated or consumed.

MATERIAL BALANCES FOR PROCESSES INVOLVING REACTION

For a closed, unsteady-state system the flows in and out would be zero

$$\xi = \frac{n_i^{final} - n_i^{initial}}{v_{\mathrm{i}}}$$

This can be applied to each species that reacts, the resulting set of equations will all contain the extent of reaction . For the species that do not react, $\xi = 0$.

MATERIAL BALANCES FOR PROCESSES INVOLVING REACTION

In terms of the total molar flow in and the total molar flow out:

$$F^{out} = \sum_{i=1}^{S} n_i^{out}$$

$$F^{in} = \sum_{i=1}^{S} n_i^{in}$$

where ***s*** is the total number of species in the system. The material balance for the total molar flow is:

$$F^{\mathrm{out}} = F^{\mathrm{in}} + \xi \sum_{i=1}^{S} \nu_i$$

MATERIAL BALANCES FOR PROCESSES INVOLVING REACTION

If you are given the value of the fraction conversion of the limiting reactant; ξ is related to f by:

$$\xi = \frac{(-f)\, n^{\text{in}}_{\text{limiting reactant}}}{\nu_{\text{limiting reactant}}}$$

MATERIAL BALANCES FOR PROCESSES INVOLVING REACTION

Example: The chlorination of methane occurs by the following reaction

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$

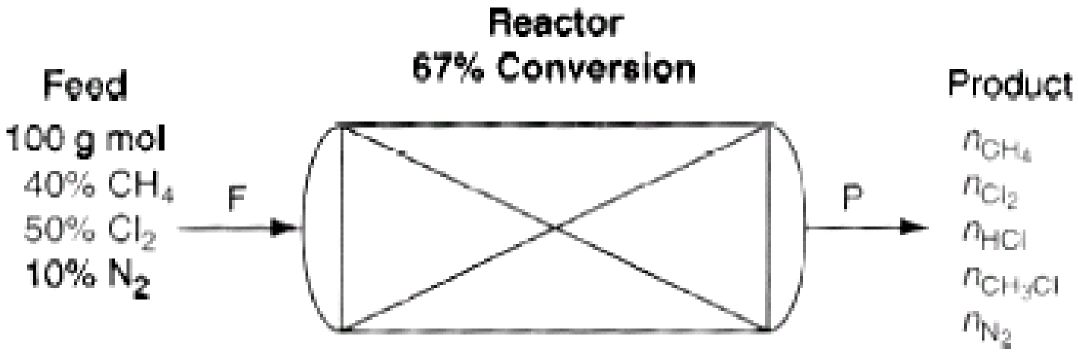
You are asked to determine the product composition if the conversion of the limiting reactant is **67%,** and the feed composition in mole % is given as: 40% CH_4**,** 50% Cl_2, and 10% N_2.

MATERIAL BALANCES FOR PROCESSES INVOLVING REACTION

Solution

Steps 1,2,3, and 4

Assume the reactor is an open, steady-state process. The following figure is a sketch of the process with the known information placed on it.



Step 5

Basis 100 g mol feed

Step 4

You have to determine the limiting reactant

$$\xi^{\max}(CH_4) = \frac{-n^{\text{in}}_{CH_4}}{\nu_{CH_4}} = \frac{-40}{(-1)} = 40$$

$$\xi^{\max}(Cl_2) = \frac{-n^{\text{in}}_{Cl_2}}{\nu_{Cl_2}} = \frac{-50}{(-1)} = 50$$

Therefore, CH_4 is the limiting reactant.

$$\xi = \frac{-f\, n^{\text{in}}_{lr}}{\nu_{lr}} = \frac{(-0.67)(40)}{-1} = 26.8 \text{ g moles reacting}$$

MATERIAL BALANCES FOR PROCESSES INVOLVING REACTION

Steps 6 and 7

The next step is to carry out a degree-of-freedom analysis

Number of variables: 11

$$n^{\text{in}}_{CH_4},\ n^{\text{in}}_{Cl_2},\ n^{\text{in}}_{N_2},\ n^{\text{out}}_{CH_4},\ n^{\text{out}}_{Cl_2},\ n^{\text{out}}_{HCl},\ n^{\text{out}}_{CH_3Cl},\ n^{\text{out}}_{N_2},\ F,\ P,\ \xi$$

Number of equations: 1 I

Basis: F = 100

Species material balances: 5

$$CH_4,\ Cl_2,\ HCl,\ CH_3Cl,\ N_2$$

MATERIAL BALANCES FOR PROCESSES INVOLVING REACTION

Specifications: 3

Two of $\{x^{\text{in}}_{\text{CH}_4}, x^{\text{in}}_{\text{Cl}_2}, x^{\text{in}}_{\text{N}_2}\}$ and f (used to calculate ξ)

Implicit equations: 2

$$\Sigma n_i^{\text{out}} = P \text{ and } \Sigma n_i^{\text{in}} = F$$

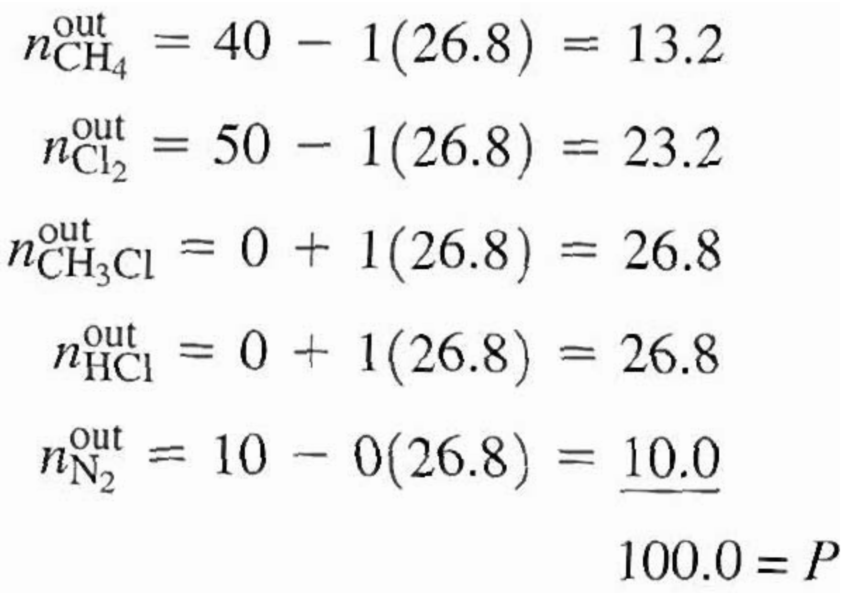
The degrees of freedom are zero.

MATERIAL BALANCES FOR PROCESSES INVOLVING REACTION

Steps 8 and 9

- The species material balances (in moles) give a direct solution for each species in the product:

$$n_i^{out} = n_i^{in} + v_i\xi$$



$$\begin{aligned}
n_{CH_4}^{out} &= 40 - 1(26.8) = 13.2\\
n_{Cl_2}^{out} &= 50 - 1(26.8) = 23.2\\
n_{CH_3Cl}^{out} &= 0 + 1(26.8) = 26.8\\
n_{HCl}^{out} &= 0 + 1(26.8) = 26.8\\
n_{N_2}^{out} &= 10 - 0(26.8) = \underline{10.0}\\
&\qquad\qquad\qquad 100.0 = P
\end{aligned}$$

- Therefore, the composition of the product stream is: 13.2% CH_4, 23.2% Cl_2, 26.8% CH_3Cl**,** 26.8% HC1, and 10% N_2

10.1 -2 Processes Involving Multiple Reactions

- To extend the concept of the extent of reaction to processes involving multiple reactions, you should include in the species material balances only the ξ_i associated with a set of independent chemical reactions called the minimal set of reaction equations.

Example:

$$C + O_2 \rightarrow CO_2$$

$$C + {}^1\!/_2 O_2 \rightarrow CO$$

$$CO + ½\ O_2 + CO_2$$

Only two of the three equations are independent

MATERIAL BALANCES FOR PROCESSES INVOLVING REACTION

- For open, steady-state processes with multiple reactions, moles for component ***i:***

$$n_i^{\text{out}} = n_i^{\text{in}} + \sum_{j=1}^{R} \nu_{ij}\, \xi_j$$

where

ν_{ij} is the stoichiometric coefficient of species ***i*** in reaction ***j*** in the minimal set.

ξ_j is the extent of reaction for the jth reaction in the minimal set.

R is the number of independent chemical reaction equations (the size of the minimal set).

MATERIAL BALANCES FOR PROCESSES INVOLVING REACTION

- The total moles, *N*, exiting a reactor are:

$$N = \sum_{i=1}^{S} n_i^{\text{out}} = \sum_{i=1}^{S} n_i^{\text{in}} + \sum_{i=1}^{S} \sum_{j=1}^{R} v_{ij}\xi_j$$

where *S* is the number of species in the system.

MATERIAL BALANCES FOR PROCESSES INVOLVING REACTION

Example: Formaldehyde (CH_2O) is produced industrially by the catalytic oxidation of methanol (CH_3OH) according to the following reaction:

$$CH_3OH + 1/2O_2 \rightarrow CH_2O + H_2O \qquad (1)$$

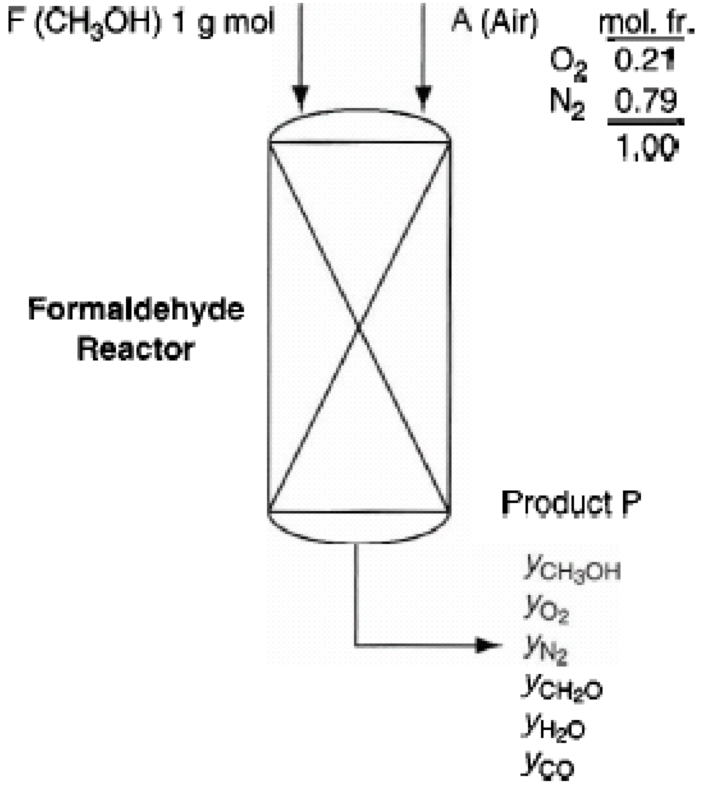
Unfortunately, under the conditions used to produce formaldehyde at a profitable rate, a significant portion of the formaldehyde reacts with oxygen to produce CO and H_20, that is,

$$CH_2O + 1/2O_2 \rightarrow CO + H_2O \qquad (2)$$

Assume that methanol and twice the stoichiometric amount of air needed for complete conversion of the CH_3OH to the desired products (CH_2O and H_2O) are fed to the reactor. Also assume that 90% conversion of the methanol results, and that a 75% yield of formaldehyde occurs based on the theoretical production of CH_2O by Reaction 1. Determine the composition of the product gas leaving the reactor.

Solution:

Steps 1,2,3, and 4



MATERIAL BALANCES FOR PROCESSES INVOLVING REACTION

Step 5:

Basis: 1 g mol F

Step 4

You can use the specified conversion of methanol and yield of formaldehyde to determine the extents of reaction for the two reactions. Let ξ_1 represent the extent of reaction 1.

$$\xi = \frac{(-f)n^{\text{in}}_{\text{limiting reactant}}}{\nu_{\text{limiting reactant}}}$$

$$\xi_1 = \frac{-0.90}{-1}(1) = 0.9 \text{ g moles}$$

The yield is related to ξ as follows

MATERIAL BALANCES FOR PROCESSES INVOLVING REACTION

By reaction 1: $n^{out,1}_{CH_2O} = n^{in,1}_{CH_2O} + 1(\xi_1) = 0 + \xi_1 = \xi_1$

By reaction 2: $n^{out,2}_{CH_2O} = n^{in,2}_{CH_2O} - 1(\xi_2) = n^{out,1}_{CH_2O} - \xi_2 = \xi_1 - \xi_2$

The yield is $\dfrac{n^{out,2}_{CH_2O}}{F} = \dfrac{\xi_1 - \xi_2}{1} = 0.75$ or $\dfrac{0.9 - \xi_2}{1} = 0.75$

$\xi_2 = 0.15$g moles reacting

The amount of air (A) that enters the process. The entering oxygen is twice the required oxygen based on Reaction 1, namely

$$n^{A}_{O_2} = 2\left(\frac{1}{2}F\right) = 2\left(\frac{1}{2}\right)(1.00) = 1.00 \text{ g mol}$$

MATERIAL BALANCES FOR PROCESSES INVOLVING REACTION

$$A = \frac{n^A_{O_2}}{0.21} = \frac{1.00}{0.21} = 4.76 \text{ g mol}$$

$$n^A_{N_2} = 4.76 - 1.00 = 3.76 \text{ g mol}$$

Steps *6* and 7

The degree-of-freedom analysis is

Number of variables: 11

$$F,\ A,\ P,\ y^P_{CH_3OH},\ y^P_{O_2},\ y^P_{N_2},\ y^P_{CH_2O},\ y^P_{H_2O},\ y^P_{CO},\ \xi_1,\ \xi_2$$

MATERIAL BALANCES FOR PROCESSES INVOLVING REACTION

Number of equations: 11

Basis: F = 1 g mol

Species material balances: 6

$CH_3OH, O_2, N_2, CH_2O, H_2O, CO$

Calculated values in Step 4: **3**

A, ξ_1, ξ_2

Implicit equation: 1

$$\Sigma y_i^P = 1$$

MATERIAL BALANCES FOR PROCESSES INVOLVING REACTION

$$P = \sum_{i=1}^{S} n_i^{in} + \sum_{i=1}^{S}\sum_{j=1}^{R} v_{i_j}\,\xi_j$$

$$= 1 + 4.76 + \sum_{i=1}^{6}\sum_{j=1}^{2} v_{i_j}\,\xi_j$$

$$= 5.76 + [(-1) + (-{}^1\!/_2) + (1) + 0 + (1) + 0]\,0.9$$

$$+ [0 + (1/2) + (-1) + 0 + (1) + (1)]\,0.15 = 6.28 \text{ g mol}$$

MATERIAL BALANCES FOR PROCESSES INVOLVING REACTION

The material balances after entering the values calculated in Step 4 are:

$$n^{\text{out}}_{CH_3OH} = y_{CH_3OH}\,(6.28) = 1 - (0.9) + 0 = 0.10$$

$$n^{\text{out}}_{O_2} = y_{O_2}\,(6.28) = 1.0 - (\tfrac{1}{2})(0.9) - (\tfrac{1}{2})(0.15) = 0.475$$

$$n^{\text{out}}_{CH_2O} = y_{CH_2O}\,(6.28) = 0 + 1\,(0.9) - 1\,(0.15) = 0.75$$

$$n^{\text{out}}_{H_2O} = y_{H_2O}\,(6.28) = 0 + 1\,(0.9) + 1\,(0.15) = 1.05$$

$$n^{\text{out}}_{CO} = y_{CO}\,(6.28) = 0 + 0 + 1\,(0.15) = 0.15$$

$$n^{\text{out}}_{N_2} = y_{N_2}\,(6.28) = 3.76 - 0 - 0 = 3.76$$

10.2 Element Material Balances

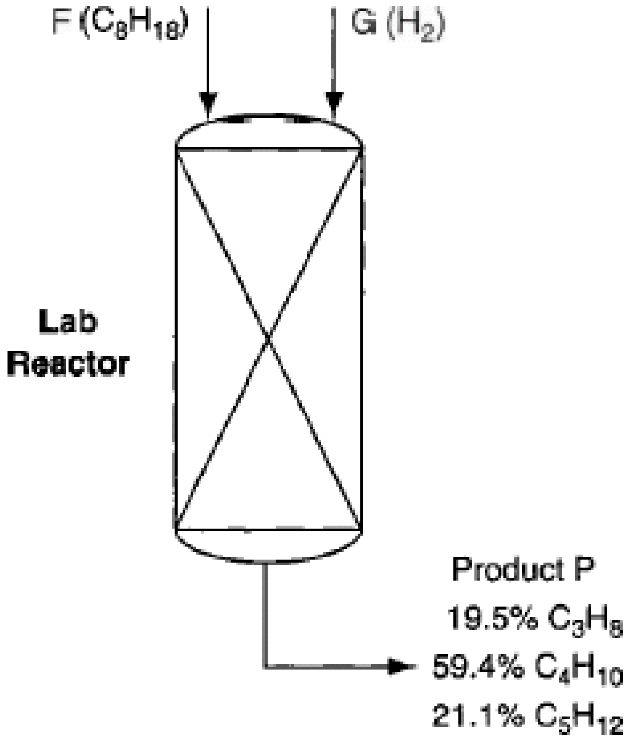
- elements in a process are conserved, and consequently you *can not* apply material balance equation (eq.(10.1)) to the elements in a process. Because elements are not generated or consumed, the generation and consumption terms in (eq. (10.1)) can be ignored.

MATERIAL BALANCES FOR PROCESSES INVOLVING REACTION

Example: Hydrocracking is an important refinery process for converting low-valued heavy hydrocarbons into more valuable lower molecular weight hydrocarbons by exposing the feed to a zeolite catalyst at high temperature and pressure in the presence of hydrogen. Researchers in this field study the hydrocracking of pure components, such as octane (C_8H_{18}), to understand the behavior of cracking reactions. In one such experiment for the hydrocracking of octane, the cracked products had the following composition in mole percent: 19.5% C_3H_8, 59.4% C_4H_{10}, and 21.1% C_5H_{12}. You are asked to determine the molar ratio of hydrogen consumed to octane reacted for this process.

Solution:

Steps 1,2,3, and 4

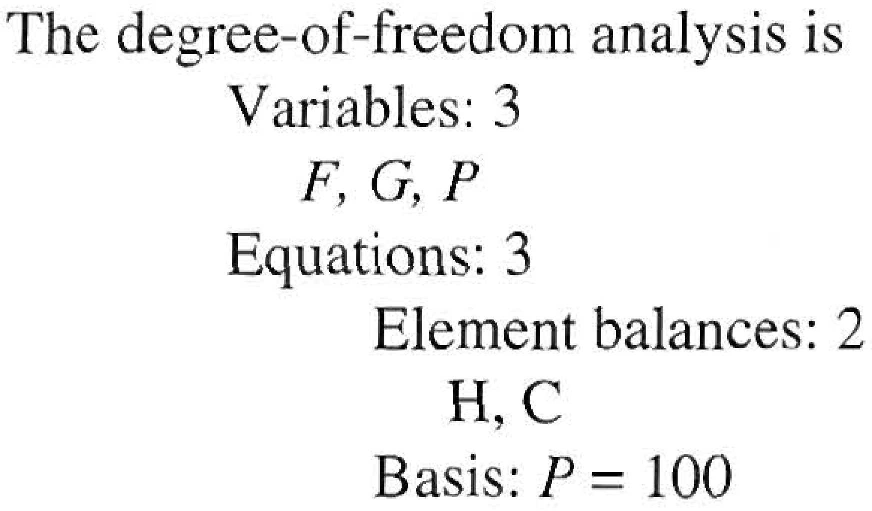


MATERIAL BALANCES FOR PROCESSES INVOLVING REACTION

Step 5:

Basis: P= 100 g mol

Step 6,7:



The degree-of-freedom analysis is

Variables: 3

F, G, P

Equations: 3

Element balances: 2

H, C

Basis: $P = 100$

MATERIAL BALANCES FOR PROCESSES INVOLVING REACTION

Step 8:

The element balances after introducing the specification and basis are:

$$C: F(8) + G(0) = 100[(0.195)(3) + (0.594)(4) + (0.211)(5)]$$

$$H: F(18) + G(2) = 100[(0.195)(8) + (0.594)(10) + (0.211)(12)]$$

$$F = 50.2 \text{ g mol} \qquad G = 49.8 \text{ g mol}$$

$$\frac{H_2 \text{ consumed}}{C_8H_{18} \text{ reacted}} = \frac{49.8 \text{ g mol}}{50.2 \text{ g mol}} = 0.992$$

10.3 Material Balances involving Combustion

- Combustion is the reaction of a substance with oxygen with the associated release of energy and generation of product gases such as H_2O, CO_2, CO, and SO_2

- Most combustion processes use air as the source of oxygen, assume that air contains 79% N_2 and 21% O_2, neglecting the other components and can assume that air has an average molecular weight of 29.

- In combustion, some terminologies require special attention such as:

  - Flue or stack gas: all the gases resulting from a combustion process including the water vapor, sometimes known as a wet basis.
  - Orsat analysis or dry basis: all the gases resulting from a combustion process not including the water vapor.
  - Complete combustion: the complete reaction of the hydrocarbon fuel producing CO_2, SO_2, and H_2O.

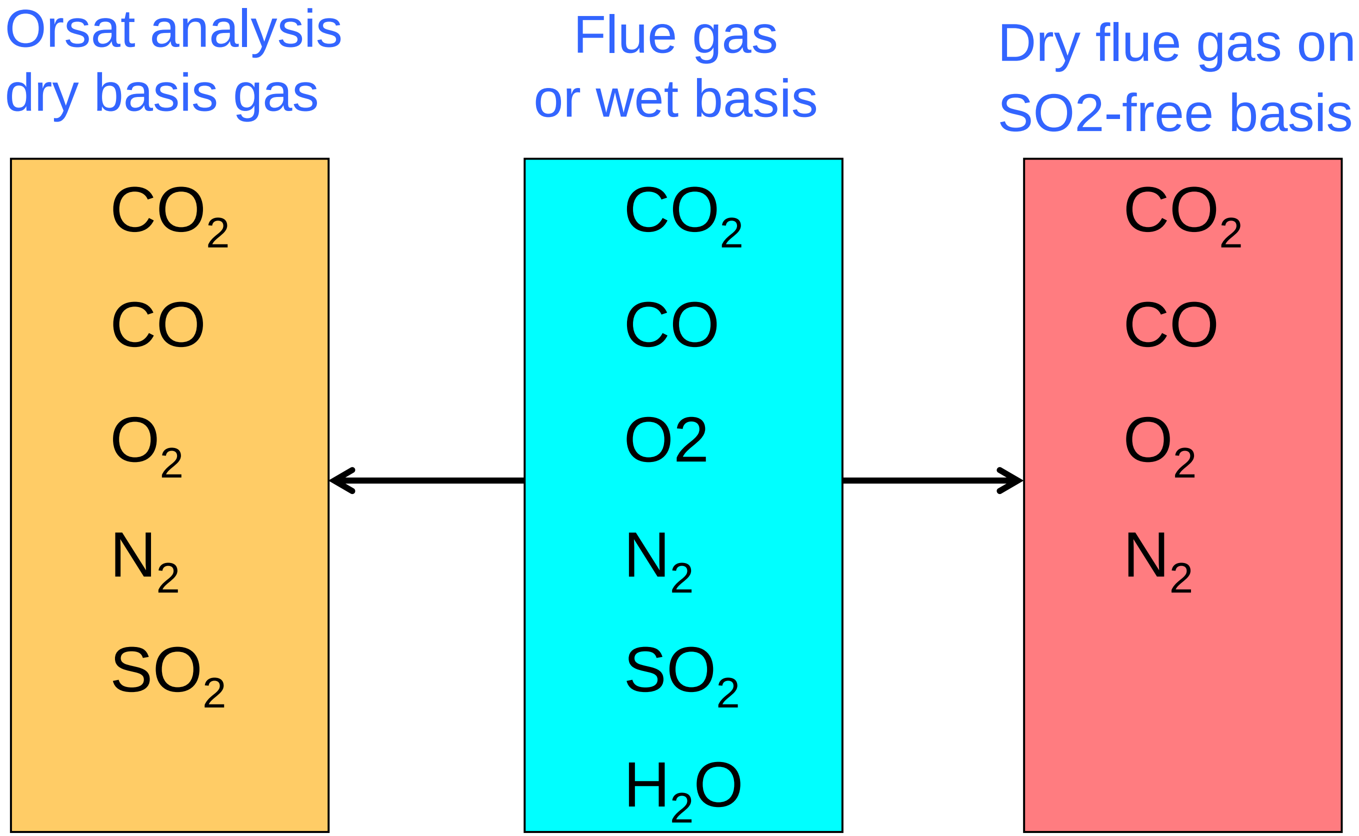
MATERIAL BALANCES FOR PROCESSES INVOLVING REACTION

- Partial combustion: the combustion of the fuel producing at least some CO.

- Theoretical air (or theoretical oxygen): the minimum amount of air (or oxygen) required to be brought into the process for complete combustion. Sometimes this quantity is called the required air (or oxygen).

- Excess air (or excess oxygen): in line with the definition of excess reactant given before, excess air (or oxygen) is the amount of air (or oxygen) **in excess of that required for complete combustion.**

MATERIAL BALANCES FOR PROCESSES INVOLVING REACTION



Orsat analysis
dry basis gas

CO_2
CO
O_2
N_2
SO_2

Flue gas
or wet basis

CO_2
CO
O2
N_2
SO_2
H_2O

Dry flue gas on
SO2-free basis

CO_2
CO
O_2
N_2

MATERIAL BALANCES FOR PROCESSES INVOLVING REACTION

- **Assumption:** The calculated amount of *excess air does not depend on how much material is actually burned* but what is possible to be burned. Even if only partial combustion takes place, as, for example, C burning to both CO and CO_2, the excess air (or oxygen) is computed as if the process of combustion went to completion and produced only CO_2.

- The percent excess air is identical to the percent excess O2

$$\%\ \text{excess air} = 100\,\frac{\text{excess air}}{\text{required air}} = 100\,\frac{\text{excess } O_2/0.21}{\text{required } O_2/0.21}$$

MATERIAL BALANCES FOR PROCESSES INVOLVING REACTION

- Percent excess air may also be computed as:

$$\%\ \text{excess air} = 100\,\frac{O_2\ \text{entering process} - O_2\ \text{required}}{O_2\ \text{required}}$$

Or,

$$\%\ \text{excess air} = 100\,\frac{\text{excess}\ O_2}{O_2\ \text{entering} - \text{excess}\ O_2}$$

MATERIAL BALANCES FOR PROCESSES INVOLVING REACTION

Example: Fuels other than gasoline are being eyed for motor vehicles because they generate lower levels of pollutants than does gasoline. Compressed propane is one such proposed fuel. Suppose that in a test 20 kg of C_3H_8 is burned with 400 kg of air to produce 44 kg of CO_2 and 12 kg of CO. What was the percent excess air?

MATERIAL BALANCES FOR PROCESSES INVOLVING REACTION

Solution:

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$$

Basis: 20 kg of C_3H_8

- Since the percentage of excess air is based on the ***complete*** combustion of C_3H_8 to $C0_2$ and H_20, The required O_2 is:

$$\frac{20 \text{ kg } C_3H_8}{} \left| \frac{1 \text{ kg mol } C_3H_8}{44.09 \text{ kg } C_3H_8} \right| \frac{5 \text{ kg mol } O_2}{1 \text{ kg mol } C_3H_8} = 2.27 \text{ kg mol } O_2$$

- The entering O2 is:

$$\frac{400 \text{ kg air}}{} \left| \frac{1 \text{ kg mol air}}{29 \text{ kg air}} \right| \frac{21 \text{ kg mol } O_2}{100 \text{ kg mol air}} = 2.90 \text{ kg mol } O_2$$

MATERIAL BALANCES FOR PROCESSES INVOLVING REACTION

- The percentage of excess air is:

$$\% \text{ excess air} = \frac{\text{entering } O_2 - \text{required } O_2}{\text{required } O_2} \times 100$$

$$\% \text{ excess air} = \frac{2.90 \text{ lb mol } O_2 - 2.27 \text{ lb mol } O_2}{2.27 \text{ lb mol } O_2}\left|\frac{100}{}\right. = 28\%$$

MATERIAL BALANCES FOR PROCESSES INVOLVING REACTION

- In calculating the amount of excess air, remember that the excess is the amount of air that enters the combustion process over and above that required for complete combustion.

Example: A gas containing 80% C_2H_6 and 20% O_2 is burned in an engine with 200% excess air. Eighty percent of the ethane goes to $C0_2$, 10% goes to CO. and 10% remained unburned. What is the amount of the excess air per 100 moles of the gas?

MATERIAL BALANCES FOR PROCESSES INVOLVING REACTION

Solution:

Basis: 100 g mol of gas

- First, you can ignore the information about the CO and the unburned ethane because the basis of the calculation of excess air is *complete combustion.* Specifically C goes to CO_2, S to SO_2, H, to H_2O, CO goes to CO_2, and so on.

- Second, the oxygen in the fuel cannot be ignored. Based on the reaction

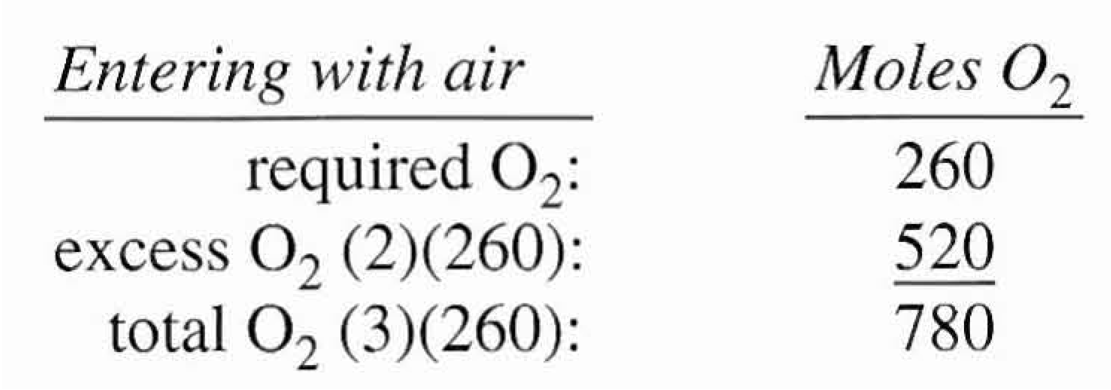
$$C_2H_6 + \frac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O$$

- For complete combustion: 80 moles of C_2H_6 require 3.5(80) = 280 moles of O2

MATERIAL BALANCES FOR PROCESSES INVOLVING REACTION

- The amount of O2 entering with air = 280 - 20 = 260 moles are needed in the entering air for complete combustion.

- Therefore, 260 moles of O_2 are the required O_2, and the calculation of the 200% excess O_2 (air) is based on 260, not 280, moles of O_2:



Entering with air	*Moles O_2*
required O_2:	260
excess O_2 (2)(260):	520
total O_2 (3)(260):	780